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ENGINEERING EXPERIMENT STATION
SERIES 23

EXPERIMENTS ON THE EXTRACTION AND RECOVERY OF RADIUM FROM TYPICAL AMERICAN CARNOTITE ORES

Including

Contributions to Methods of Measuring Radium

by

HOWARD H. BARKER

With the Collaboration
of
HERMAN SCHLUNDT

ISSUED THREE TIMES MONTHLY; ENTERED AS SECOND-CLASS MATTER AT THE POSTOFFICE AT COLUMBIA, MISSOURI—2,000

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Experiments on the Extraction and Recovery of Radium from Typical American Carnotite Ores.

INTRODUCTION

During the past decade a number of processes have been proposed for the treatment of carnotite and other uranium-bearing ores for the extraction and recovery of the valuable constituents, namely, radium, uranium, and in most instances vanadium. Some of the methods proposed have found commercial application while others have never gotten beyond the experimental stage. In considering the merits of a new process, or modifications of an established process, two important points must not be overlooked: (1) How does the new method compare with other and better-known methods as to efficiency and cost of operation? (2) Is the new method applicable to all types of ores or perhaps only to the type of ore which the investigator has been working with? These are two points which are sometimes passed over too hastily and the result is that new processes when operated under changed conditions not infrequently prove to be failures. Therefore in developing a new process the investigator should be thoroughly familiar with the limitations of other standardized or well-known processes and secondly he should not be satisfied when he finds that his process is successful with a single type of ore, but he should immediately test his methods on different and varied types of ores. After this has been done the real merits of the process may be judged, and comparisons made with other methods or processes which have been subjected to the same rigid investigation. Proceeding in this way the limitations of a new process are discovered and the value of its claims approximately determined.

Objects of Investigation.—With these ideas in mind, and the fact that up to the present time no careful comparative study of the better-known processes for treatment of carnotite has been published, as well as their adaptability to different ores, it seemed that such a study would be of considerable importance, both to those at present interested in the industry as well as those who contemplate entering it, and even parties owning mining claims or properties, as it is hoped that the results of this investigation indi-

cate the amenability of various types of ores to some of the standard or better-known processes. In order to obtain data on methods comparable to plant conditions, experimental equipment was installed to treat batches of ores as high as one hundred pounds.

The study of this problem involved a great deal of analytical work, and in this connection some attention was given to the development of new methods and the improvement of existing procedures with the view of simplifying the analytical operations. These experiments were directed primarily to the quantitative methods for the estimation of radium in the various products obtained, and to minor improvements in the methods of determining the uranium and vanadium content of the various ore samples used. On account of some delay in the publication of this work as a whole, one part pertaining to the analytical phase has been published (1), but is assembled and unified in another section, (pp. 54) of this bulletin.

At the outset of this work it was quite impractical to carry on at the same time the operations for taking the vanadium and uranium through to the finished form, consequently these elements were precipitated as calcium-uranium-iron vanadate from the solutions by the addition of lime, filtered and the lime cake stored for later study. This phase of the work is still in progress and consequently is not incorporated in this bulletin.

The objects of this investigation may be summarized as follows: (1) To compare the different general methods of treating American carnotite ores for the extraction and recovery of radium; (2) to test the applicability of the various methods to the different types of ores in various fields; (3) to devise new methods of treatment, and modifications of existing processes for the efficient extraction of radium from virgin ore; (4) to study and compare the different methods for the recovery of uranium and vanadium to determine their respective efficiency, and the quality of product obtained; (5) to study the electrical and analytical methods involved in determining radium in the various products obtained in its commercial production.

Funds for the Investigation.—This work was undertaken by the Engineering Experiment Station in cooperation with the Department of Chemistry. The major expense was borne by the funds of the Engineering Experiment Station. Some money was obtained from the Chemistry Department's allotment from the University fund for Scientific Laboratories. Minor revenues were

obtained from the Chemical Service Fund of the Department of Chemistry, and from individual contributors.

A technological laboratory was installed in the basement of the Chemistry Building on Francis Quadrangle at an approximate cost of five thousand dollars, and while the equipment purchased was primarily for use in connection with this investigation, still the installation was so designed and arranged that it can be readily adapted to the study of other commercial problems.

Acknowledgment to Donors of Ores.—Inasmuch as this work was purely experimental in character and did not have the commercial production of radium as an objective, it was decided to invite some of the American producing concerns to contribute lots of one thousand pounds of ore, typical of certain ores which they were undertaking to treat. In this connection a most hearty response was received and acknowledgment is hereby made to the following concerns and individuals for ore and concentrates contributed:

To the Radium Company of Colorado, for two lots of ore of one thousand pounds each, characteristic of ores obtained from Temple Mountain, Utah.

To the United States Radium Corporation, for one thousand pounds of ore characteristic of the ores mined in the Paradox Valley, except that this lot was a little lower in quality than the grade which is ordinarily termed "shipping ore".

To the Keystone Metals Reduction Company, for one thousand pounds of ore typical of their mines in the Polar Mesa region of Utah.

To the W. L. Cummings Chemical Company, for furnishing concentrates upon which some work was done.

To Mr. L. M. Hughes, for furnishing various odd lots of "dust",* which he held in his possession.

Personnel of Investigators.—The Director of the Engineering Experiment Station, Dean E. J. McCaustland, was in general charge of this investigation. The planning of the work, the methods to be pursued, as well as the details of the problem were left to Professor Herman Schlundt, and the author, and it was under their direction that the work was carried out. The laboratory experiments were conducted by the author or by the author with the help of assistants. Special phases of the problem were assigned, as individual units, to various graduate students in the Department of Chemistry, who most ably and efficiently assisted in their part

*Very finely divided ore concentrated by air separation.

of the work. Mr. R. O. Humphrey, besides assisting with the major part of the work in the technological laboratory pertaining to the recovery and extraction of radium, is making a study of the methods of recovery of vanadium and uranium. Mr. R. H. LeRoy, investigated the adaptability of the gamma-ray method as a means of determining the quantity of radium in ore samples and various products obtained in plant operation. Mr. LeRoy also assisted in devising a new and unique method of maintaining a constant potential for use in charging electroscopes. He constructed this apparatus and devised most of the details. Mr. C. E. Baumgarten made a careful study of the emanation method for determining the quantity of radium in various specimens. Mr. H. D. Crowe ably assisted during the summer months of 1922 with the analytical work. Acknowledgment is also made to Mr. D. C. Stark, who gave minor assistance in various phases of the work.

Cost of Production.—No attempt has been made to compare the costs of operation of the different methods studied as that is dependent upon too many variable factors, such as overhead and administration expense, efficiency of process, economy of plant operation, cost of chemicals in the locality of the reduction works, cost of labor, etc. Nevertheless, a few general statements of approximate cost will be presented.

Of fundamental importance to the successful operation of any plant engaged in the production of radium, is an assured ore supply. The large manufacturers have found by experience that the best means of securing such a supply is to own and operate their own mining properties.

Perhaps next in importance is the cost to produce a ton of average grade ore, say 2 per cent uranium oxide, from such claims as are being operated. There are a number of items which must be borne in mind in this connection, such as, amortization of properties, cost of development and exploration work, which is a constantly increasing item with the depletion of the readily available ore, cost of transportation to the railroad, mining, administration expense, freight from shipping point to reduction plants, and actual mining costs. It has been pointed out by reliable authorities, who are familiar with the type of mining involved in the production of carnotite or uranium ore, that even under favorable conditions of mining the cost to produce a ton of 2 per cent uranium oxide ore will be at least one hundred and fifty dollars.

The cost of processing a ton of ore is somewhat problematical and difficult to estimate unless there is at hand such basic information as the tonnage to be treated per month, the processes used and the recoveries obtained, cost of chemicals, labor, etc., and the overhead and administration expense. However, it is probably safe to estimate that the cost ranges from one hundred to one hundred and fifty dollars per ton. The cost of recovering the vanadium and uranium has not been taken into account in this figure.

Taking the average of the figures given for the cost of processing plus the cost of the virgin ore, we see that approximately two hundred and seventy-five dollars is invested in the radium recoverable from one ton of 2 per cent uranium oxide ore*. Assuming that a recovery of 85 per cent is obtained, the cost per milligram will be approximately sixty-two dollars. Add to this the cost of selling, plus the cost of maintaining the service which certain companies have established, the total cost to put radium into the hands of the consumer doubtless amounts to seventy-five dollars per milligram. In order to obtain the price which radium should sell for, a fair margin of profit must be added, depending upon the capital invested, etc. Certainly a profit of one-third of the manufacturing cost would not be unreasonable and it seems that for conservative investment this margin should be increased on account of several special elements of risk involved in the undertaking.

These estimates are undoubtedly conservative and as time goes on and the readily available ore deposits become depleted the mining cost will undoubtedly rise as pointed out by George Kunkle (2), and obviously with the increased cost of obtaining the virgin ores will come an increased cost of producing the finished product.

As stated before, no allowance for either the cost of production or possible profit in the by-products of uranium and vanadium have been taken into consideration. At one time this was quite an important factor, but the present market conditions makes a profit in either product somewhat uncertain. It is probable that a small margin may be realized on the vanadium, as the demand for vanadium products seems to be gradually increasing. Eventually these products will undoubtedly mean a substantial source of revenue to the producers.

About the time that the major part of this investigation was completed (fall of 1922) there was a marked decline in the selling price (3) of radium, due to the announcement of very rich deposits of uranium ore in the Belgian Congo, West Africa. The grade of

*A ton of 2 per cent uranium oxide ore contains 5.24 milligrams of radium element.

the ore is reported to be some fifteen to twenty times as rich in radium as the commercial American ores, consequently the cost of producing the finished product is materially reduced. Some of the American producers realized that it was going to be difficult to process their ores and meet competition from abroad. Therefore, instead of facing the probable dissolution of their entire organizations, agreements with the foreign syndicate have been formed, whereby certain American producers now act as sales agents for certain territories. The result has been that relatively little American ore has been processed since the summer of 1922, and there seems to be small immediate hope for any change in the present situation. At any rate, American producers and owners of mining properties will have to bide their time until the quality of the ore originating from the Belgian Congo will be on a par with that from American claims, before they can hope for any material resumption of production in this country.

It might be well to call attention to the fact that there has been a small quantity of "high grade" (ore containing well above 2 per cent uranium oxide) ore mined during this period of general inactivity. In most instances the ore mined has been readily available and the mining costs have been nominal. Also, most of this "high grade" ore has been processed as it is obvious that the cost to process a ton of such ore is practically the same as to process a ton of average grade ore, consequently the net cost per milligram of radium element produced from the rich ore is much less than from the lower grade ore. This combination of circumstances has enabled certain operators to produce radium from American ores and still meet competition from abroad.

CLASSIFICATION OF METHODS FOR EXTRACTION OF RADIUM FROM URANIUM ORES

The following classification will assist in showing the relation of the various methods investigated.

1. Direct Solution from Ore.
   - A. Direct solution in acid
     - a. Use of hydrochloric acid
     - b. Use of nitric acid
       Recovery of uranium and vanadium
     - c. Use of sulfuric acid
   - B. Solution in acid after conversion of the radium and barium to acid soluble form, as carbonates
2. Concentration of Radium by Reducing Gang* Material
   - A. By direct solution of the gang material
   - B. By breaking down ore with acid or nitre cake, followed by sliming off values and recovery of radium from slimes by,
     - a. Volatilization of the silica
     - b. Solution of silica
     - c. Solution of radium
     - d. Solution of radium after conversion into form soluble in acids, generally carbonates.
3. Miscellaneous Methods for the Recovery of Radium.

Practically all methods for the extraction and recovery of radium from virgin ores may be assigned to some section of the above classification, which is simple and quite self-explanatory. The classification is one which might be adapted to practically any metallurgical process involving the separation of certain constituents from crude ores. It must be borne in mind that some preliminary preparation of the ore such as grinding, is necessary, before subjecting it to chemical treatment. The matter of properly grinding the ore for treatment is one which should be given careful consideration, as the percentage extraction of radium and the cost of several of the operations will be very materially affected by this initial step.

1A. Direct Solution from Ore.—Hydrochloric, nitric (4), and sulfuric (5) acids of the proper degree of concentration and under suitable operating conditions may be utilized for the extraction of radium from crude uranium ores.

a. Hydrochloric acid.—This acid has been used to some extent for leaching radium from crude ores, although the method has not proven very satisfactory where it is desired to effect solution of the radium at the outset. It is essential that the acid be practically free from sulfate and the ore must be exceedingly low in gypsum or other sulfate content, otherwise, the greater part of the radium is precipitated as the sulfate and remains with

*The term "gang material" as used in this work refers to the bulk of non-valuable constituents of the ore (as silica, iron, aluminum, etc.) However, it is noted that in some instances the uranium and vanadium remain associated in part at least with the gang material on initial treatment and in such cases, it is necessary to give consideration to the subsequent recovery of these elements.

the residue or sand. With ore free from gypsum or sulfates it is possible to obtain 80 and in some instances 90 per cent extraction of the radium by the use of an equal weight of 13° Baumé acid (sp. gr. 1.10). The filtration must take place while the acid is hot and the residue should be washed with hot acid and then with distilled water. Hydrochloric acid is a good solvent for both vanadium and uranium, but for the direct extraction of radium from most ores it is not practical.

b. Nitric acid.—While hot concentrated hydrochloric acid is a solvent for radium as well as barium to a certain extent, still nitric acid is very much more effective, a fact which is the basis for the method devised by the U. S. Bureau of Mines (4) and used in the plant of the National Radium Institute at Denver, Colorado. The method consists essentially in leaching the ore, which has been ground to pass 20 mesh, with hot nitric acid in the proportion of 121 pounds of 100 per cent nitric acid to 500 pounds of ore, the acid being diluted to 38 per cent strength. After digestion for fifteen to twenty minutes the acid is run onto filters, and the sand remaining in the leaching pots is given a wash with acid about one-third the strength of the original leach. The sand is then transferred to the filters and given two washings with distilled water. The sand is discarded and the washings are combined with the original leach and diluted still further with water. Most of the excess of acid is then neutralized with sodium hydroxide, after which about two pounds of barium chloride per ton of ore is added and the liquid thoroughly stirred. The radium and barium are next precipitated by the addition of a suitable quantity of sulfuric acid, agitated, and the radium and barium sulfate allowed to settle in conical-bottomed tanks. The solution is allowed to settle three to four days, after which the liquor is siphoned off and treated further for the recovery of the secondary products, uranium and vanadium. The radium-barium sulfate in the bottom of the tank is transferred to earthenware suction filters, filtered, and the cake thoroughly washed. The high-grade radium-barium sulfates thus obtained are dried and delivered to the crystallizing department for further treatment.

Recovery of uranium and vanadium. The liquors containing the uranium and vanadium which are siphoned or decanted off after the radium-barium precipitation, are pumped into a tank containing an excess of boiling sodium carbonate solution, where the iron, calcium and most of the aluminum are precipitated and the uranium and vanadium remain in solution. The solution is then boiled vigorously after which the iron cake is separated by filtration. The sodium carbonate liquor is nearly neutralized with nitric acid and most of the carbon dioxide removed, after which sodium hydroxide is added to the boiling solution until the uranium is completely precipitated as sodium uranate. The precipitate of sodium uranate is then separated by filtration and the liquors are treated for the recovery of vanadium. The sodium uranate thus produced always contains from 7 to 8 per cent vanadium oxide and has to be further purified.

The hot solution from the sodium uranate is completely neutralized with nitric acid, and air is blown into the liquid to eliminate the carbon dioxide. Ferrous sulfate is then added, while the liquid is vigorously agitated, after which the precipitate of iron vanadate is filtered and washed. The grade of the product varies from 30 to 40 per cent vanadium oxide, V_2O_5, depend-

ing upon the final acidity of the solution. There is usually quite a loss of vanadium due to incomplete precipitation.

The process as outlined in Bulletin 104 of the Bureau of Mines (4) yielded a very satisfactory extraction of the radium and uranium, but in the case of vanadium the recovery was only 40 to 50 per cent. This is due to the fact that the vanadium has a tendency to separate out as vanadic acid during the initial treatment of the ore after going into solution with nitric acid. Even the addition of a small quantity of hydrochloric acid at the outset, as was later used by the Bureau of Mines (4), does not materially decrease the tendency of the vanadium to separate as vanadic acid. The costs of production of uranium, vanadium, and radium as outlined on pages 114 to 117 of Bulletin 104 (4) are exceedingly low and undoubtedly are costs which can not be maintained at the present time due to higher costs of ore, chemicals, and labor.

Like hydrochloric acid, the successful use of nitric acid for direct solution of radium is limited to ores practically free from sulfates (gypsum) and carbonaceous material. Where gypsum is present too high a percentage of the radium and barium precipitate out and remain in the residues. The presence of more or less carbonaceous material is objectionable as the mechanical difficulties are very much increased by violent frothing when the acid and ore are mixed, resulting from the oxides of nitrogen set free.

In this process a good part of the nitric acid in the liquor is finally recovered as sodium nitrate from which the comparatively expensive acid can be regenerated.

c. Sulfuric acid.—Otto Paul Bredt (6) proposes treating successively with concentrated sulfuric acid as a method for the direct solution of radium and barium from virgin ores. He then precipitates the radium and barium by dilution of the acid liquors and proceeds to concentrate the radium by treatment of the precipitated residues with a limited quantity of concentrated sulfuric acid to dissolve the sulfates present that are more soluble than radium.

H. Schlundt (5), (7), has applied the fact that boiling hot concentrated sulfuric acid is a solvent for barium sulfate in devising a method for the extraction of radium from carnotite ores. He has found that above 90 per cent of the radium may be extracted by treating carnotite ore with twice its weight of hot 60° Baumé acid. The radium may be recovered from the solution by diluting the acid with ten-fold its weight of water and allowing the radium and barium sulfate to settle from three to four days, after which the supernatant liquors, containing the uranium and vanadium may be separated by siphoning. The radium-barium sulfate obtained is of a high degree of purity and is ready for delivery to the crystallizing department.

1B. Solution in Acid after Conversion of the Radium and Barium to Acid Soluble Form as Carbonates.—Evidently, several investigators have attempted to convert the radium in virgin ores into a form which would be readily soluble in a fairly dilute solution of acid. Among the earliest experimental work along this line is probably that of Haynes and Engle (8). The object of their process is primarily the recovery of uranium and vanadium, for at the time the patent was taken out there was little or no interest in radium. The process involves the boiling of the ore, which has been crushed

to 12 mesh, with a solution of sodium or potassium carbonate until both the uranium and vanadium are dissolved. The strength of the carbonate solution and the length of time required for boiling are determined by the proportion of uranium and vanadium in the ore. The originators claim that 100 pounds of sodium carbonate per ton of ore for each 1 per cent of uranium and vanadium or either, present, will give good results. The time required for boiling should be about one hour. The solution is then separated from the residues and the uranium and vanadium recovered from the solution.

F. Ulzer and R. Somner (9) have devised a method for the production of crude sulfates enriched with radium. They propose to treat the radium-containing material with hot concentrated sulfuric acid or else fuse with acid sulfate, followed by washing with water and filtration. The residue so obtained is then treated under increased pressure with alkali or alkali carbonates or mixtures of the two, or it may be fused with the alkali carbonates. The residue after washing and treating with dilute sulfuric acid produces a crude sulfate enriched with radium.

Warren F. Bleecker (10) proposes to take the residues obtained from a procedure such as that outlined by Haynes and Engle and dissolve out the radium with dilute acid, preferably hydrochloric or nitric. The radium together with the barium may be recovered from the acid solution in a fairly high degree of purity by precipitation with sulfuric acid. The leaching of the residues with acid increases the extraction of uranium and vanadium over the method proposed by Haynes and Engle.

Another patent was issued to Bleecker (11) covering some modifications of the process outlined. Under the later patent the ore is boiled with a solution of an alkaline hydroxide, and, if desired an alkaline carbonate solution may be added. After leaching the ore with alkaline hydroxide for the removal of the vanadium, it is treated with an alkaline carbonate for the removal of the uranium. The residue, after thorough washing to remove the carbonates and sulfates is leached with an 8 per cent hydrochloric or nitric acid solution. The radium and barium may be recovered from the acid solutions by precipitation as the sulfates.

In the fall of 1922 a third patent (12) was issued to Bleecker in which he proposes to treat radium-bearing ores in a finely divided condition with an alkaline carbonate and a liquid at a high temperature and under pressure, after which the residue is treated with about 25 per cent of hydrochloric acid of 16° Baumé, for solution of the values.

William A. Schlesinger (13) proposes a method essentially the same as that proposed by Bleecker (12). One ton of the ore to about 30 per cent soda ash (by weight) is treated under pressure to render the sulfate radical in the ore acid soluble. The residue is then thoroughly washed and the radio-active constituents extracted by suitable means.

While we are not dealing with the recovery or extraction of radium from pitchblende, still it is of interest to note that the first radium produced in any quantity was extracted by fusing pitchblende ores with sodium sulfate. The method was originally used by the Austrian Government for treatment of their ores obtained from government mines at St. Joachimstahl. The fusion with sodium sulfate converts the uranium into sodium uranate, which is

readily soluble in dilute sulfuric acid. The radium remains with the residue, and prior to its discovery these residues were discarded.

Haitinger and Ulrich (14) have described quite fully the recovery of the radium from the residue and the method as outlined by them is essentially the one which the Austrian Government used for the extraction of the radium from its pitchblende residues. The process is long and tedious, and can hardly be classified as a modern method for the extraction of radium from even pitchblende ores, therefore details will be omitted here. A good abstract appears on p. 21, Bulletin 104, U. S. Bureau of Mines, and full details are given by Haitinger and Ulrich (14). Briefly, the process consisted in boiling the residues with sodium hydroxide, separation of the solution by decantation and washing the residues by decantation also. The residues thus obtained were then boiled with dilute hydrochloric acid, the liquors again separated by decantation and the residues washed. The residue from the hydrochloric acid leach was next boiled with sodium carbonate, leached with acid, and this operation repeated as many as three times, or until the residues were practically free from radium. The various hydrochloric acid extracts were combined and the radium precipitated as the sulfate. The sulfates were reconverted into carbonates by repeated boiling with sodium carbonate solution and the radium was then again taken into solution in dilute hydrochloric acid. The lead was removed next by precipitation with hydrogen sulfide, after which the liquors were evaporated to dryness. The residues obtained from evaporation were dissolved in concentrated hydrochloric acid. The most of the radium and barium chlorides (which are only slightly soluble in concentrated hydrochloric acid) remained as a residue, which was finally dissolved in water and the radium concentrated by fractional crystallization.

2A. Concentration of Radium by Direct Solution of Gang Material.— Solution of the gang material, which consists principally of silica, may be accomplished by fusing the ore with an excess of either soda ash or caustic soda, or a mixture of the two, whereby the silica is rendered soluble in water. After fusion the melt may be either allowed to cool and then dissolved in water or the hot melt poured directly into a large excess of water which is vigorously agitated. The sodium silicate goes into solution forming water glass and the carbonates of radium, barium, iron, calcium, magnesium, etc., may be separated from the solution of water glass by filtration. With some types of ores the carbonates obtained are of a high enough purity for direct delivery to the crystallizing department, but usually they require further purification. This may be accomplished by dissolving the carbonates in a dilute acid and precipitating the radium and barium by the addition of sulfuric acid or Glauber's salt. The method does not lend itself to commercial application at the present time as the cost of chemicals required is prohibitive. However, during the earlier periods of the commercial production of radium and at a time when soda ash could be purchased at a much more reasonable price than now the method was used to some extent.

Otto Paul Bredt (15) proposes a method primarily for the concentration of radium residues, which falls under this classification. He proposes the fusion of the radium residues with insufficient alkali to convert all the radium and barium to the carbonates, and he states that the material not converted will consist largely of radium. By repeating the fusion procedure,

the author claims that it is possible to produce a radium product of high purity.

2B. Breaking Down Ore with Acid or Nitre Cake Followed by Sliming off Values.—In view of the fact that the methods whereby either the radium is taken into solution, or the gang material is completely removed from virgin ores require a large quantity of chemicals, a number of methods have been devised for making a chemical concentration of the ore which claim a saving of this item. In most of these methods concentrates are first obtained by chemical treatment of the ore. The radium is then separated from the concentrates by either solution of the radium or the gang material. Under this caption we shall refer to a number of methods for production of a concentrate, containing most of the radium that was in the virgin ore, and weighing from one-eighth to one-twelfth of the original weight of ore.

Fleck, Haldane and White (16) have devised a method primarily for the extraction and recovery of uranium and vanadium from virgin ore, but the process also lends itself to a fair recovery of radium. The process in general consists in agitating ore, which has been ground to 20 or 40 mesh, with 15 to 20 per cent sulfuric acid solution, and enriching this solution by treating a second batch of fresh ore with the acid from the first batch. The solution is thus enriched in its uranium and vanadium content to the desired strength, after which it is separated from the residues and the remaining uranium and vanadium values in the ore are removed by washing with dilute sulfuric acid. For the recovery of radium, the residues may be agitated with water and after the larger part of the coarser material has settled, the slimes may be separated by decantation, and allowed to settle. The slimes may then be separated from the liquors by again decanting, and the radium recovered from the sediment by one of the standard methods described below. The method as outlined by the authors, in all probability does not give a very high yield of the radium content, but the recovery will depend quite materially on the type of ore treated.

H. N. McCoy (17) has devised a method which involves the treating of carnotite and similar ores with either dilute or concentrated sulfuric acid to form a mud, raising the temperature at first to 100° C. and finally to 300° C. or higher if necessary to produce a solid mass when cold. The mass is ground and leached with water which dissolves out the vanadium, uranium, iron, etc. By sliming off the liquors containing the soluble salts most of the radium will be obtained in the slimes, which may be separated from the liquors by allowing them to settle and then decanting.

H. Schlundt (18), also Loomis and Schlundt (19) have devised and studied a method of heating ore with hot 60° Baumé sulfuric acid for disintegration, followed by dumping the mass while hot into a large excess of water violently agitated. The solution containing the uranium and vanadium, together with the slimes and radium values are then decanted, and the liquor separated from the solids by filtration or other suitable means.

Schlundt (19), (20) has also utilized the by-product, nitre cake, from the manufacture of nitric acid as a source of supply for sulfuric acid. The commercial grade of nitre cake, which is normally sodium acid sulfate, contains from 30 to 33 per cent of free sulfuric acid. By fusing the crude ore with two to three times its weight of nitre cake it is possible to quite thoroughly

disintegrate the ore and convert the radium and barium present to the sulfates. The fused mass may be either allowed to cool, ground and lixiviated with water, or dumped while hot into water vigorously agitated. After digestion for a few minutes, the coarser particles are allowed to settle and the liquors containing the uranium and vanadium in solution, fine slimes, and finely-divided radium-barium sulfate are separated by decantation. The coarse residue is washed at least two times with water and the decantation repeated to remove the last traces of uranium and vanadium as well as the slimes containing the radium and barium sulfate. A concentration of from eight to twelve times is obtained, containing from 85 to 95 per cent of the radium, practically all of the uranium and from 90 to 97 per cent of the vanadium.

Radcliffe (21) has a method which is applicable to certain types of uranium-bearing ores, containing a much larger percentage of thorium than the average ore from either Colorado or Utah. The ore upon which Radcliffe worked is amenable to magnetic concentration and he then fused these concentrates, which represent about 30 per cent of the weight of the original ore with three times their weight of nitre cake in a reverberatory furnace. The fused mass is crushed to pass an 8-mesh sieve and put into wooden vats equipped with agitators. Cold water is fed continously into the vats at the bottom, and an overflow is provided at the top. By proper adjustment of the flow and agitation of the water it is possible to remove the finer material, consisting principally of silica, together with the radium and barium sulfates, in the overflow liquors. After allowing the slimes to settle for twelve hours in lead-lined vats the liquor is separated and treated for the recovery of uranium and vanadium. Radcliffe proposes to further treat the slimes with half their weight of concentrated sulfuric acid and allow to stand for several days, which quite materially reduces the bulk of slimes. The slimes are separated from the liquors by filtration, washed by decantation and treated further with sodium carbonate in steel boilers. The radium and barium as carbonates are dissolved out in acid and precipitated as high-grade sulfates with sulfuric acid. It is sometimes necessary to give the slimes a second treatment with sodium carbonate to completely remove the radium.

H. D. d'Aguiar (22) outlines a method whereby the ore is wetted with water and then treated with sufficient hydrochloric acid to take into solution the values of uranium, vanadium and radium. Sufficient sulfuric acid is then added to precipitate the barium, calcium, and radium, the mass diluted with water, digested, and the heavier sands allowed to settle. The fine material, consisting of finely divided silica, radium-barium sulfates, etc., is decanted off and the concentrates separated from the solution by filtration. The concentrates or slimes so obtained are then treated in pressure kettles with sodium carbonate solution to convert the radium and barium to a form soluble in acids. After filtration and thorough washing to remove the sulfates and free carbonates the cake is treated with dilute hydrochloric acid, which takes the radium and barium into solution. The author states that it is usually necessary to re-treat the residues after the acid leach as the radium content is too high to warrant discarding. The residues are accumulated for a period of time and then re-treated in the pressure kettles as described above.

J. H. Burfeind (23) has devised a method for the extraction of uranium, vanadium, and radium from ores by treating the ore with an aqueous solution of sulfur dioxide to dissolve the uranium and vanadium and convert the radium-bearing constituents of the ore into an amorphous mud. The uranium and vanadium may be separated from the solutions and the radium from the mud by standard methods.

L. F. Vogt (24) proposes the treatment of carnotite ore by roasting in air or steam, with subsequent leaching with water and sulfuric acid to dissolve the uranium and vanadium. The author proposes to fuse the residues containing the radium and barium with sodium carbonate, leaching with water, and then with hydrochloric acid to dissolve out the radium and barium. The radium and barium are then recovered as a high-grade sulfate for delivery to the crystallizing department.

Inasmuch as the methods proposed above for the extraction and recovery of radium nearly all involve the production of a slime, it will be necessary to consider the methods which may be used for separating the radium from the slimes produced. Generally the same methods of procedure may be applied to the slimes with slight variations as to the original ore.

2Ba. Volatilization of the silica in the slimes.—The slimes usually consist principally of silica, and compounds of iron, calcium, magnesium, and vanadium. H. N. McCoy (25) has proposed the use of hydrofluoric acid for the removal of the silica in slimes obtained by his process (pp. 14). It may be stated that the slimes obtained according to the method outlined by McCoy are practically identical to those obtained by the methods of others: H. Schlundt (20), H. D. d'Aguiar (22), and Radcliffe (21). McCoy proposes the treatment of 220 pounds of the concentrates or slimes with 200 pounds of water mixed with 20 pounds of concentrated sulfuric acid and 900 pounds of 30 per cent aqueous solution of hydrofluoric acid to furnish a sufficient proportion of hydrogen fluoride to combine with the silica present. The mass is stirred for three to eight hours to complete the reaction. The undissolved residue which usually weighs about 20 pounds contains practically all the radium together with the sulfates of calcium and barium.

2Bb. Solution of the silica in the slime.—The slimes or concentrates may be fused with an excess of caustic soda or soda ash or a combination of the two to render the silica soluble in water. The melt may be allowed to cool and then digested with water, or poured while hot into water vigorously agitated. The carbonates of radium, barium, calcium, iron, etc., may be separated by filtration, thoroughly washed for the removal of soluble carbonates and sulfates and then dissolved in sulfate free hydrochloric acid. It has been found that the costs of chemicals may be somewhat lessened by not fusing the original slimes or concentrates with an excess of caustic or soda ash, as is necessary to render all of the silica soluble, but to use only enough alkali to yield a molten mass at a temperature of 600° to 800° C., and then pour the melt into a tank of water as before. The insoluble material may be separated and treated with dilute boiling acid, preferably sulfuric, which materially further reduces the bulk. The residues of sulfates thus obtained are again fused with a mixture of soda ash and caustic soda and treated as above. The final sulfates obtained under a procedure such as this are usually of high enough purity to warrant delivery to the crystallizing department.

2Bc. Solution of the radium in slimes by acid.—Neither nitric nor hydrochloric acids have proven to be very satisfactory for dissolving the radium out of slimes or concentrates obtained by the several methods described above. Under very favorable and carefully controlled conditions it is possible to get a fair recovery by the use of nitric acid, while hydrochloric acid has proven to be entirely unsatisfactory. However, the mechanical difficulties in filtering a nitric acid solution of the concentrates makes the method unsatisfactory for commercial application.

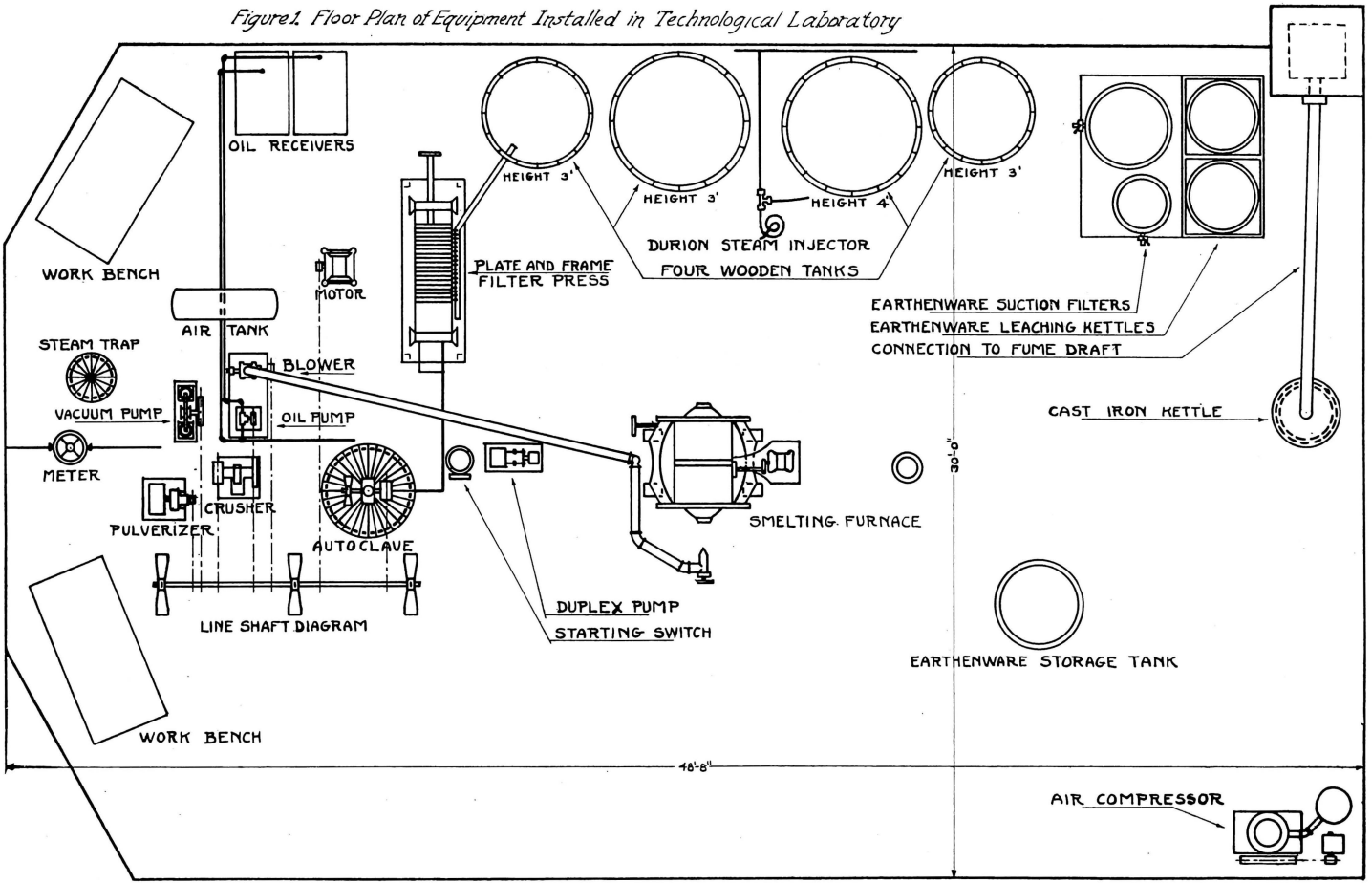
Sulfuric acid has been used to some extent for the extraction of radium from these slimes with a fair amount of success so far as the percentage recovery is concerned. The principle of the use of sulfuric acid on the slimes or concentrates is the same as that applied by H. Schlundt (5) to the extraction of radium from carnotite ores with concentrated sulfuric acid. While the method is capable of yielding satisfactory results as far as the recoveries are concerned, still the mechanical operation and difficulties encountered are so bad that the method has not found much favor. One commercial concern in the eastern part of the United States attempted to use the method for a time, but eventually gave it up on account of the mechanical trouble involved as well as the difficulty in getting the workmen to perform the required operations on account of the sulfur trioxide fumes.

2Bd. Solution of radium after conversion into form soluble in acids, generally carbonates.—As previously stated, it is possible to convert the radium in virgin ores into a more soluble form by boiling with a solution of sodium carbonate at either atmospheric pressure or under higher pressures. The problem of extracting the radium from the slimes or concentrates by means of a carbonate boil has doubtless been more or less carefully studied, but the data and results obtained have never been published. The method consists in boiling the slimes or concentrates with a mixture of sodium carbonate and caustic soda under pressure, separation of the mother liquor by filtration, and subsequent washing of the cake to remove the last traces of sulfates. The radium-barium carbonate is then leached from the cake by boiling with dilute hydrochloric acid and filtering off the solution. The radium and barium may be recovered in a high degree of purity by precipitation from the hydrochloric acid solution with sulfuric acid. In many instances it has been found that the residues contain too large an amount of radium to be discarded and often have to be re-treated as suggested by H. D. d'Aguiar (22).

3. Miscellaneous Methods for the Recovery of Radium.—Erich Ebler (26) has devised a method for separating radio-active compounds from liquids by the addition of colloidal silica, and violently mixing, whereupon the silica absorbs the radio-active products. The colloidal silica which has absorbed the radio-active compounds is then separated from the liquid and the radio-active constituents recovered by some suitable procedure.

Danforth, Samuels, and Martersteck (27) propose the subjection of complex refractory carnotite ores to a plain oxidizing roast followed by treatment with a strong solution of warm sulfuric acid to remove practically all of the uranium and vanadium from the sands and to fix the radium as the sulfates which remain with the residues. The radium may be subsequently recovered from the residues and the uranium and vanadium from the acid liquors.

Figure 1. Floor Plan of Equipment Installed in Technological Laboratory



GENERAL DESCRIPTION OF EQUIPMENT AND INSTALLATION

A technological laboratory was equipped with the apparatus and machinery required for an efficient study of the various commercial processes for the extraction of radium. In the installation as well as the selection of apparatus, there has been an endeavor to equip a technological laboratory that will be of general service to the University as well as for the study of problems in applied chemistry. The floor plan, Figure 1, shows the general arrangement of the equipment.

The equipment installed may be grouped under five main heads, as follows: (1) General, (2) equipment for treatment with acids, (3) equipment for operations with alkalis, (4) miscellaneous equipment and (5) equipment for crystallization of radium.

(1) General.—All of the apparatus requiring power for operation was driven from one line shaft, which in turn was operated by a five H. P. motor. While it would have been more desirable to have had some of the machines individually driven, the funds available imposed restrictions. The grinding and crushing equipment consisted of one small Braun jaw crusher of the usual type and one Braun disc pulverizer. While this equipment is better adapted for handling laboratory samples rather than material on a semi-plant scale, it was nevertheless found serviceable. Connections were made with the air compressor of the Chemistry Department, and a small vacuum pump equipped with a receiving tank and necessary accessories was installed. These additions to the existing equipment of the room made available for use with each unit tap-water, distilled water, gas, steam, air, and vacuum.

(2) Equipment for treatment with acids.—Two acid-proof stoneware leaching pots with round bottoms were installed as boiling pots for treatment of ore with acids. The pots, surrounded by hay as packing material to hold them firmly in position were housed in boxes and mounted on elevated platform. One of the plots had a capacity of 24 gallons and the other 37. In the larger one charges of ore up to 100 pounds could be treated at one time. Water, air, and steam lines were brought to convenient points above the platform.

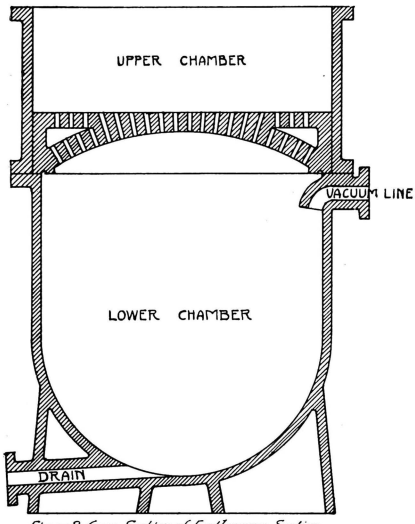


Figure 2. Cross Section of Earthenware Suction Filter

For filtration of the acid solutions from the pots two acid-proof stoneware suction filters, Figure 2, were set up nearby on a lower level so that the contents of the pots could be siphoned directly onto the filters (see plate 1). The larger filter had a capacity of 45 gallons, upper and lower chambers, while the smaller had an upper chamber of 11 gallons and a lower holding 22. For

a filtering medium, duck asbestos filter cloth, encircled by sand as described in Bulletin 104, U. S. Bureau of Mines (4), was used.

By exercising moderate caution these stoneware units give satisfactory service, withstanding the heat shock when live steam is passed into a mixture

PLATE NO. 1. LEACHING POTS, BOXED, AND SUCTION FILTERS.

of ore and acid, and conversely, when cooled from the boiling point of 38 per cent nitric acid by running in cold water.

For the storage of acid liquors and precipitation, conical acid-proof stoneware pots, 110 gallons capacity, were slightly elevated and set at a dip so that the contents drained completely from the outlet. A large cast iron kettle served for cooking ore with concentrated sulfuric acid, and sodium bi-sulfate.

Minor accessories included stoneware jars and buckets, wooden and fiber pails, and dippers.

(3) Equipment for operations with alkali.—Since most of the processes using alkali leaches on the ore were conducted under pressure, an autoclave, Plate 2, was installed. A seamless steam-jacketed cast-iron kettle equipped with a bolt-on cast iron cover was selected for these experiments. It had

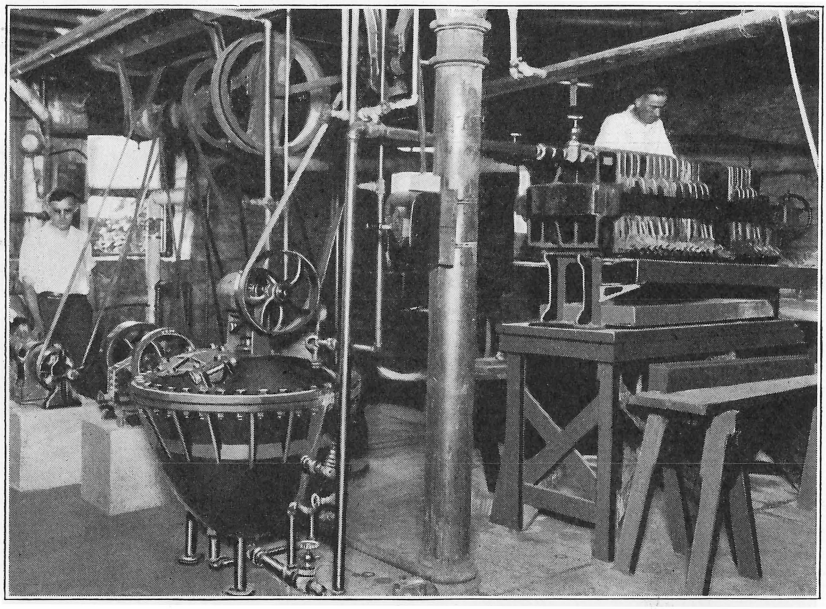


PLATE NO. 2. AUTOCLAVE AND FILTER PRESS.

a capacity of 50 gallons, and was equipped with a bridge type stirrer attached to a driving mechanism. It may be connected for pressure or vacuum. The autoclave had a man-hole plate in the cover for charging and cleaning and was equipped with pressure and vacuum gauges. Besides the jacket, steam could be introduced at the top or at the bottom of the apparatus.

The outlet at the bottom of the autoclave was connected by means of a 2-inch iron pipe to a filter press, (Plate 2). It is further described technically as a square, corner feed, two-eyed, open delivery, washing, flush plate and frame filter press. The press contained 18 frames, each 18 inches by 18 inches, and was also equipped with a dummy plate, so that it was possible to utilize only such a portion of the press as was desired. The press was equipped for back-washing as well as for air drying. It was mounted on an elevated platform so that the discharge liquors ran by gravity into a series of wooden tanks.

Evidently, the direct connection of the autoclave to the filter press utilizes the autoclave as a blow case, thereby doing away with the use of a pump or a supplementary blow case for charging the press. However, for washing, a small duplex steam pump was connected into the feeder line of the press, to force wash waters through the press when charged.

(4) Miscellaneous equipment.—Four circular wooden tanks, low form, were included in the equipment: 1 redwood and 1 cypress, each 3′ x 4′, 204 gallons; 1 redwood 3′ x 5′, 316 gallons; 1 fir 4′ x 5′, 444 gallons. The tanks were elevated about one foot from the floor and set on a slight incline to make them easy to drain. Steam, air, and water connections were made available for use in all of the tanks.

For transferring solutions from one receptacle to another a 1-inch Duriron steam injector was installed.

For roasting ores prior to chemical treatment the furnace shown in Plate 3 was installed. The furnace was equipped with both rotating and tilting mechanisms and was heated by means of an oil blast burner. For some

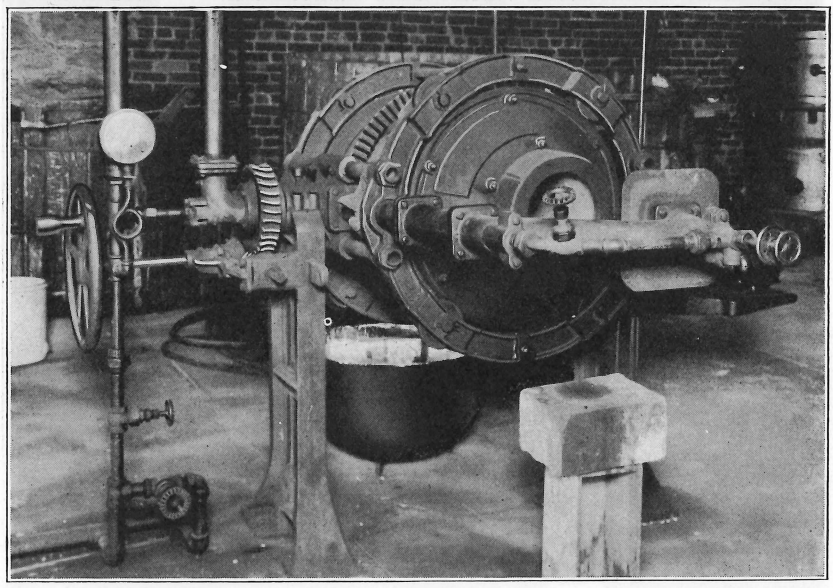


PLATE NO. 3. SMELTING FURNACE.

uses this furnace would doubtless be ideal, but it was not well adapted for the experiments on roasting we had projected.

(5) Equipment for crystallizing radium.—One of the smaller rooms in the basement of the Chemistry Building was equipped for crystallization. While the equipment installed was neither extensive nor particularly unique, it served well for the amount of crystallizing which was done in connection with this work.

The evaporation of the plant liquors containing the radium and barium as chlorides, and the earlier fractionations were conducted in a series of glass enameled evaporators which consisted of two 10 gallon steel pots shown on Plate 4, and three 10 gallon cast-iron pans, also shown in Plate 4, loaned by the Welsbach Company through the courtesy of Dr. H. S. Miner. As the concentration of the radium increased large porcelain evaporating dishes graduating to smaller sizes were used for the crystallizations.

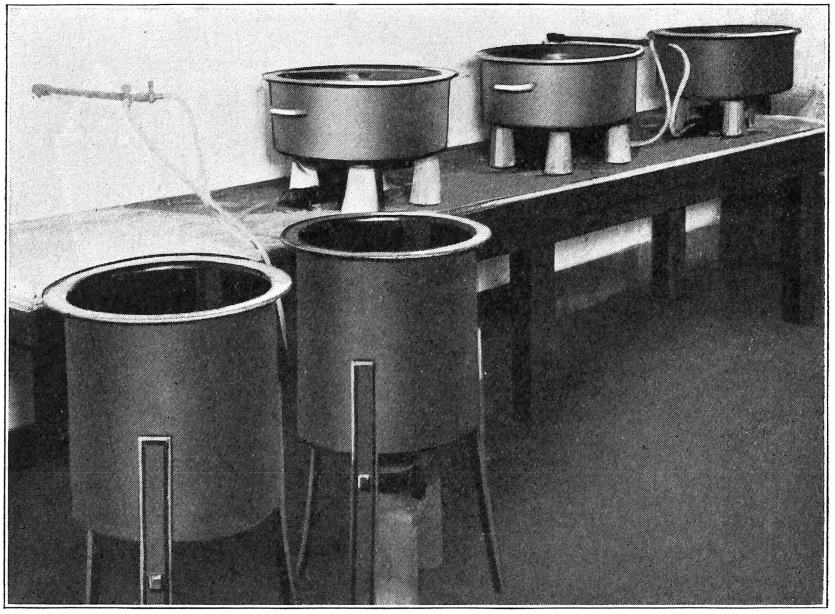


PLATE NO. 4. STEEL AND CAST IRON, GLASS ENAMEL EVAPORATORS.

After conversion of the values into bromides, porcelain dishes were used for a time but most of this work was done in fused silica ware, shown on Plate 5.

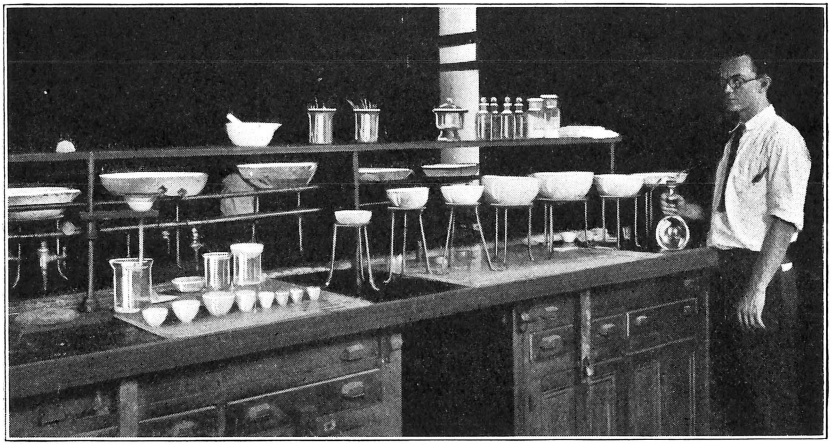


PLATE NO. 5. BROMIDE CRYSTALLIZING SYSTEM.

For the fractionation of very high-grade bromides small transparent silica dishes were used, and the solution of the crystals and evaporation were conducted on a water bath.

OCCURRENCE OF CARNOTITE ORES

The main producing areas in the United States are to be found in southwestern Colorado and southeastern Utah. In fact, the area may be completely included in a huge elipse whose major axis extends ninety-five miles west and thirty miles east from the La Sal Mountains, which are located in southeastern Utah very close to the Colorado border. Limiting it more definitely, the northern boundary starts in Utah and includes Green River, Thompson, and Cisco and continues east and slightly to the south to the Utah-Colorado border where the Dolores River crosses, and continues up the river to Gateway. From this point the boundary is drawn east to the foot of the Uncompahgre Plateau and thence southeast to include what is known as the Grub Stake Camp on Mesa Creek. The line then runs a little east of south to the mouth of Tabequatch Creek and thence south into East Paradox Valley, passing east of Thunderbolt Camp. From this camp the boundary runs southwest around the head of Gypsum Valley and Klondyke, and thence southeast to the canyon of the Dolores River, from which point it runs west to the edge of the state and continues toward Monticello, Utah, to include the deposits along the edge of Dry Valley, and thence west toward the junction of the Grand and Green rivers, and thence southwest to include the Henry Mountains. It is then extended west and north around the San Rafael Swell and joins the points including Green River, Thompson and Cisco. The region is shown in Figure 3, which is drawn to scale.

The above description of the carnotite fields of Utah and Colorado as well as the geology of this region has been compiled largely from the following sources: a report by R. C. Coffin (28) on the Radium, Uranium and Vanadium Deposits of Southwestern Colorado; a professional paper by H. E. Gregory (29), on the Navajo Country; a professional paper by B. S. Butler (30), and an article by Frank L. Hess (31), on Uranium-Bearing Asphaltite Sediments of Utah. Carnotite is by no means limited to the area outlined, but any deposits found occurring in other regions have not produced ore in commercial quantities.

The geology of this region throws some light on the physical characteristics of the ore deposits. Four formations are exposed in the region, namely, Dolores, La Plata, McElmo, and Post McElmo. The Dolores formation belongs to the Triassic system and consists of 1000 feet or more of shale and sandstone, with a massive bed near the top. The La Plata formation belongs to the Jurassic system. It consists of one, and in most places south of the Paradox Valley, of two massive cross-bedded sandstones which are separated by a few feet of shaly sandstone or limestone. The McElmo formation, which belongs to the Cretaceous or Jurassic system, is from 700 to 1000 feet thick over a goodly part of the area. It contains at least four and in most places five bodies of very resistant sandstone, separated by layers of shale or limestone.

The Post McElmo formation belongs to the Cretaceous system, and occurs persistently at or near the base of the McElmo formation. The underlying rocks are less resistant sandstone and shales.

With but few exceptions, one of which will be presented later, all occurrences of uranium-bearing ores in the territory mentioned have been limited

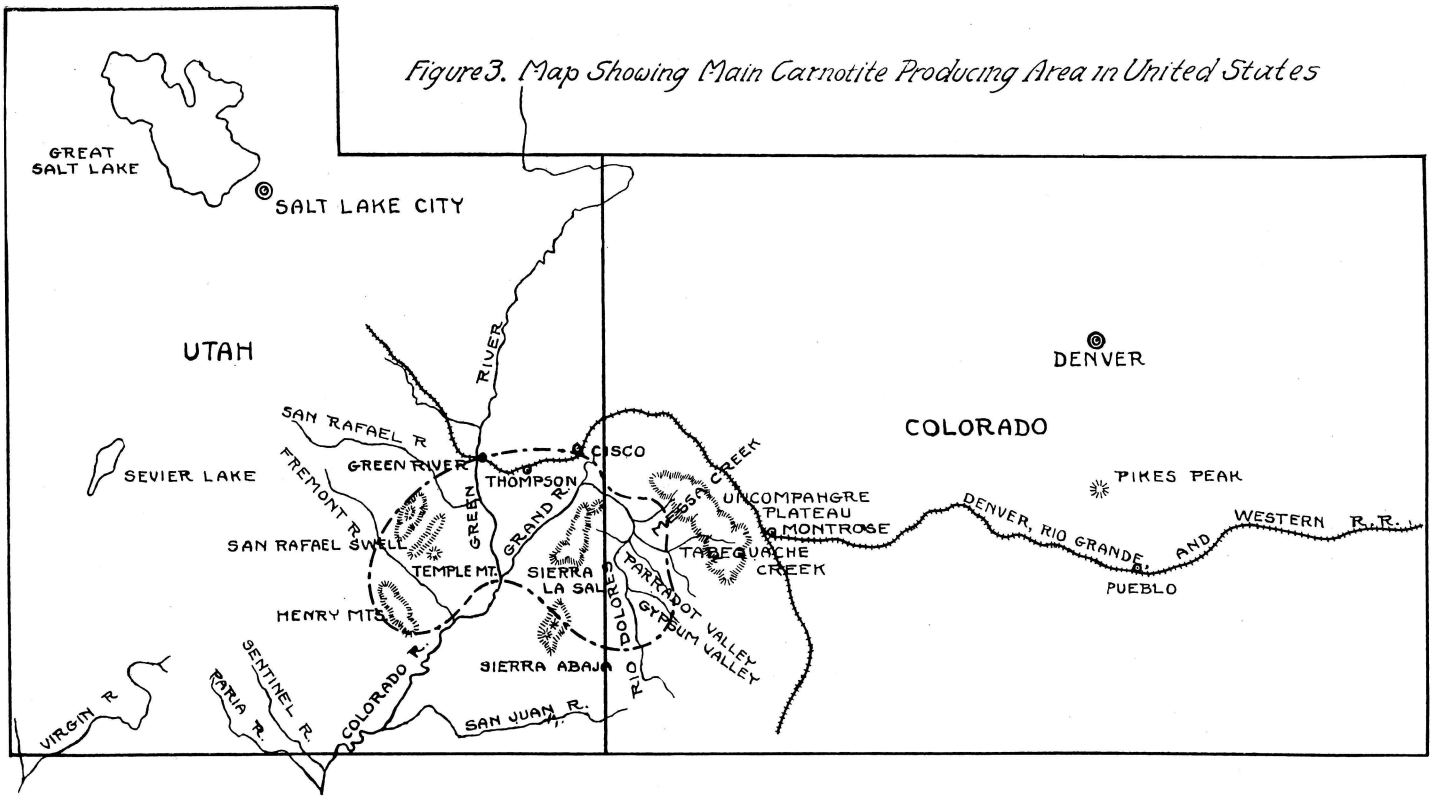


Figure 3. Map Showing Main Carnotite Producing Area in United States

to the McElmo formation, and for the most part in two zones, an upper one from 275 to 325 feet above the base, and a lower one from 60 to 125 feet above the base of the formation. The outcrop of these beds is so constant wherever they are horizontal that a generalized section represents conditions in many places, Figure 4. It does not necessarily follow that the ore

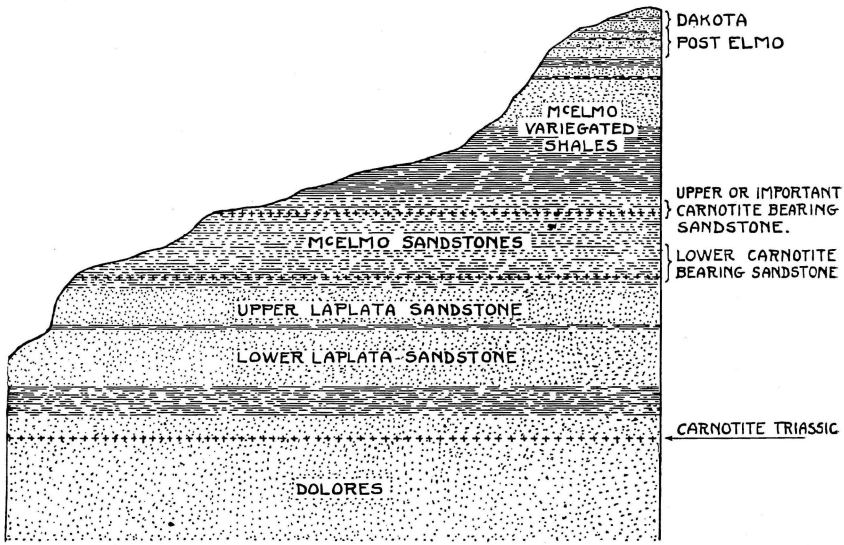


Figure 4. General Section of Strata, Showing Relation of Carnotite Zones

will be found in both zones in the event that it is found in one, although it is often found at two or more zones within the same bed.

The upper limit of the important producing zone approximates the dividing line between the easily eroded shale portion of the formation above, and the resistant sandstone portion below. This arrangement brings many ore bodies near or at the top of the bench which results from the uneven weathering of this formation. The position of the lower productive zone is easily followed, and its location with respect to the base of McElmo is nearly constant. This zone, which is made up of massive beds of sandstone separated by lenses and seams of shale, includes the first prominent bed above the La Plata formation. This bed comes within the limits assigned, from 60 to 125 feet from the base of the formation.

Whether or not carnotite exists in formations above the sandstone of the McElmo formation awaits further investigation. The existing surveys have not revealed the occurrence of carnotite in commercial quantities at higher levels.

However, in formations below the McElmo the vanadium-bearing minerals found in the Chinle formation (Triassic) of the Navajo Country (29), and the vanadium ore in the La Plata formation at Placerville, and the uranium-vanadium deposits (30) in the Triassic shales of the San Rafael Swell suggest that some of those formations, particularly the Triassic, are productive.

Frank L. Hess (31) devotes the major part of his work to the discussion of the Temple Mountain of Utah, and he states that the uranium and vanadium deposits are with one exception in the Asphaltite and therefore mostly in the Shimarump (Upper (?) Triassic) Conglomerate. Most of the commercial ore coming from this section has been produced from the South Temple Wash and the North Temple Wash, a short distance from the point where the Shimarump passes under the debris. On the North Temple Wash workings, uranium and vanadium ore have been found in the white sandstone interstitial deposits, which are in a soft layer of the Jurassic, probably 50 feet below the summit of the mountain.

The interesting feature about the occurrence of ore in this region is that the major part of the ore produced comes from the Shimarump (Upper (?) Triassic) formation while the ores from all other sections of the known carnotite-producing beds of America are found in the McElmo formation. May not herein lie the real cause for the difficulty encountered in attempting to treat the ores originating from Temple Mountain by the various processes as compared with the treatment of ores from other known regions?

LOCATION OF ORE SAMPLES

In the selection of ores to be studied, an endeavor was made to get typical ores from different districts, and to include ores from the two distinct formations in which carnotite and other similar ores have been found in commercial quantities.

Inasmuch as the ore from the Temple Mountain district occurs in an older formation—the Dolores—two samples were secured. One termed low-grade ore, was not only relatively low in radium, but also low in carbonaceous content, and the other average-grade ore and rather high in carbonaceous content. In the Temple Mountain ores the uranium has apparently been deposited by chemical precipitation induced by asphaltic material in the Dolores formation, which is generally ascribed to the Triassic. One sample of ore came from the Long Park region, where the uranium occurs in the McElmo formation, which is ascribed to either the Jurassic or Cretaceous. Two other samples from the McElmo formation were studied, one from the San Rafael Swell and the other from the Polar Mesa region. Altogether, these five ores were studied. They henceforth will be designated as follows: (1) Temple Mountain Ore No. 1 (low grade), (2) Temple Mountain Ore No. 2 (average-grade), (3) Long Park Ore, (4) San Rafael Ore, (5) Polar Mesa Ore.

ANALYSIS OF ORES

About 1000 pounds of each ore sample were secured and after careful sampling the ores were analysed for the important constituents which come under consideration in processing them. The analytical results follow in Table I.

TABLE I.—PARTIAL ANALYSIS OF ORE SAMPLES.

Item	Temple Mt. Ore No. 1	Temple Mt. Ore No. 2	Long Park Ore	San Rafael Ore	Polar Mesa Ore*
Loss of wt. on ignition	11.50	18.15	3.94	6.03	3.61
Silica, SiO_2	77.44	62.03	81.32	69.54	81.21
Heavy Metals (H_2S-ppt.)	.18	.28	.13	.18	.28
Iron and aluminum as oxides	5.15	7.84	7.94	10.62	5.01
Calcium as sulfate	.54	2.64	1.49	.02	2.57
Barium as sulfate	.03	.08	1.76	.01	.15
Vanadium as V_2O_5	2.45	3.51	3.50	6.45	4.03
Uranium as U_3O_8	1.49	2.68	1.27	3.21	2.04

*The Polar Mesa ore is rather unique in that the quantity of carbonates contained is comparatively high, which accounts for the marked effervescence when acid is added.

CHEMICAL TREATMENT OF ORES

The methods studied for treating the various ores are as follows: (1) Direct leaching with nitric acid, (2) direct leaching with hydrochloric acid, (3) conversion of radium, barium, etc., into carbonates by treatment with soda ash, and followed by leaching with either nitric or hydrochloric acids, (4) disintegration of the ore with hydrochloric acid followed by sliming off the values, (5) disintegration of the ore with dilute sulfuric acid followed by sliming off the values, (6) disintegration of the ore with concentrated sulfuric acid followed by sliming off the values, (7) roasting the ore prior to chemical treatment, (8) conversion of the radium, barium, etc., to oxalates by boiling with oxalic acid followed by leaching of values with either hydrochloric or nitric acids.

(1) Direct leaching with nitric acid.—The procedure described on pages 30 to 34, Bulletin 104, U. S. Bureau of Mines (4) was closely followed. The

federal bureau of mines quite thoroughly established the best conditions under which to operate this process on certain types of ores, but did not extend the investigation to include as varied a collection of ores as is represented in our list. The experimental data obtained are summarized in Table II. It will be noted, that the acid leach contained some hydrochloric acid, and was, in fact, a mild aqua regia. In stating the weights of acids used the form given in Bulletin 104, U. S. Bureau of Mines (4) has been followed. The numbers represent weights reduced to a 100 per cent basis. Sufficient water was added to give a solution containing 38 per cent nitric acid. The values for the percentage of radium extracted were obtained by analysis of the residue, while the values for percentages of radium recovered were obtained by determining the radium recovered from the acid liquors filtered off from the treated ore. The analytical methods followed are described in another section under Methods of Measurement.

TABLE II.—TREATMENT OF ORES WITH NITRIC ACID.

Item	Temple Mt. Ore No. 1	Temple Mt. Ore No. 2	Long Park Ore		San Rafael Ore	Polar Mesa Ore
Run No.	42	7	5	6	8	60
Weight of ore, lbs.	35	50	50	50	50	50
Weight of nitric, lbs.	12	17	17	17	17	16
Wt., hydrochloric, lbs.	3	3	--	3	3	2
Per cent of residue	83.7	71.6	74.0	85.4	75.8	91.3
Per cent Ra extracted	55.3	57.0	87.1	95.2	94.2	94.5
Per cent Ra recovered	----	59.5	89.0	94.6	91.5	93.2
Percent V_2O_5 extracted	88.0	59.4	75.3	79.4	76.4	76.2

For three types of ore, the radium recoveries stand in close agreement with the values reported in Bulletin 104, U. S. Bureau of Mines (4), but it is also evident that this method fails to give economical recoveries for the two types of ore from the Temple Mountain district. The low extraction of radium from these ores is doubtless due to the reducing action of the large amount of asphaltic material (31) occurring in the ore, and is not to be attributed, as some operators have suggested, to their high gypsum content, as this is no higher than that of some of the ores (see Table I) which yielded good extractions. Evidently, the nitric acid becomes too depleted in oxidizing the carbonaceous ingredients of the ore to effect complete solution of the radium.

The percentage extraction of the vanadium contained in the virgin ores is materially higher, about 25 per cent, than was found by the Federal Bureau

of Mines (page 109, Bulletin 104 (4).) Just what factor caused this difference in vanadium extraction is not apparent unless the conditions were more favorable for retaining the vanadic acid in solution than they were in the operation of the National Radium Institute.

Of the two runs reported on the Long Park Ore, one shows a somewhat higher recovery of the radium content than the other but the operating conditions were quite the same. In run number 5, however, the material had to be transferred from one filter to another which introduced delay and resulted in cooling before the filtration was complete. This delay in filtering allows time for some of the radium to precipitate and materially reduces the recovery.

(2) Direct leaching with hydrochloric acid.—The use of hydrochloric acid for leaching of values from carnotite and other uranium-bearing minerals has not found general commercial application, although this method yields satisfactory results in some instances as will be seen from the experimental data obtained and reported in Table III. The general method of procedure followed was that outlined in part on page 9 of this report. The ore and acid were cooked for about 30 minutes with live steam and then filtered while still hot. The residues were washed in hydrochloric acid first and then with distilled water.

The one ore treated by this method which yielded satisfactory results was that originating from Long Park, and for this, the extraction of both the radium and vanadium was very gratifying. The process undoubtedly has possibilities and will warrant the installation of a plant when a large body of ore of this type is available.

TABLE III.—TREATMENT OF ORE WITH HYDROCHLORIC ACID.

Item	Long Park Ore		San Rafael Ore	
Run No.	9	11	10	24
Wt. of Ore, lbs	50	50	50	50
Wt. of hydrochloric, lbs.	30	24	24	24
Wt. of nitric, lbs.	3	3	3	4
Per cent of residue	76.4	87.0	69.8	75.8
Per cent Ra extracted	90.8	88.5	53.7	51.0
Per cent Ra recovered	81.5	89.7	53.7	----
Per cent V_2O_5 extracted	89.7	87.6	77.0	84.3

(3) Conversion of the radium, barium, etc., into carbonates by treatment with soda ash, followed by leaching with either nitric or hydrochloric acids.—The underlying idea of this procedure is not of recent origin, but the experimental conditions under which the method yields satisfactory results on a commercial scale have probably been determined and applied successfully quite recently in some producing plants. Haitinger and Ulrich (14) were among the first to apply the principle to the recovery of radium from pitchblende residues that had accumulated from the processing of pitch-

blende ores for their uranium content. As mentioned before, the earlier experiments with this method in America were by Haynes and Engle (8), but they did not sufficiently establish the conditions to warrant commercial application. From the time of their experiments, about 1910, down to the present, various modifications and improvements of the application of the principle have appeared. The method as most generally practiced at this time is that covered by two patents, one issued to Warren F. Bleecker (12), and the other to William A. Schlesinger (13). It is questionable whether either of these men can be given much credit for evolving a new and unique idea for the treatment of carnotite and other uranium-bearing ores, by treatment with sodium carbonates under varying conditions of pressure for the conversion of the radium and barium to a form readily soluble in either dilute nitric or hydrochloric acids.

The earlier investigators attempted to accomplish this conversion by boiling the mixture of ore and solution of sodium carbonate under atmospheric pressure, but the time required to render a fair percentage of the radium and barium soluble in acids was long, and as a rule the operation had to be repeated several times before the values contained in the residues were low enough to justify their discard. It is easy to see that such a procedure would be tedious as well as expensive. More recently, various experimenters have tried carrying out the reaction under pressures varying from a few pounds up to pressures of 100 pounds and higher, with the object of materially shortening the time of reaction as well as rendering a larger portion of the valuable constituents acid-soluble by raising the temperature of the reaction. At the time this investigation was started it was quite generally understood that a procedure as above described was being utilized by some of the producing concerns, although no definite information or data giving details of operation, or results, had been published. Hence, some experiments were conducted by the method above described, the results of which are in part given in Table IV. It may be stated that the experiments were completed prior to the issuing of the patents to Messrs. Bleecker and Schlesinger. However, the author claims no originality for this phase of the investigation.

The treatment with sodium carbonate solution was carried out in the autoclave under pressure. To the specified amount of soda ash and caustic soda sufficient water was added for a complete solution, after which the ore was added, the man-hole plate bolted on and the operation started. The time of cooking varied from four to six hours, at temperatures between the range, corresponding from 65 to 100 pounds of steam pressure. In most of the runs the cooking was conducted by pressure steam in the jacket of the autoclave, but in some runs the steam was passed directly into the autoclave. The cooking ended, the material was transferred to the filter press while hot and washed with tap water for several hours or until only a slight test for sulfates was noticeable in the wash water. The cake was then washed for twenty to thirty minutes with either distilled water or else tap water containing a slight excess of barium chloride. When free from soluble sulfates, the cake in the press was partially dried by blowing air through it. After removal from the press, the cake was treated with a quantity of commercial hydrochloric acid (free from sulfates) equivalent to about 40 per cent of the original charge (see lower half of Table IV).

TABLE IV.—TREATMENT OF ORES WITH SODIUM CARBONATE SOLUTIONS UNDER PRESSURE.

Item	Temple Mt. Ore No. 1			Temple Mt. Ore No. 1			Long Park Ore		San Rafael Ore			Polar Mesa Ore*
Run No.	1	33	47	13	26	45	12	43	20	36	49	
Wt. Ore, lbs.	106	50	50	63	50	50	76	50	88	50	50	
Wt. of soda ash, lbs.	20	16	20	15	20	16	20	16	23	16	16	
Wt. caustic soda, lbs.	10	3.5	3	4.5	5	3.5	6	3.5	5	3.5	3.5	
Wt. hydrochloric, lbs.	32	20	20	20	20	20	20	20	24	20	20	
Per cent of residue	72	76	71	64	68	63	73	69	65	60	66	
Per cent Ra recovered	68.6	85.0	76.0	73.0	----	64.8	79.3	88.6	80.0	84.5	79.2	
Per cent Ra recovered	----	83.8	----	69.0	----	68.7	77.6	86.4	82.6	85.0	81.4	
Per cent V_2O_5 extracted	81.7	75.0	72.2	78.4	81.7	88.0	64.3	80.8	66.4	71.5	70.8	

*The ore from the Polar Mesa region was received so near the end of the investigation that it was not found convenient to conduct any experiments with it by this method.

In most experiments enough barium chloride was added to the charge at the outset so that the ratio of barium sulfate to radium element would be about one million to one. In two experiments a little manganese dioxide was added to the original charge with a view to increasing the extraction of vanadium. While a slight increase in the extraction of vanadium was observed, the effect of manganese dioxide on the yield of soluble vanadium remains not fully conclusive. While the radium extraction falls somewhat below the previous treatments, nitric and hydrochloric acid leaches for two types of ore, the Long Park, and San Rafael, still the extraction must be considered fairly good. For the Temple Mountain ore the radium extractions rather surpass the values obtained by the previous methods of treatment.

(4) Disintegration of the ore with hydrochloric acid, followed by sliming off the values. The treatment with acid prior to sliming may be accomplished in either one of two ways, that is, by adding the strong acid to the ore and mixing well after which water is added, or by making up the desired mixture of water and acid, and adding the ore to this mixture. Regardless of the preliminary procedure followed, the charges were usually cooked for about one hour with live steam, and then just prior to siphoning off the liquors and fine slimes a little sulfuric acid was added to insure the complete precipitation of any radium or barium that might be in solution.

The quantity of acid used compared to the weight of ore varied from about 20 to 40 per cent. Where the ore was wetted with the acid prior to dilution of the acid, more acid was required than otherwise. During the boiling with live steam the acid became further diluted with water in the ratio of 1 to 1½. The contents of the pots was then allowed to settle for a few minutes. The radium-barium sulfates remained in the finely-divided suspended material which was siphoned off with the liquors. The sliming operation was repeated several times. The experimental data are summarized in Table V.

TABLE V.—HYDROCHLORIC ACID TREATMENT COMBINED WITH SLIMING.

Item	Temple Mt. Ore No. 1	Temple Mt. Ore No. 2	Long Park Ore		San Rafael Ore		Polar Mesa Ore
Run No.	54	21	19	52	18	50	61
Weight of ore, lbs.	40	76	66	40	66	35	50
Weight of hydrochloric, lbs.*	15	12	10	15	12	13	15
Weight of sulfuric, lbs.	2	1	1	2	1	1	2
Per cent of residue	81.0	57.2	59.4	63.1	71.8	68.6	73.6
Ratio of slimes to heads	13.3:1	9.5:1	4.4:1	5.6:1	5.2:1	7.3:1	
Per cent Ra extracted	89.1	80.5	92.7	95.6	84.2	85.0	78.5
Per cent Ra recovered	----	77.1	94.6	--	87.5	--	----
Per cent V_2O_5 extracted	56.0	80.3	86.5	91.3	64.7	75.7	

*The acid used was 20° Baumé (sp. gr. 1.16) commercial hydrochloric.

It is interesting to note that so far as the extraction of the radium is concerned, it is equally good with the smaller amounts of acid as with the larger, although the vanadium extraction is improved by the use of a larger proportion of acid to ore.

(5) Disintegration of the ore with dilute sulfuric acid, followed by sliming off the values.—The quantity of 66° Baumé acid used in these experiments varied from about 30 to 40 per cent of the weight of ore. The ore was thoroughly wet with water after which the acid was added and the mass cooked with live steam from 30 minutes to one hour. The acid was then further diluted and the liquors and fine slimes decanted. The residues were washed three times with water and the wash waters combined with the

original liquors. When the ratio of barium sulfate to radium element in the virgin ore was less than one million to one, sufficient barium chloride was added prior to the addition of sulfuric acid to bring the ratio up to one million to one.

The data in Table VI clearly shows that dilute sulfuric acid decomposes the ore effectively and makes possible an excellent separation of the vanadium, and the radium recovered in the slimes compares very favorably with recoveries by other methods.

TABLE VI.—TREATMENT WITH DILUTE SULFURIC ACID FOLLOWED BY SLIMING OFF VALUES.

Item	Temple Mt. Ore No. 1		TempleMt. Ore No. 2	Long Park Ore		San Rafael Ore
Run No.	17	48	25	14	44	16
Weight of ore, lbs.	88	40	72	83	50	94
Weight of sulfuric, lbs.	32	13	30	30	15	35
Per cent of residue	83.9	80.5	63.3	55.0	65.2	61.8
Ratio of slimes to heads	13.0:1	14.5:1	9.9:1	5.5:1	5.9:1	7.1:1
Per cent Ra extracted	75.9	85.0	84.5	93.1	86.4	91.2
Per cent Ra recovered	----	----	85.3	91.6	84.6	85.5
Per cent V_2O_5 extracted	86.6	76.3	93.2	97.6	97.6	96.9

(6) Disintegration of the ore with concentrated sulfuric acid, followed by sliming off the values.—Instead of cooking the ore with dilute sulfuric acid, the ore is moistened with concentrated acid after which it is cooked until the mass is converted to a stiff paste. It is then shoveled or dumped into water in violent agitation, which thoroughly disintegrates the hot mass, taking into solution the acid-soluble constituents and leaving the radium and barium precipitate with the finely divided slimes. The liquors and slimes are then decanted and the residues washed as previously described.

The quantity of acid used in these experiments is proportionately much larger than where dilute sulfuric acid was used to disintegrate the ore, and the recovery or extraction of the radium is very little if any better. However, the ratio of slimes to heads is increased, which is a very important factor in considering the subsequent cost of recovering the radium from the slimes. The higher ratio is probably due in part to the more thorough disintegration of the ore with the hot concentrated acid and the solution of some of the siliceous material, which remains undissolved in the dilute acid. The experimental data obtained are given in Table VII.

(7) Roasting the ore prior to chemical treatment.—From some experiments conducted on a laboratory scale in 1920 it appeared that a preliminary roast of some ores, at least, and probably all ores altered the physical condition and constitution of the ore and materially improved them for further chemical treatment, especially where sodium carbonate was to be used for the conversion of the valuable constituents to a readily soluble form in

TABLE VII.—TREATMENT WITH CONCENTRATED SULFURIC ACID FOLLOWED BY SLIMING.

Item	Temple Mt. Ore No. 1	Temple Mt. Ore No. 2	Long Park Ore	San Rafael Ore
Run No.	30	25	35	39
Weight of ore, lbs.	35	35	35	35
Weight of sulfuric, lbs.	26	30	28	29
Per cent of residue	78.9	62.8	73.8	63.7
Ratio of slimes to heads	11.6:1	14.4:1	13.0:1	11.2:1
Per cent Ra extracted	88.0	87.9	92.2	88.2
Per cent Ra recovered	83.4	82.0	89.6	83.0
Per cent V_2O_5 extracted	87.4	93.3	94.5	91.1

dilute mineral acids such as nitric and hydrochloric. Unfortunately, the records of that work are not all at hand and complete enough for summarizing in tabular form. However, as a result of these experiments it was quite definitely established that the carbonaceous ores from Temple Mountain (Dolores formation), and ores from the Moab district (McElmo formation) uniformly gave decidedly higher extractions of vanadium and generally somewhat better extraction of the radium after having been given a preliminary roast. Considerable work was done at that time to establish the character of roast which would yield the best results. Experiments on a laboratory scale gave fine promise when finely-ground salt, to the extent of 6 per cent by weight, was incorporated with the ore and the mixture then kept at a temperature between 600° and 700° C. for about half an hour in a decidedly oxidizing atmosphere. In extending these experiments to a semi-plant scale we met with disappointment. In our hands it was found impossible to maintain the desired conditions for the roast with the furnace previously described. It was found difficult to maintain an oxidizing atmosphere and at the same time keep the temperature down to 700° C. The air blast was so strong that the ore was continually blown out the back end of the furnace. The furnace is also constructed for operating at much higher temperatures than were desired for this operation.

However, a few roasts were made on the various types of ores, both with and without salt, and the roasted ore was subsequently subjected to chemical treatment for extraction of radium, uranium, and vanadium by the various methods already described. Simple roasting without the addition of salt materially reduced the percentage extraction of radium and vanadium. Neither were the extractions bettered by roasting the ores with salt and then subjecting them to the same methods of treatment as the original ores, except by one method,—boiling the ore with sodium carbonate solution to convert the valuable constituents to an easily-soluble form. (See Table VIII.) Even here the recovery of radium runs low except with one ore, but it is interesting to note that the recovery of vanadium is quite materially better. The use of a preliminary roast has one very decided advantage

which should not be overlooked, and that is, the reduction in weight of the ore (which lowers the expense of handling the products later, and saves chemicals). These items alone would probably bear the extra expense involved in roasting the ore.

TABLE VIII.—ROASTING THE ORES BEFORE THE CHEMICAL TREATMENT.

Item	Temple Mt. Ore No. 1	Temple Mt. Ore No. 2		San Rafael Ore
Run No.	35	32	53	57
Weight of ore after roasting, lbs.	50	35	40	40
Weight of soda ash, lbs.	16	14	16	16
Weight of caustic soda, lbs.	3.5	3.5	3.0	3
Weight of hydrochloric, lbs.	20	4	16	16
Weight of residue	35.1	21.3	22.5	20.7
Per cent V_2O_5 extracted	90.0	91.6	79.2	95.0
Per cent Ra recovered	63.4	21.0	55.0	87.8

The percentage of radium recovered and vanadium extracted in Table VIII are calculated on the basis of the quantity of these materials in the roasted ores. Inasmuch as the mechanical loss during the operation of roasting was large, due to the type of furnace used, little or no significance could be attached to the weight of ore obtained after roasting compared to the original weight.

(8) Conversion of the radium, barium, etc., to oxalates by boiling with oxalic acid followed by leaching the values with dilute nitric acid or preferably hydrochloric acids.—Two outstanding facts encouraged experimentation utilizing oxalic acid in solution for conversion of radium and barium in virgin ores to the oxalates. These salts are readily soluble in dilute mineral acids, such as nitric and hydrochloric. Oxalic acid solutions, as Mr. H. F. Kriege has found in his experiments with Missouri clay, decompose the silicates in clays as completely as do the ordinary mineral acids of the same concentration.

Since carnotite ores contain clay-like constituents with which the major part of the radium becomes associated in sliming processes, some experiments were made with oxalic acid solutions to ascertain how effective this reagent is in converting the radium into readily soluble form. Most authorities are of the opinion that the valuable constituents of ores are not disseminated in the sand grains, but merely in the fine and more clay-like covering over the grains and in the cracks and crevices of the grains.

Assuming that such is the case, one would expect that oxalic acid solutions with their powerful disintegrating action on clays would be very effective in loosening radium from the sand grains. At the same time, what will be the chemical action of the oxalic acid on the radium compounds? It has been shown that sodium carbonate solutions convert radium and barium

into carbonates in accordance with the laws of mass action and the effect of temperature on chemical equilibrium. The conversion of radium and barium present in the ore, probably as silicates or sulfates, into oxalates by oxalic acid will doubtless proceed according to the same laws. But the oxalates of the alkaline earth metals are nearly four times as soluble in water as the carbonates, and in oxalic acid solution, the solubility of the oxalates is further increased. Hence, a part of the radium should appear in the oxalic acid liquors. By experiment it was found that from 10 to 20 per cent of the radium remains in solution in the oxalic acid solution from which it may be precipitated along with barium in the form of sulfates.

Several experiments were first conducted on a laboratory scale to determine the quantity of oxalic acid required and the minimum concentration to secure efficient recoveries of radium. At the outset but little attention was given to the extraction of the vanadium. Experiments with different types of ore indicated that a quantity of oxalic acid ranging from 8 to 10 per cent of the weight of the ore to be treated was most effective in converting the radium into soluble form. As a result of these laboratory experiments the ratio of ore, water, and acid finally settled upon, for the larger scale experiments, was about as follows: 100 parts of ore, 150 parts of water, and 8 to 10 parts of oxalic acid. In several experiments much larger quantities and higher concentrations of oxalic acid were used but the extractions were thereby not increased. When the quantity of acid was reduced below 8 per cent of the weight of the ore a marked falling-off in the extraction of radium resulted.

The mixture of oxalic acid solution and ore was boiled for forty-five minutes to one hour with live steam after which the residues were separated from the liquors by filtration and washed until free from sulfates. The residues were then treated with a quantity of 20° Baumé (sp. gr. 1.16) hydrochloric acid varying from 30 to 40 per cent of the weight of the original ore. The 20° Baumé acid was diluted to 15° Baumé (sp. gr. 1.10) before addition of the ore. The hydrochloric acid solution was boiled for a few minutes after which the residue was thoroughly washed. The oxalic acid liquors and hydrochloric acid solutions were then combined and the radium and vanadium recovered. The experimental data are given in condensed form in Table IX.

It will be noted that the recovery of radium in one of the runs on Temple Mountain Ore No. 1 is quite materially better than the other, even though the proportions of ore and oxalic acid are about the same. This difference is doubtless to be attributed to incomplete washing of the residues after the oxalic acid leach, and prior to leaching with hydrochloric acid. Temple Mountain Ore No. 2 yielded very poor results and doubtless for the same reason which caused the low extraction with nitric acid; namely, the large amount of carbonaceous matter present preempts the acids. It is questionable whether this particular ore will be amenable to any sort of direct acid treatment unless the ore is first given a preliminary treatment to rid it of the large amount of organic material it carries.

There is quite a variation in both the recoveries of the radium and vanadium in the two runs reported on the San Rafael ore. The proportion of oxalic acid to ore used in run 37 was quite a little less than in the case of run 34, with the result that the extraction of radium was materially de-

TABLE IX.—TREATMENT WITH OXALIC ACID.

Item	Temple Mt. Ore No. 1		Temple Mt. Ore No. 1	Long Park Ore		San Rafael Ore	
Run No.	14	46	56	41	51	34	37
Weight of ore, lbs.	35	35	35	35	35	30	35
Weight of oxalic, lbs.	2.5	3.5	4	2.5	2.5	2.5	1.8
Weight of hydrochloric, lbs.	14	14	14	14	14	12	14
Per cent of residue	79.5	65.2	50.5	76.3	65.5	65.0	69.7
Per cent Ra extracted	67.6	88.0	37.4	93.2	84.8	89.4	66.4
Per cent Ra Recovered	60.6	86.4	----	96.6	87.2	90.5	62.9
Per cent V_2O_5 extracted	74.4	74.1	74.4	64.6	60.2	76.8	84.3

creased, which result was checked by further laboratory experiments and thus establishes a minimum for the quantity of oxalic acid at about 8 per cent of the weight of the ore treated for normal recoveries of radium. However, why the vanadium extracted should be so much better in the run where the smaller quantity of acid was used, is more difficult to explain.

The use of oxalic acid unquestionably has possibilities for efficiently extracting both the radium and the vanadium from carnotite and similar ores, and the method is worthy of quite detailed and special investigation.

Sulfuric Acid for Direct Leaching of Values.—No new experiments falling under this head were conducted. The author found in repeating the experiments of Schlundt (5) on a larger scale with Temple Mountain ore that the mechanical difficulties of handling hot concentrated sulfuric acid together with the large amounts of acid required prohibited its commercial use.

Comments Regarding the Use of Sodium Acid Sulfates for Disintegration of the Ore, Followed by Sliming off the Values.—As patented by H. Schlundt (20), fusing the ore with sodium acid sulfate (a by-product in the manufacture of nitric acid containing from 30 to 33 per cent of free sulfuric acid) may be used as a substitute for either concentrated or dilute sulfuric acid in the disintegration of virgin ores, followed by sliming off the values. Sodium acid sulfate was at one time, and still is, in some localities a cheap substitute for sulfuric acid. For this reason, it was used at one time in a commercial radium-producing plant, even though the extractions obtained were no higher than treatment with sulfuric acid itself. Inasmuch as the author of this work operated the method in a commercial plant for a time on ores originating from practically all localities, no additional experiments with this reagent were considered necessary. The results obtained agree very closely with those given for concentrated and dilute sulfuric acid (Tables VI and VII). Since the industrial uses of sodium acid sulfate are growing and its cost is rising, the use of sulfuric acid itself will probably take the place of nitre cake in commercial plants.

Treatment of Slimes or Concentrates for the Recovery of the Radium Contained.—In processes involving sliming, concentrates are obtained weighing from one-fourth to one-fifteenth that of the virgin ore treated, and containing from 75 to 95 per cent of the radium in the ore. When sulfuric acid is used to disintegrate the ore the slimes contain sulfates which constitute an important factor in the subsequent treatment of such concentrates. For the further concentration of the radium in such material some of the methods applied to virgin ore often lead to the goal.

Direct extraction of the radium with acids such as hydrochloric or nitric has been found unsatisfactory, and while sulfuric acid does remove the radium directly, the mechanical difficulties make this method impractical. The use of hydrofluoric acid has been proposed for reducing the silica content of concentrates, leaving a relatively small residue containing all of the radium and barium from which radium may be recovered by one of the standard methods.

A method which has been operated successfully on a commercial scale consists of fusing the concentrate—one part, with caustic soda two and one-half parts, and soda ash one-fourth part, in a large cast-iron kettle either oil or coal fired. By dumping the fused mass directly into water and agitating, most of the silica passes into solution as water glass, while iron, radium, and barium remain in the residue as carbonates. Treatment of the washed residue with hot dilute sulfuric acid removes iron and leaves radium in the residue with the alkaline earth metal as sulfates along with un-decomposed silicates. A second and sometimes a third fusing with caustic soda and soda ash must be made to free the residue from silica before the hydrochloric acid solution of the carbonates attains the purity required for further enrichment of the radium by fractional crystallization. While the recovery of radium by this process is very high, it is too expensive and time-consuming for competitive commercial operation.

Our experiments in refining the concentrates which had been accumulated in the course of the work were confined largely to conversion of the radium-barium into carbonates by boiling with solutions of sodium carbonate under pressure and thus to render the values soluble in dilute mineral acids. Several preliminary experiments were first conducted on a laboratory scale to establish the conditions that would yield the best results. A small autoclave was constructed for this purpose by capping a piece of 4-in. iron pipe and equipping with an agitator that was driven by a small fan motor. To establish the quantity of sodium carbonate required, a series of runs was made varying the quantity from one-fourth to two times the weight of the slimes. Apparently, no advantage is gained in using the very large excess of sodium carbonate. Some of the laboratory runs in which a quantity of sodium carbonate equal to one-fourth the weight of the concentrates was used, showed quite satisfactory extractions of radium by leaching the residue with hydrochloric acid. However, as will be noted later, the experiments conducted on a larger scale did not yield as good results when the quantity of sodium carbonate was so reduced. The quantity of carbonate required, it seems, is dependent upon other factors than the radium and barium content of the concentrates. The laboratory experiments were conducted at pressures varying from 60 to 100 pounds. As a rule, a little caustic soda was also added.

It was apparent that a very vital factor in this work was thorough washing of the residues after the sodium carbonate treatment to remove the last traces of sulfates before taking the radium and barium into solution in dilute hydrochloric acid. This condition is quite difficult to obtain, especially where sulfuric acid has been used for disintegrating the ore. Special precaution must be taken in washing or a large percentage of the radium will be re-precipitated from the hydrochloric acid solution by the soluble sulfates retained in the residue. In runs where hydrochloric acid was used to disintegrate the ore, the removal of the last traces of the sulfates is not nearly so difficult.

In carrying out the experiments on a semi-plant scale the same general method of manipulation was followed as described for the treatment of virgin ores under pressure (pp. 30). The mixture of slimes, soda ash, caustic soda, and water was cooked from six to eight hours in the autoclave at pressures varying from 80 to 110 pounds. In some instances where it was found difficult to remove the last traces of the sulfates by washing in the filter press the cake was removed, put back into the autoclave and mixed thoroughly with water, again filtered and washing continued. This extra step usually accomplishes the removal of the last traces of sulfates from the residues. The treatment with dilute (1:1) hydrochloric acid for the solution of the radium was carried out in acid-proof stoneware pots and the material filtered on earthenware suction filters. In some runs the hydrochloric acid solution could be taken directly to the crystallizing kettles, but usually it was found better to precipitate out the radium and barium from solution with sulfuric acid, thereby eliminating practically all foreign substances. The matter of converting the high-grade radium and barium sulfate back to an acid soluble-form is not difficult.

It is quite probable that the residues from the hydrochloric acid leach will often require a second treatment in commercial operation to bring the radium content of the slimes down to a point that will justify their discard. When it is considered that the weight of the concentrates compared with that of the original ore is small, and that the residue after leaching is further reduced about one-half, the matter of a re-treat is not a serious objection.

The concentrates investigated on a semi-plant scale were produced by the disintegration of an ore originating from the Gypsum Valley district, where the ore occurs in the McElmo formation. The ore was cooked with dilute sulfuric acid, the liquors and slimes decanted off and the slimes separated from the liquors by filtration. The slimes were quite free from any carbonaceous material, but the quantity of soluble sulfates retained was above normal, a factor which can be greatly reduced in regular plant operation. Table X gives a summary of the data obtained on the runs made.

It is seen that the runs in which a quantity of sodium carbonate less than one-half of the original weight of material used, yielded very poor extractions of radium. Runs 58 and 62 may be considered typical of what can be accomplished on a plant scale. Other investigators report extractions as high as 95 per cent and over where equal weights of carbonate and concentrates were used. Experiments of this kind are being continued.

In Tables XI to XIII inclusive, giving the condensed experimental data obtained in processing the ores, there are two items, one giving the percentage of radium extracted, and another giving the percentage of radium

TABLE X.—TREATMENT OF CONCENTRATES WITH SODIUM CARBONATE SOLUTION.

Run No.	Weight of concentrates lbs.	Weight of soda ash lbs.	Weight of caustic soda, lbs.	Weight of hydrochloric lbs.	Per cent Radium Extracted
2	69.5	14.0	7.0	40.0	24.7
3	59.0	12.0	3.5	30.0	65.6
4	60.0	25.0	5.0	20.0	30.1
23	40.0	20.0	4.0	16.0	75.0
58	42.5	21.0	4.0	17.0	89.6
62*	92.3	30.0	4.5	30.0	88.7

*The material used in this run was the combined residues of Runs 2 and 4; which showed very low extraction of the radium contained.

recovered. The values for the former were obtained by careful alpha ray comparison of the tailings with the heads, while the values under the caption of per cent radium recovered, are based upon radium analysis of the solutions or concentrates obtained, as the case may be. In a number of instances the quantity of radium extracted and the quantity recovered apparently do not show that close agreement one is accustomed to expect in analytical results, but these discrepancies are not unusual or serious when one considers the difficulties encountered in sampling either solids or solutions containing radium.

TABLE XI.—PERCENTAGES OF RADIUM RECOVERED BY DIFFERENT METHODS.

Method	Temple Mt. Ore No. 1	Temple Mt. Ore No. 2	Long Park Ore	San Rafael Ore	Polar Mesa Ore
Nitric acid direct	55.3*	59.5	94.6	91.5	93.2
Hydrochloric acid direct	-----	-----	89.7	50.0	78.5
Carbonate Conversion	83.8	69.0	86.4	86.0	----
Hydrochloric acid - sliming	89.1*	77.1	94.6	87.5	87.5
Dil. sulfuric acid - sliming	85.0*	84.5	93.1	91.2	91.4
Conc. sulfuric acid - sliming	83.4	82.0	89.6	83.0	----
Oxalic acid acid	86.4	37.4	96.6	90.5	----

*Values are for per cent extracted rather than for per cent recovered.

The last item in the tables, designated as the per cent of V_2O_5 extracted, is based throughout upon vanadium determinations made on the residues. In making the calculations it was assumed that the quantity extracted went into solution and would be at hand in this form for recovery. At the time the runs were made the vanadium was not recovered in finished form, but was precipitated out of solution by the addition of an excess of lime and stored for future recovery.

Summary of Work.—Table XI gives a summary of the percentages of radium recovered from the different types of ores by the various methods of treatment studied. Table XII gives a summary of the percentage of vanadium extracted by the various processes.

TABLE XII.—PERCENTAGES OF VANADIUM EXTRACTED BY DIFFERENT METHODS.

Method	Temple Mt. Ore No. 1	Temple Mt. Ore No. 2	Long Park Ore	San Rafael Ore	Polar Mesa Ore
Nitric acid direct	88.0	59.4	79.3	76.4	76.2
Hydrochloric acid direct	----	----	89.7	84.3	
Carbonate conversion	81.7	81.7	80.0	71.5	----
Hydrochloric acid - sliming	56.0	80.3	91.3	75.7	
Dil. sulfuric acid -sliming	86.6	93.2	97.6	96.9	
Conc. sulfuric acid - sliming	87.4	93.3	94.5	91.1	----
Oxalic acid	74.4	74.4	64.6	84.3	

A glance at Table XI, showing the percentages of radium recovered, quickly discloses that ores originating from Temple Mountain are much more difficult to treat than those originating from any of the other sources studied. These types are probably representative carnotites from the Dolores formation. The ores from Long Park, San Rafael Swell, and Polar Mesa Regions are usually ascribed to the McElmo formation. It is evident that they are more amenable to treatment and that they are quite similar in their reaction to the different methods of treatment.

Table XIII shows the final recoveries of radium which may be obtained on the various types of ores by the different methods, assuming that it is possible to recover 90 per cent of the radium from the slimes in processes where they are produced. In all processes involving the production of slimes the radium that will be ultimately realized was calculated by taking 90 per cent of the radium in the slimes.

TABLE XIII.—FINAL PERCENTAGES OF RADIUM RECOVERED BY THE DIFFERENT METHODS.

Method	Temple Mt. Ore No. 1	Temple Mt. Ore No. 2	Long Park Ore	San Rafael Ore	Polar Mesa Ore
Nitric acid direct	55.3*	59.5	94.6	91.5	93.2
Hydrochloric acid direct	----	----	89.7	50.0	78.5
Carbonate conversion	83.8	69.0	86.4	86.0	----
Hydrochloric acid - sliming	8 .9*	69.4	85.1	78.7	78.7
Dil. Sulfuric acid -sliming	76.5*	76.0	83.8	82.1	82.2
Conc. Sulfuric acid - sliming	75.0	73.8	80.6	74.7	----
Oxalic acid	86.4	37.4	96.6	90.5	----

*Values are for per cent extracted rather than for per cent recovered.

From the above table it is observed that the methods which yield uniformly the best results on the various types of ores, are the carbonate conversion and the methods involving the production of slimes. Direct leaching with nitric acid (U. S. Bureau of Mines process) gives very gratifying recoveries of radium on ores originating in the McElmo formation, but it is also evident that this process fails when applied to Temple Mountain ores. The oxalic acid conversion followed by leaching with hydrochloric acid gave very encouraging results on all ores tried except Temple Mountain Ore No. 2. There is an important factor that should be kept in mind in considering the merits of the various processes, and that is, all processes involving the treatment of concentrates or slimes for the recovery of radium involve a much longer time factor than any of the other methods.

At the present price of heavy chemicals no one of the methods stands out above the others for cheapness of operation. The individual producer must therefore give careful consideration to such items, as type of ore, location of plant, etc., before deciding upon a method of procedure to follow. Perhaps the ideal arrangement for the most economical production of radium would be to have the plant so designed and constructed that the ore could be leached directly for its values, or subjected to one of the the sliming processes.

REFINING OF RADIUM BY FRACTIONAL CRYSTALLIZATION

In the commercial production of radium, barium, if not present in sufficient quantity in the ore, is added at early stages in the extraction to protect the radium from going into solution. The radium then accompanies the barium in successive operations until the radium and barium are recovered together in the form of high-grade sulfates. It is evident then that the second stage of operation in radium refining involves the separation of the radium from the large bulk of barium salts (usually present in the ratio of one million parts of barium to one part of radium).

In the first step of the standard method of procedure, the sulfates are converted into a soluble form. The concentration of radium from the solution then follows by successive fractionations, generally by crystallization or to some extent by precipitation.

Operating on a commercial scale, the sulfates delivered to the crystallizing department are, as a rule, nearly free from silica, iron, aluminum, and other impurities. For the conversion of the sulfates to a readily-soluble form, reduction with charcoal as described in Bulletin 104, U. S. Bureau of Mines (4), has proven to give very satisfactory results. The radium-barium sulfate is reduced to sulfide which is readily soluble in dilute hydrochloric acid. Where the sulfates are contaminated with silica, it has been found advantageous to either fuse these sulfates with a mixture of caustic soda and soda ash or boil under pressure with a sodium carbonate solution, whereby the radium and barium are converted to carbonates, a form soluble in dilute acids, while the silica is rendered soluble in water.

The common method employed for the concentration of radium, is by fractional crystallization from a dilute acid solution, usually hydrochloric at the outset and hydrobromic later. The progress made in the concentration of radium from these solutions is very dependent upon their purity. The presence of silica very materially retards progress. When silica persists in the chlorides it has been found possible to remove the major part by dissolving the sulfides or carbonates in rather strong hydrochloric acid, boiling with live steam, and allowing to stand for twenty-four hours. The silica usually separates as a gel that is insoluble in water. By breaking up the gel and treating with water, it is possible to dissolve out the radium and barium and leave the silica as a residue that may be separated by filtration. The residue usually contains a relatively large percentage of radium and has to be re-treated. This simple procedure has been found to be very effective in removing the objectionable silica.

In fractionating chlorides or bromides the radium continues to be enriched in the crystal fractions and impoverished in the successive mother liquors. The chlorides and bromides of radium are less soluble than the barium salts, a relation that favors the enrichment of radium in the crystals. L. M. Henderson and F. C. Kracek (32) have found that in the concentration of radium from chromate solutions by fractional precipitation a similar relation exists. On the other hand, the solubility of the hydroxides of the alkaline earth metals increases with the increase of atomic weight, and in the fractional separation of the hydroxides radium enriches in the solution (33).

The factor of concentration or enrichment, also called the crystallization factor, in each step of the chloride fractionation is about 1.5 to 1.6 (4) and 2 to 2.2 in the acid bromide systems. The enrichment is considered more favorable in acid than in neutral solutions. It is evident, however, that the crystallization factor depends primarily on the fraction of salt that crystallizes out. The factors given refer to the conditions followed in practice of evaporating the solutions to the point where approximately half of the barium in solution separates on cooling, which may be roughly ascertained by noting when a stream of air blown on the surface of the hot solution just causes the formation of crystals. The fraction of crystals that separates under this condition, however, varies more or less with the acidity of the solution.

The term "crystallization factor" is the ratio of the concentration of radium in the crystals or precipitates separated to the concentration in the original crystals used in preparing the solutions, concentration usually being given in milligrams of radium per gram or kilogram of anhydrous crystals. This factor serves directly in computing the radium content of the head crystals in fractionation, as this factor raised to the nth power—n being the number of crystallizations—gives the desired multiplier. In this connection it is of interest to note that the crystallization factor by definition must be less than 2, when the solution is concentrated enough to crystallize out 50 per cent of the solute. For, assuming the factor as 2, and one-half of the solute as crytsals, it follows that all of the radium appears in the crystals,

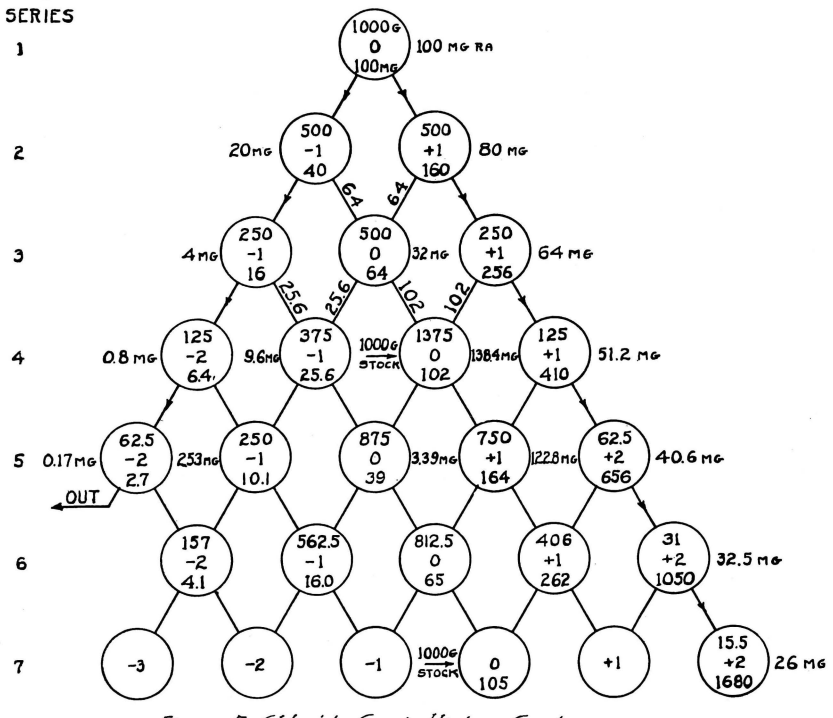


Figure 5. Chloride Crystallizing System

a result that is contrary to experiment. For example, the crystallization factor in the case of chlorides is assumed to be 1.6 (4) where 50 per cent of the barium chloride in a given solution crystallizes out, while in the case of the bromides the factor is assumed to be 2.2 when 42 per cent of the barium bromide crystallizes out.

To make the matter concrete, consider a stock solution of chloride liquor containing 100 milligrams of radium per kilogram. The problem is (1) to deduce the quantity of salt and the radium content in the crystals and the mother liquors obtained in each dish in the successive series of fractionations, and (2) to work out from these results a crystallization system with the minimum number of dishes or transfers. The concentration of radium in the chloride of the mother liquor, of course, should be approximately the same as in the crystals with which it is combined for further fractionation.

The solution of the problem is shown in Figure 5. Beside the number of the dish each circle in the diagram contains the weight in grams of salt in the dish and the concentration of radium. The amount of radium in each dish stands to the right on the plus side and to the left on the minus side. The crystals pass up in successive series whereas the mother liquors pass toward the minus side, and the crystals and liquors of the same concentration always meet and will continue to do so unless somewhat disturbed by the introduction of fresh stock liquor, as shown in the zero dish of series 4, the proper point at which stock liquor should be introduced.

As long as the fraction of crystals separated remains constant, liquors and crystals of the same concentration will always meet when this simple plan of transfer is followed.

As 50 per cent of the salt crystallizes, 500 grams of crystals will be obtained upon the first fractionation whose concentration is 160 milligrams per kilogram, making the total radium in the crystals 80 milligrams or 80 per cent, and 20 per cent or 20 milligrams of radium in the mother liquors which also contain 500 grams of salt. Hence, the concentration of radium in the salt remaining in solution is 20÷500 or 40 milligrams per kilogram of anhydrous chloride. As the crystals contain 160 milligrams radium per kilogram, the ratio 160÷40 equals 4, shows how many times more concentrated radium is in the crystals separated than in the salt of the mother liquor. Another relation is of interest;—as 80 per cent of the radium is in the crystals and 20 per cent in the mother liquors, it is seen that in the parting four times as much radium appears in the crystals as remains in the mother liquors.

This example supplies the fundamental constants to be applied to each crystallization throughout the entire fractionation process.

Distribution of salt in the process of concentration:—

Salt in crystals, percentage, p.	.50
Salt in mother liquors, percentage	.50
Corresponding crystallization factor, c.	1.60
Radium in crystals, percentage, pc.	.80
Radium in mother liquors, percentage, pl.	.20
Concentration of radium in crystals to salt in liquor	4.00

Finally, the crystals contain four times as much radium as remains in the mother liquid.

The data given in the diagram were computed and checked by using these constants.

The system here outlined may be applied to crystallizations from bromide solutions and the values in the dishes of the series may be readily calculated. Assuming the crystallization factor is 2.2 when 42 per cent of the salt is separated as crystals (35) and that the given stock solution contains 18 milligrams of radium per kilogram of dry salt, how many series of crystallizations, n, will have to be made to obtain head crystals containing 10,000 milligrams per kilo or 1 per cent radium salt? From the data at hand:—

$$2.2^n = \frac{10{,}000}{18}, \text{ and } n = 8.$$

Likewise, the number of crystallizations required to take material of any given concentration of radium to a higher concentration in either the bromide or chloride series can be calculated.

The underlying idea of this system is to have the steps in the concentration from dish to dish in each series as great as possible. The number of dishes is thus reduced to a minimum. Additional intermediate dishes as Scholl (36) describes may be at times a convenience but the extra dishes are not necessary and merely make the steps in concentration from dish to dish in any series smaller, and greatly increase the number of transfers of liquors and crystals. In operating any crystallizing system, care must be taken in adding stock liquor to the system at a point where it will be combined with crystals (or mother liquor) of approximately the same concentration of radium.

Nierman (34) showed in his work on the fractional crystallization of the bromides of mesothorium that the value of the crystallization factor depends primarily upon the fraction of salt separated. Since mesothorium and radium are isotopes the same relations hold. A simple exponential relation appears to exist between the percentages of mesothorium (35), and therefore, radium, in the crystals and the crystallization factor, as expressed in the equation $Q_1 = Q_0\, e^{-kp}$ where Q_1 represents the fraction of radium remaining in the mother liquor, when Q_0 the amount of radium in solution to be crystallized equals 1. The percentage of salt separated as given by p, and k is a constant expressing the continuous partition of radium between mother liquor and crystals. The experimental relation indicates that the enrichment of radium in the crystals is proportional always to the amount remaining in solution. Then, since Q_c, the fraction of radium in the crystals, is $1 - Q_1$ we have $Q_c = 1 - e^{-kp}$ and since $Q_c = cp$, it follows that the value of c, the crystallization factor corresponding to different percentages of crystals separated, can be computed when the value of k is known.

It has been pointed out that the relation is not rigorous, for when p becomes 1, Q_c does not become 1 in $Q_c = 1 - e^{-kp}$ also, as it should for an exact relation.

H. Schlundt (35) has calculated a value for k in fractionation of bromide and chloride solutions of mesothorium. Schlundt's calculations may also be applied directly to the fractionation of radium solutions. For calculating k for neutral bromide solutions Schlundt used an experimental value obtained by Nierman (34), namely, that approximately 12 per cent of the mesothorium remained in the mother liquors when 44 per cent of the salt crystallized out,

and the liquor was drained off well from the crystals. When these values are substituted in the above equations, the value of k is 4.8.

Applying the same exponential formula to chloride fractionation, one finds that the characteristic partition coefficient k has a value of approximately 3. This value is based on plant operation in which more or less mother liquor remains with the crystals in making transfers. The value 3 for k is based upon the factor of enrichment of 1.55 when 50 per cent of the chloride is separated as crystals. The actual partition coefficient for chlorides probably has a somewhat higher value, and in acid solutions the value seems to be a little higher still. Doubtless, certain experimental conditions, such as the rapidity of separation of crystals and the degree of supersaturation, influence the value of enrichment. Nierman found that the crystallization factor remains constant up to a concentration of 2 milligrams per gram, but the experimental work recorded by Schlundt would seem to indicate that the factor remained fairly constant for higher concentrations of mesothorium. Even when the crystals that separate were as active, weight for weight, as pure radium bromide, no decline in the crystallization factor was observed. Whether or not the crystallization factor still remains constant for radium-barium bromide mixture as the radium approaches or exceeds the barium present has not been investigated.

Description of Experiments.—For experimental work on the concentration of radium by fractional crystallization a lot of concentrates was obtained from a radium producer. The radium and barium were present in the form of sulfates and carbonates, a concentration of one part of radium per 3,250,000 parts of material. The values were converted to acid-soluble form by treatment in the autoclave under pressure with sodium carbonate solutions. The carbonates were separated by filtration and thoroughly washed with distilled water, after which they were dissolved in 20° Baumé hydrochloric acid free from sulfates. The liquors were then ready for fractionation and it may be stated that they were practically free from silicic acid, or at least the quantity was so small that no interference in the fractionation was encountered by the formation of gelatinous silica. The plan of fractionation outlined was followed rather closely, except in the very last steps in the production of high grade salt.

A total of 1212 liters of chloride solution which contained 134.25 kilos of anhydrous barium chloride and 102.8 milligrams of radium element was introduced into the crystallizing system. The initial concentration of radium in the liquors averaged about .76 milligrams per kilo of pure chlorides. It may be stated that this ratio is somewhat lower than is ordinarily obtained in regular plant operations, but it could not be controlled as the processing of nearly all the radium for these experiments prior to fractionation was done in a commercial plant.

Ordinarily it is considered desirable to raise the concentration of the radium per kilo of salt to a minimum of 20 milligrams in the chloride series, after which the salts are converted to the bromides. When ample facilities are available for handling these solutions it is feasible to raise the concentration of radium per kilo to 60 milligrams before beginning fractionations with bromide solutions. Since the equipment was limited, it was deemed advisable to convert to the bromide series at a concentration ratio of 20

milligrams of radium per kilo of salt. To determine the number of crystallizations necessary to raise the factor of enrichment to 20 milligrams per kilo we have:

$$1.6^n = \frac{20}{.76}, \text{ and } n = 7.$$

That is, seven fractionations would be required, assuming that the factor is 1.6 when 50 per cent of the barium was separated in the fractionation. In actual practice, between 8 and 10 fractionations were made from fairly strong acid solutions, by which procedure more than 50 per cent of the crystals separate.

After the chlorides had been fractionated eight to ten times, a concentration of 20 parts of radium per kilo had been reached in the crystals, they were converted to the bromides, the lead present first being removed. For this purpose the chloride solution was made slightly alkaline with ammonia and then saturated with hydrogen sulfide. The precipitate of sulfide settled quickly, and was readily filtered off on a large funnel. To the filtrate a saturated solution of pure sodium carbonate was added which quickly precipitated the radium and barium. After settling over night most of the supernatant liquid was poured off, and the rest went on a large Büchner funnel where it was filtered, and washed several times with hot water. In regular plant operation the filtrate would be returned to the tanks in the plant in which radium products were treated. In these experiments the filtrate was discarded.

The moist barium carbonate was next dissolved in 20 to 30 per cent chemically pure hydrobromic acid. From this point the fractionation was conducted, for the most part, in fused silica dishes. To ascertain the number of fractionations that would be required to raise the concentration of the salt to 1 per cent radium, we have to determine n from the following expression:—

$$2.2^n = \frac{10{,}000}{20}, \quad n = 8.$$

As the concentration of radium in the head crystals of bromides reached about 1 per cent they were removed from the system from time to time preparatory to an analysis of the several products that had accumulated up to this point in the refining process. The data thus obtained have been arranged in the form of a balance sheet showing the distribution of radium. The combined head crystals, 8.75 grams anhydrous salt, were sealed, and after allowing sufficient time for the radium to become partially in equilibrium with its decay products, a series of gamma-ray measurements showed the tube to contain 96.04 milligrams of radium element.

TABLE XIV.—RADIUM DISTRIBUTION—FIRST BALANCE SHEET.

1.	Radium introduced as mother liquor (chlorides)		102.80 mg.
2.	Radium discarded in tail liquors (chlorides)	2.29 mg.	
3.	Radium discarded in tail bromide liquors	.47 mg.	
4.	Radium accumulated in lead residues	1.70 mg.	
5.	Radium taken from system as 1.1 per cent salt (8.75 g.)	96.04 mg.	
6.	Radium not accounted for	2.30 mg.	
		102.80 mg.	102.80 mg.

Only a small part of the 2.3 milligrams not accounted for is to be assigned to mechanical losses. The apparent loss results largely from inaccuracies in sampling the chloride liquors.

The quantity of radium discarded in the chloride and bromide liquors, items 2 and 3, represent the real loss in fractionation. For instance, the ratio of radium to anhydrous barium chloride, item 2, is about .017 milligrams per kilo, and in item 3 very little higher. As it is rather laborious to recover so small a quantity of radium associated with such large amount of barium salt, the expense is usually more than the value of the finished product. Sometimes instead of discarding the chloride liquors outright, the barium is recovered for use in the first stage of processing the ore. The discard liquor from the bromide fractionation is usually treated for the recovery of hydrobromic acid. Assuming the loss to be representative of large-scale operations, and neglecting the quantity of radium not accounted for, the actual loss would be about 2.6 per cent. The quantity of radium remaining with the lead residue of item 4 is recoverable and in regular plant operations may be re-introduced at some appropriate place.

In the final stage of concentration, from 1.1 per cent salt to approximately 90 per cent salt the general scheme of fractionation outlined was again followed, except of course, there is no stock solution of mother liquor. By such a procedure it is quite possible to obtain 80 per cent of the total quantity of radium introduced in the form of approximately 90 per cent salt, but it is often desirable and sometimes quite necessary to remove a larger proportion of the radium introduced as a high-grade salt. It thus becomes necessary to deviate somewhat from the process outlined. As the volume of the liquors gradually becomes smaller it also becomes more difficult to control the fraction of salt separating out as crystals, with the evident result of greatly increasing the number of fractionations in the final stages.

In our crystallizing experience several observations have been made which have contributed to efficient manipulation in the final stage: (1) Fractionation is facilitated by the removal of ammonium salts. Such salts may be removed by taking to dryness and carefully heating to smoke off the volatile salts. (2) In operating with small volumes of solution there is a tendency for salt to deposit on the dish at the rim of the liquid when the concentration of acid happens to get too high. The fractionation of values is thereby greatly reduced. (3) By continuing the fractionations the first 50 to 60 per cent of salt can be taken out as head crystals nearly 100 per cent pure, which makes it possible to get a larger percentage of the total radium present to a high state of purity, say 90 per cent. (4) Rather than fixing attention on radium in the head dish, give strict heed to the amount of radium in the discard liquors, for eventually nearly all of the radium will be in the head crystals and quite free from barium. (5) Rather than pour the liquors from one dish to another in the final stages of fractionation it is better to pipette them out. Of course, care must be exercised not to use the same pipette for liquors of high and low radium content, otherwise little or no progress will be made.

Table XV gives the final distribution of radium in the various fractions as sealed.

TABLE XV.—FINAL STAGE IN RADIUM REFINING.

1.	Radium to start with, 1.1 per cent salt, 8.75 g.		96.04 mg.
2.	Radium taken out as 88 per cent salt	92.66 mg.	
3.	Radium taken out as 1.46 per cent salt	3.51 mg.	
4.	Radium taken out as .08 per cent salt	.52 mg.	
5.	Apparent excess		.65 mg.
		96.69 mg.	96.69 mg.

A simple calculation shows that 96.5 per cent of the total amount of radium element started with as 1.1 per cent salt was fractionated up to 88 per cent purity.

It is noted that apparently more radium was removed from the system than was introduced. The absorption of gamma rays by the large amount of barium salt initially present easily accounts for this discrepancy.

For fractionation of the high-grade salt a comparatively small, but well-equipped laboratory is required. It should be at least several hundred feet away from the laboratory for radio-active measurements, and preferably in a different building in order to guard against infecting the measurements laboratory or instruments with high-grade radio-active products.

RECOVERY OF VANADIUM AND URANIUM

At the time that the ore was treated for the extraction and recovery of radium it was not convenient to carry the vanadium and uranium through to the finished products, consequently the solutions containing the uranium and vanadium from which the radium had been removed were treated with an excess of lime, which precipitated practically all of the values as complex calcium salts, a form in which they could be easily stored. The Ore Products Corporation of Denver utilized the same procedure for obtaining the vanadium and uranium in a form that could be stored when it was necessary to defer processing these products. The method was also used as a means of concentrating these values in acid liquors. After adding an excess of milk of lime to a tank of acid solution, the supernatant liquor was decanted and then the dilute acid liquor from another run was added to the precipitated uranium and vanadium, which effected their solution, thereby materially raising the concentration of the solution as to the uranium and vanadium content and at the same time reducing the acidity of the solution.

The production of the lime cake of uranium and vanadium was not objectionable for the later study of the methods of recovery, inasmuch as the re-solution of the vanadium and uranium in any desired form is not difficult. Then too, the study of methods of recovery of the valuable constituents from the lime cake presents an important problem for investigation.

The production of lime cake carrying uranium and vanadium is a regular step in several of the commercial processes of radium production. Experiments on the recovery of vanadium and uranium from the lime cake are in progress, but the experimental results are not complete enough to be incorporated in this paper.

Inasmuch as the vanadium is the valuable product to an operating concern, primary consideration is usually given to its recovery while the recovery of the uranium is made subordinate. With the knowledge at hand there appear to be three main lines of attack worthy of careful consideration.

(1) Vanadium may be effectively precipitated from dilute acid solution as iron vanadate by the addition of ferrous sulfate. In commercial processes where the vanadium is obtained in solution, the uranium, iron, etc., are also in solution. For obtaining a marketable product of iron vanadate from such solutions it is usually necessary to first remove the uranium, iron, etc. Such a procedure was employed by the National Radium Institute (4) where the best conditions for carrying out the reaction were carefully worked out.

(2) H. M. Plum (37) studied the various methods for the recovery of radium, vanadium, and uranium from American carnotite ores. He suggests a method of procedure for the recovery of vanadium which has been used commercially in a somewhat modified form. The carnotite ore is treated successively with a boiling hot solution of sodium carbonate, after which the filtrates are combined and concentrated by evaporation. At a specific concentration of the solution a yellow precipitate appeared, which proved to be sodium uranyl carbonate. After the removal of the double carbonate and further evaporation of the liquor, it was possible to crystallize out a large part of the unused sodium carbonate, leaving the greater part of the vanadium in solution. The vanadium could be recovered by evaporating to dryness or precipitating as iron vanadate. Plum states that the method did not completely remove the vanadium from the virgin ores, which is in accord with the work of Haynes and Engle (8). Karl B. Thews (38) extended the method to the recovery of the vanadium from the precipitated lime cake, where the vanadium is present in a form much easier to remove. Thews proposes treating lime cake with a solution of sodium carbonate under pressure, to which a small quantity of manganese dioxide is usually added. The carbonate solution extracts the vanadium and uranium from the lime cake. Upon concentration by boiling a yellow precipitate of sodium uranyl carbonate is thrown out from the carbonate solution. The vanadium may then be recovered from the alkaline solution by precipitation with ferrous sulfate or as the oxide. It is sometimes necessary to remove the phosphorous prior to the recovery of the vanadium, which may be accomplished by treatment with sodium aluminate.

(3) Barker and Schlundt (39) in studying the removal of small quantities of vanadium from a commercial sodium uranate produced by the National Radium Institute (4), found that vanadium could be precipitated almost quantitatively from dilute acid solutions containing rather large quantities of other materials, such as uranium, iron, calcium, etc. The Chemical Products Company of Denver later extended the application of this idea to the recovery of vanadium from both acid and alkaline solutions. In the treatment of acid solutions the large excess of acid was partially neutralized with lime to the point where the vanadium and uranium were just held up in solution, after which the precipitate of calcium sulfate was removed and neutralization further continued with sodium carbonate until the desired concentration of acid was obtained. In the event that the vanadium present was not in the highest state of oxidation a little sodium chlorate was added

and the solution boiled. The vanadium was thus thrown out of solution as a mixture of vanadic acid and iron vanadate, practically free from uranium. By such a procedure it was found possible to precipitate 97 per cent of the vanadium in solution and retain practically all of the uranium in solution. Later, it was found that the vanadium could be precipitated just as effectively by heating the solutions to 70° C. and bubbling air through for a time. The product thus obtained averaged well above 30 per cent vanadium oxide (V_2O_5), where the virgin ore contained 3 per cent or more. Any copper present in the virgin ore was removed from the acid solution with sodium sulfide prior to precipitation of the vanadium.

From alkaline solutions the vanadium was recovered by first acidifying, and then boiling to expel carbon dioxide. Continued boiling finally precipitates practically all of the vanadium as the acid. The final product obtained usually contained from 80 to 90 per cent vanadium oxide, which percentage could be still further raised by heating to a high temperature to expel the last traces of water.

When the uranium is obtained as an impure sodium uranyl carbonate, it may be quite easily purified and the uranium obtained as sodium uranate or as the sodium uranyl carbonate. By the other standard method the uranium is precipitated with sodium hydroxide as sodium uranate, but iron must first be removed from the solution. But when the uranium is precipitated prior to the removal of the vanadium, the sodium uranate produced usually contains a considerable quantity of vanadium and has to be purified. When the vanadium is removed first (method 3), the sodium uranate produced is practically free from vanadium.

At the present time uranium has a limited market either in the form of the black oxide or as the yellow salt, which is generally a sodium uranyl salt. The black oxide may be produced by reducing either the sodium uranate or the sodium uranyl carbonate with charcoal as described by the Federal Bureau of Mines (4). The yellow salt may be produced by purifying the sodium uranyl carbonate or precipitation of the uranium from a slightly alkaline solution with sodium hydroxide. By careful regulation of the conditions of precipitation, the color of the salt produced may be pretty well controlled, that is, from the yellow to the orange shades. The black oxide is used in the manufacture of c. p. uranium salts and in the production of uranium metal and the ferro compounds. The yellow salt is used primarily in the ceramic industry.

Mr. R. O. Humphrey is making a careful study of the various methods suggested for the recovery and purification of both vanadium and uranium to determine their efficiency and the purity of the products.

MEASUREMENT OF RADIUM

General Discussion.—For control work in plant operation and the measurement of radium in general, three methods have become standard in use: (1) Emanation method, (2) gamma-ray method, and (3) alpha-ray comparison. The emanation method probably occupies the foremost place, although the utilization of the gamma radiation for estimating the radium content of materials is coming more and more into general use. The gamma-

ray method is simple in operation and has become the standard way of determining the radium content of commercial preparations, while for the accurate measurement of the quantity of radium in virgin ores and various other intermediate products which are obtained prior to commercial preparation, the emanation method has been more generally used. The alpha-ray method, which is the simplest of the three and very sensitive, is used for qualitative and very rough quantitative work. Instruments for alpha-ray work are very generally used in prospecting, ore sorting, and milling, and even in the control of radium plant operations. Its shortcomings for quantitative purposes have been given in some detail by S. C. Lind (40).

More detailed descriptions of these methods and the types of instruments devised by different investigators may be found in reference books and journals. However, some time was devoted to special problems in this field and included herewith are some new experiments by Mr. C. E. Baumgarten and the author on obtaining quantitatively the emanation from carnotite ores where sulfuric acid is used as a solvent; we have also studied the use of phosphoric acid in radium determinations by the emanation method. Following the account of these experiments a section is given to experimental work by Mr. R. H. LeRoy on the application of the gamma-ray method for determining radium in concentrates and in ores.

The Emanation Method.—The emanation method is based upon the fact that the gaseous disintegration product of radium—the emanation—can be completely separated from radio-active materials, and that the equilibrium quantity is proportional to the radium content. The emanation is capable of very accurate measurement by electrical methods for which purpose carefully standardized electroscopes have come into general use. Since solids containing radium usually emit, at ordinary temperatures, variable proportions of the emanation continually produced it is usually necessary in quantitative determinations to first expel the emanation, that is, reduce it to zero, then seal up the sample, allow it to stand for a definite period, and again separate the accumulated emanation and collect in a suitable electroscope. The equilibrium quantity is then conveniently obtained by reference to a table of growth of radium emanation (41).

Calibration of Instruments.—All of the electroscopic measurements were made with three instruments of the Lind (42) interchangeable type. The instruments were calibrated by (1) a specimen of pitchblende standardized by Randall (43), (2) a specimen of pitchblende standardized by Lind and Roberts (44), (3) a standard radium solution prepared here, and designated as the University of Missouri Standard Solution. The solution was prepared by dissolving a specimen of radium bromide containing 0.978 mg. of radium element in 2200 cc. of 1.2 normal hydrochloric acid solution containing 1 g. of barium chloride per liter. Twenty cc. of this stock solution, which will be designated as "A" was carefully and accurately pipetted out and diluted to 1000 cc. with 1.2 normal hydrochloric acid containing 1 g. of barium chloride. Next, 40 cc. of this stock solution, which will be designated as "B", was accurately measured out and diluted with 500 cc. of 1.2 normal acid containing 1 g. of barium chloride per liter. This stock solution will be designated as "C". For a calibration 20.035 cc. of stock solution "C" at 20° C. was used, which contains 1.4297×10^{-8} g. of radium ele-

ment. The specimen of salt used in the preparation of the standard solution had been carefully standardized by the U. S. Bureau of Standards, and checked in the radium measurements laboratories of the University. All pipettes, flasks, and weights used in this work were carefully calibrated.

The electroscopes were calibrated at 22° C. and 740 mm. pressure, and in the event that readings were made under other conditions Lester's (45) corrections were applied. For converting the calibration values found by using the pitchblende standards, the radium-uranium ratio, 3.4×10^{-7} reported by Lind and Roberts (44) was used.

TABLE XVI.—CALIBRATION OF INSTRUMENTS.

No. of Instrument	Vol. of ionization chamber in liters	Curies of radium per div. per sec. x 10^9		
		Randall Pitchblende	Lind & Roberts Pitchblende	U. of M. Std. Ra. solution
10	4	9.530	-----	9.524
11	4	8.993	9.003	-----
12	10	8.884	-----	9.053

DETERMINATION OF RADIUM IN CARNOTITE ORES

The rapid and accurate determination of radium in carnotite ores presents several difficulties.

Direct solution in nitric acid and storage prior to collecting emanation has been found impractical as part of the radium salt is absorbed by the colloidal silicic acid which is set free by the nitric acid and consequently values obtained by such a procedure are usually low.

The carbonate fusion and solution method as described by Lind (46) yields fairly satisfactory results. However, the method is long and tedious, and unless special precautions are taken the results are apt to run 10 to 15 per cent low as reported by Schlundt (47).

The bisulfate method as described by Barker (48) has been found to yield accurate results, as well as supplying a method which minimizes the number of operations required to collect the emanation for measurement.

Schlundt and Underwood (49) have used concentrated sulfuric acid as a storing solution for radium with excellent results. However, it has been found necessary to treat a carnotite ore with a little concentrated nitric acid (47) for decomposition of the ore prior to treatment with sulfuric acid.

A representative carnotite ore was selected for study and the percentage of uranium was carefully determined by chemical analysis, and its radium content calculated assuming that the radium-uranium ratio for pitchblende holds for carnotite (50).

The radium content was then determined directly by: (a) the carbonate fusion and solution method, (b) the bisulfate method, and (c) a modified sulfuric acid procedure of Schlundt and Underwood (49). The results obtained are tabulated in Table XVII, and while the values obtained by the bisulfate and sulfuric acid methods are found to check the values calculated from the uranium content, it will be noted that the carbonate fusion and

solution method yielded low results, which confirms the findings reported by Schlundt.

TABLE XVII.—RADIUM CONTENT OF CARNOTITE ORE No. 1.

Method	No of Determinations	g. Ra. per g. x 10^9
Uranium detd. analytically		12.00
Bisulfate Method	3	12.02
Conc. HNO_3 & H_2SO_4 De-emanated by boiling both times	6	12.06
Carbonate fusion and solution method	3	10.44

The experimental conditions necessary to reduce the ore sample to zero activity and to collect the accumulated emanation after a definite period of storage will be described.

The ore sample, 1 to 3 g., is first treated with the solvent—30 cc. concentrated sulfuric or phosphoric acid in a pyrex test tube, 2.5 x 20 cm. to dissolve the radium and remove the emanation. After being fitted with stoppers and tubes as shown in Figure 6, the tube is set aside for a definite period of growth of emanation. For collection of the emanation, the test

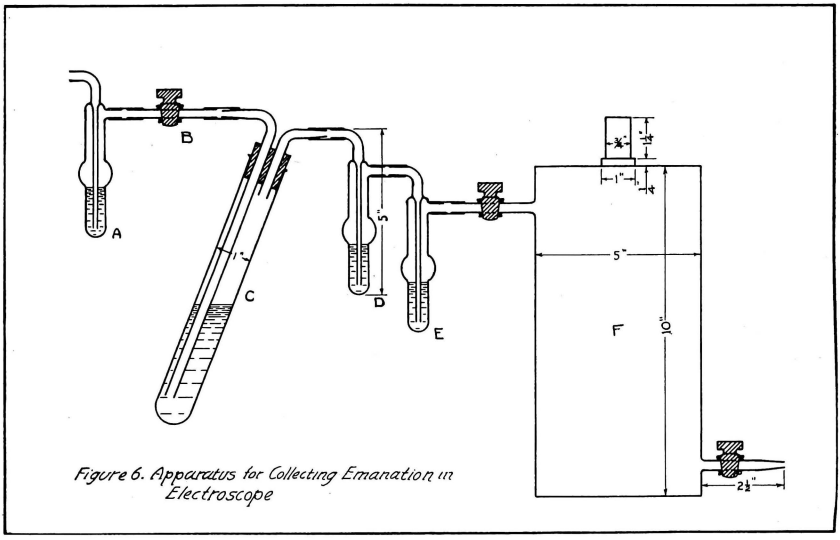


Figure 6. Apparatus for Collecting Emanation in Electroscope

tube C is connected in series with two micro-drying bulbs, D containing caustic soda solution to catch any acid spray or sulfur trioxide, and E, containing concentrated sulfuric acid to dry the air and emanation prior to entering the emanation chamber F. The aspirating bulb A is filled with either water or sulfuric acid and is there primarily for noting the inflow of air into the system. All rubber connections are wired and the capillary tips of the glass tubes are not broken until all connections have been made and the inter-

mediary system placed under a slight vacuum. By adjusting the stop cocks of the ionization chamber, the flow of air through the chain may be regulated. Heat may now be applied to the test tube C.

The results of this section of the work are reported in Table XVIII, and a word of explanation for each series follows. It will be recalled from Table XVII that the radium content of the ore used was 12.03×10^{-9} g. of radium per g. of sample.

TABLE XVIII.—DATA OBTAINED ON CARNOTITE ORE, SHOWING DIFFERENT METHODS OF SEPARATING EMANATION.

Series Number	Method of Reducing to Zero Activity	Method of de-emanating for collection	Solvent Used	No. of Determinations.	G. of Ra per g. of sample x 10^9	Per cent Deviation from accepted value
1.	Asp. with air in cold.	Asp with air in cold.	HNO_3 & H_2SO_4	2	8.85	25 low
2.	Asp. with air and boiling	Asp. with air in cold	HNO_3 & H_2SO_4	2	10.43	13 low
3.	Asp. with air and boiling	Asp. with air in cold	H_2SO_4	6	10.30	14 low
4.	Asp. with air at 100° C.	Asp. with air at 100° C.	H_2SO_4	2	10.34	14 low
5.	Asp. with air at 100° C.	Asp. with air at 100° C.	HNO_3 & H_2SO_4	5	11.30	6 low
6.	Asp. with air and boiling.	Asp. with air and boiling.	H_2SO_4	2	11.38	5 low
7.	Asp. with air and boiling.	Asp with air and boiling.	HNO_3 & H_2SO_4	6	12.06	------
8.	Asp. with air and boiling.	Asp. with air and boiling	H_3PO_4	2	11.95	------
9.	Asp. with air and boiling.	Asp. with air and boiling.	HNO_3 & H_3PO_4	2	11.99	------
10	Sealed for 30 days	Asp. with air and boiling.	H_3PO_4	1	11.94	------

Series 1. The ore was moistened with concentrated nitric acid and evaporated to dryness. The sulfuric acid was added cold and about 5 liters of air slowly bubbled through the solution. The sample was then sealed and stored to allow the emanation to accumulate, which was eventually transferred to an electroscope by drawing 2 to 3 liters of air through the cold solution.

Series 2. The ore was treated with concentrated nitric acid as in Series 1, then boiled five to seven minutes with concentrated sulfuric acid and sealed. The emanation was collected as in Series 1.

Series 3. The procedure was the same as in Series 2, except that the ore was not decomposed with nitric acid at the outset.

Series 4. In the experiments of this series, concentrated sulfuric acid was added to the ore, the test tube placed in boiling water and air drawn through the solution to reduce to zero activity. After allowing the emanation to accumulate it was collected under the same conditions as for reducing to zero activity.

Series 5. The procedure for reducing to zero activity and collecting the emanation was the same as in Series 4, except that the ore was first decomposed by evaporating to dryness with a little nitric acid.

Series 6. The ore was reduced to zero activity by boiling with concentrated sulfuric acid and the emanation later collected by again boiling and drawing a current of air through the solution.

Series 7. The ore was decomposed by nitric acid, after which sulfuric acid was added and the solution boiled to reduce to zero activity. The accumulated emanation was later collected by again boiling the solution accompanied by drawing through a current of air.

Series 8. Phosphoric acid (85 per cent) was substituted for sulfuric. The sample was reduced to zero activity by boiling the solution and the emanation later collected by boiling and drawing through a current of air.

Series 9. The procedure was the same as for Series 8, except that the ore was decomposed with a little nitric acid prior to the addition of the phosphoric acid.

Series 10. A sample of the ore was added to 30 cc. of phosphoric acid, sealed and allowed to stand until in equilibrium (30 days), after which the emanation was collected by boiling and drawing through a current of air.

From the foregoing data we must conclude that for insuring the accurate estimation of the radium in a specimen of ore by the use of sulfuric acid as solvent, it is necessary to decompose the ore with a little nitric acid followed by boiling with concentrated sulfuric acid to reduce the activity to zero, and for the subsequent collection of the emanation it is again necessary to boil the solution, and to aspirate with air.

We must also conclude that phosphoric acid may be used as a solute for radium, and substituted for sulfuric acid in the quantitative estimation of radium in carnotite ore. As will be noted, both phosphoric acid alone and a combination of phosphoric and nitric acids were tried for reducing the activity to zero, with equal success.

Phosphoric Acid Method.—Encouraged by the satisfactory results obtained by substituting phosphoric acid in determining the quantity of radium in a carnotite ore, its service for determining radium in other products was investigated. Inasmuch as phosphoric acid (85 per cent) is far more viscous than concentrated sulfuric acid, it did not seem necessary to study the possibilities of reducing to zero activity or collecting the emanation by aspiration without the aid of heat.

A series of preliminary experiments showed that barium sulfate is somewhat soluble in hot phosphoric acid. It was found that 100 cc. of 85 per cent ortho phosphoric acid will dissolve approximately 1 g. of barium sulfate at the boiling point, 170° C. and that 5 g. of barium sulfate go into solution in 100 cc. of pyro phosphoric acid when the temperature is raised to 300° C.

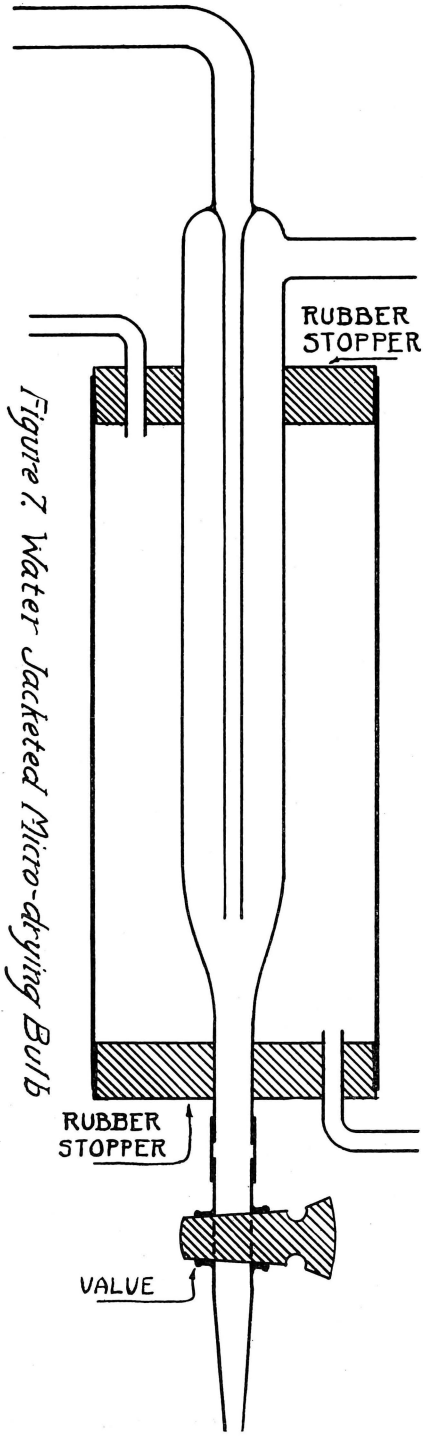


Figure 7. Water Jacketed Micro-drying Bulb

From these data it is quite obvious that 30 cc. (the quantity of acid used in the experimental work) is sufficient to take into solution the amount of barium sulfate usually associated with radium in ore samples or concentrates.

In reducing the activity to zero, it was noted that the acid began to boil quietly when the temperature reached 250° C., after which the boiling was usually continued for a few more minutes in order to insure raising the B. P. of the acid to 300° C. However, caution must be exercised not to boil the solution too long as there may be a tendency to dehydrate the acid past the pyro stage and meta phosphoric acid will separate out. Barium meta phosphate, which is insoluble in acids, will be found at this stage, and of course would interfere with the subsequent collection of the emanation.

Manipulation.—The required quantity of the specimen to be analyzed was weighed out into a pyrex test tube and 30 cc. of 85 per cent phosphoric acid added. The mixture was boiled until it boiled quietly, which usually required from five to seven minutes. Boiling was then continued from one to two minutes to make certain that a temperature of 300° C. is reached. The tubes were then sealed while hot with a two hole rubber stopper fitted the same as the stoppers used for sealing the sulfuric acid solutions, except that one tube extended to within 2 to 3 cm. of the surface of the liquid instead of to the bottom of the tube.

The set up for collecting the emanation is practically the same as for collecting the emanation from the sulfuric acid solutions, which has been described and shown diagrammatically in Figure 6. It was found advantageous although not absolutely necessary to substitute a micro-drying bulb equipped as shown in Figure 7 for D of Figure 6. The bulb so equipped with a water jacket serves to condense the water vapor passing over when the phosphoric acid solution is boiled. In collecting the emanation the acid was usually boiled from six to ten minutes and then air drawn through five to ten minutes longer. Even then there is usually a little vacuum left in the ionization chamber which serves to guard against the loss of emanation during the three hours which intervene before readings are taken.

Table XIX shows the products examined by the phosphoric acid method. The results obtained establishes quite conclusively that the method is applicable to practically all materials obtained in radium extraction and concentration, with as high a degree of accuracy as the bisulfate method, and other methods of measurement.

The accepted values assigned to Carnotites 1 and 2 are the average of check uranium and radium determinations, the radium having been determined by the bisulfate method. The accepted value of Residue 1 was determined by the bisulfate fusion method. The accepted values for concentrates 1 and 2, and Sulfate 2 were determined by running bisulfate fusions on the respective samples. Sulfate 1 was analyzed by the carbonate fusion and solution method and concentrated sulfuric acid methods. The accepted value for Carbonate 1 is the result of check values obtained by a direct solution method and gamma-ray measurement.

The principal advantage which the phosphoric acid method offers over the bisulfate method lies in the fact that it is much easier to reduce the average specimen to zero activity. The mixture of bisulfate boils rather

TABLE XIX.

Materia	Weight of sample in g.	Accepted value in g. Ra per g. x 10^9	Determined value by use of H_3PO_4. g. Ra per g. x 10^9	Number of Determinations by H_3PO_4.
Carnotite Ore 1----	1.50	12.02	11.97	4
Carnotite Ore 2----	3.00	3.96	3.88	3
Residue 1----------	3.00	1.83	1.79	2
Concentrate 1------	0.50	377.20	37.20	3
Concentrate 2------	1.00	25.24	25.30	1
Sulfate 1----------	0.02	1102.	1100.	2
Sulfate 2----------	0.20	187.1	183.0	3
Carbonate 1-------	0.03	674.	670.	2

vigorously at times which makes it difficult to retain the melt in the test tube.

The use of bisulfate requires very careful and constant attention during the period of reducing to zero activity, while in the use of phosphoric acid it is possible to so adjust the flame under the boiling acid that the operator can go away and leave the boiling solution for a short period of time.

The mortality of the determinations is not as great with the use of phosphoric acid as a solute as with bisulfate, which is due to the fact that the phosphoric acid is a liquid and does not cause cracking of the tubes on account of differences of coefficients of expansion.

The Gamma-Ray Method.—The gamma-ray method involves comparing the rate of electroscopic discharge produced by the gamma radiation from a standard salt or preparation containing a known amount of radium, with the gamma radiation from an unknown salt or preparation, the conditions of measurement being, of course, identical. It is obvious that the accuracy of the method is dependent upon the standard used for comparison, and therefore care should be exercised to select as a standard a preparation whose radium content is definitely known.

In the technique of operation, the net discharge in divisions per second of the electroscope for the known may be compared with the net discharge in divisions per second of the unknown, taking into consideration such correction factors as are necessary. It is also possible to determine the value of "Eve's number"* or "K" for the given instrument under certain specified conditions and then make the proper corrections for readings of the unknown made under other conditions.

For accurate work several corrections must be considered: (1) Absorption of radiation by the specimen itself, (2) variations in the ionization cur-

*$I = \frac{KQ}{r^2} e^{-ur}$ where I is the ionization at a distance r from a point source of Q grams of radium, and u is the coefficient of absorption of the gamma rays by air, and K is the constant which represents the number of ions per cubic centimeter due to one gram of radium as a point source at a distance of one centimeter (51).

rents observed resulting from changes of pressure and temperature and (3) when the specimen under test is not in radio-active equilibrium, it is necessary to make corrections for emanation regenerated in the sealed container. For specimens of radio-active salt, where the activity is zero at the time of sealing, measurements may be made after a few days by taking the percentage rate of accumulation of emanation (and, consequently, the gamma radiation) according to the expression $I_t = 1-e^{-\lambda t}$ in which I_t is the percentage accumulation at any time t. The function "$e^{-\lambda t}$", for various time intervals, is solved in the Kolwrat Table (41). When specimens to be measured are not in equilibrium at the time of measurement, or the data regarding the time of sealing a commercial preparation are not available, it is necessary to make a series of measurements allowing a definite time interval between the successive readings. It is obvious that the second reading will be higher than the first one and the quantity of equilibrium may be calculated by the formula.

$$q = q_0 + \frac{q_1 - q_0}{1 - e^{-\lambda (t_1 - t_0)}}$$

where q_0 is the quantity at the time of the first reading, t_0, and q_1 is the quantity at the time of the second reading, t_1, and λ is the decay constant of radium emanation expressed in the same units as t_0 and t_1. (See Appendix)

V. F. Hess (52) has described an instrument for making accurate gamma-ray measurements on specimens where the radium content is 10^{-8} grams radium per gram of sample. More recently, Hess (53) has described an apparatus for measuring specimens whose activity is as low as 10^{-10} g. Ra per g. of sample, and in some instances, 10^{-11} g. Ra per g. N. Dorsey (54) describes a type of instrument which he has been using for measuring the content of radium specimens whose activity is as low as 7×10^{-8} g. Ra per g. of sample. He also states that the instrument may be used with a precision of at least 10 per cent for material containing 7×10^{-9} g. Ra per g. In the work of both Hess and Dorsey, the instruments were calibrated against radium standards whose activity, weight for weight, very often was many times that of the specimen to be tested. This procedure necessarily involves such correction factors as coefficients of absorption, volume distribution, and the specific gravity of the material, all of which have to be determined experimentally for each specimen. It is necessary to take into consideration temperature and pressure variations, unless the instruments are calibrated daily, or are under control. Oftentimes the determination of the correction factors is a more arduous task than the determination of the radium content by the emanation method.

Our procedure differs from that of Hess and Dorsey in the following respects: (1) The instruments were not calibrated in absolute (electrical) units. All measurements are made by direct comparison of the unknown with a standard similar to the unknown in (a) the order of magnitude of the radium content, (b) physical characteristics, thereby obviating the use of correction factors. (2) The more penetrating beta rays were not entirely screened off, for 10 to 15 per cent of the observed ionization was contributed by beta rays.

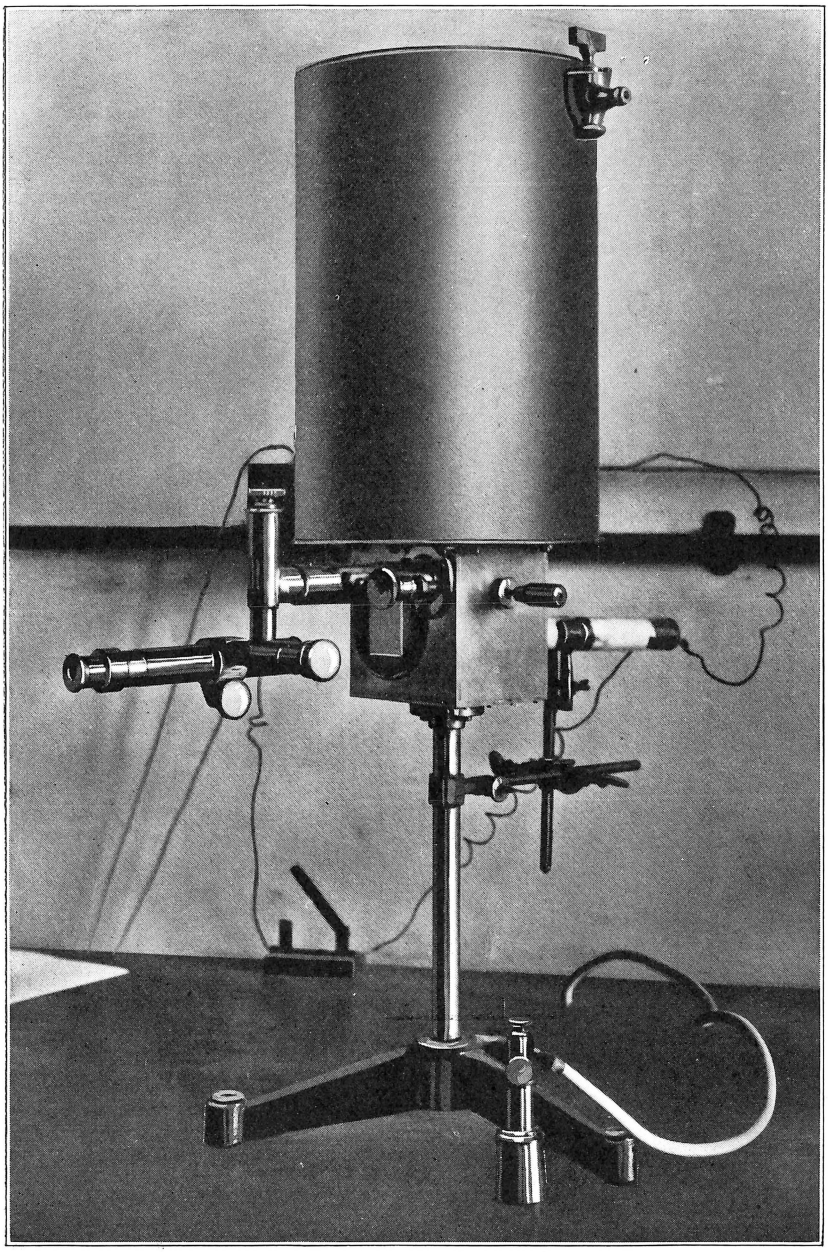


Plate VI

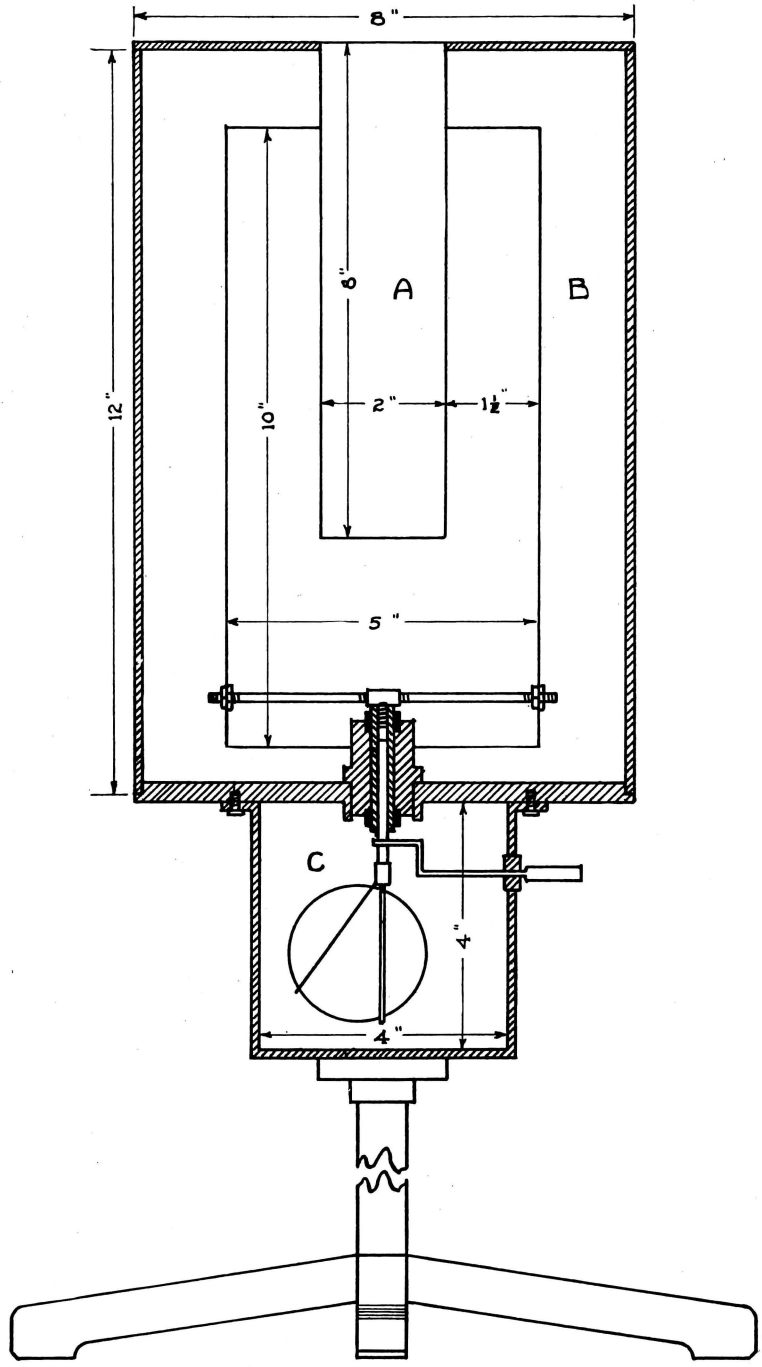


Figure 8. Modified Curie Type of Gamma-ray Instrument

In the application of the gamma-ray method to weakly-active materials, such as ores and concentrates, the main difficulties encountered are: (1) Securing a satisfactory sensitivity, (2) determination of the correction for volume distribution of the material, and (3) the determination of the correction for the absorption of the radiation by the material itself.

High sensitiveness in an electroscope may be secured by: (1) Reducing the electrostatic capacity of the electrode system, and (2) increasing the volume of the ionization chamber. The rate of discharge will, of course, depend largely upon the weight of sample for which the instrument is designed. Hess (53) ingeniously surrounds a small electrode system mounted in a spherical ionization chamber of relatively small volume by a very large sample of material to be tested. In the Dorsey (54) type, closely modeled after the Curie form, the electrostatic capacity is relatively high, but the ionization chamber is large. The instrument described by Bothé (55) resembles the Curie (56) type in most features but its electrode system is much smaller. However, the method of introducing the specimen to be measured is objectionable.

The instrument used in our experiments was patterned after the Curie form (56). It was found that the sensitiveness of the instrument could be quite materially increased by using a different type of electrode and not screening off completely the beta radiation. Ordinarily in gamma-ray measurements the beta rays are completely screened off, but in our method of making comparisons the activity of the standards used was weight for weight close to that of the samples. There is thus no necessity of screening off the beta rays, and correction factors are also eliminated.

Description of the instrument. A cross section of the instrument is shown in Figure 8. It may be described as a "triple cylinder, or re-entrant ionization chamber attached to an electroscope". Plate 6 shows the mounting of the reading microscope by means of which it can be adjusted in three planes at right angles to each other.

The sample, hermetically sealed in a pyrex tube, occupies a position in the center of the ionization chamber. The electrodes surround the sample,

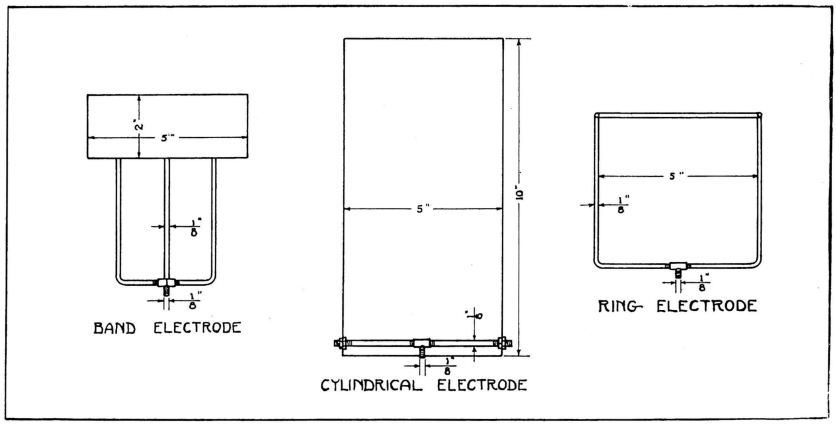


Figure 9. Electrodes for Curie Gamma-ray Instrument

equidistant from the outer wall and the inner wall of the ionization chamber, which, in turn, surrounds the sample. The electrode is supported by the rods that connect it to the leaf system. The leaf system, a single gold leaf, is of the usual type, mounted in amber insulation. Three forms of electrode were used, shown diagrammatically in Figure 9, (1) cylinder, (2) band, and (3) ring type.

The object of our experiments was to ascertain the degree of accuracy that can be attained in making gamma-ray measurements in place of the usual radium determinations by the emanation method on low-grade products which require analysis in plant operation. About ten representative samples were selected and prepared for the test by grinding to pass through a 40-mesh sieve and drying at 90° C. The radium content of all the samples was first carefully determined by the emanation method, and in samples containing uranium these values were checked by uranium determinations. The gamma-ray activity of the samples was then determined.

Tared test tubes were filled to within one centimeter of the top, weighed again, and hermetically sealed, and measurements were made after equilibrium had been attained. The technique is simple. The specimen is placed in the sample chamber (A, Fig. 8) of the instrument and the rate of drift of the leaf noted. The leaf system was always charged to the same potential prior to readings, and the drift of the leaf taken over not only the same number of divisions of the scale in the eye-piece, but also over the same section of the scale.

The behavior of the instrument with the different electrodes was first tested. After the natural leak had been taken for each electrode the rates of discharge were measured for four samples with each electrode. The second, third and fourth columns of Table XX give the observed discharge expressed in divisions per gram per second for the respective electrodes, cylinder, C. E., band, B. E., and ring, R. E. and the other columns express ratios.

TABLE XX.—RATES OF DISCHARGE FOR THE THREE ELECTRODES.

Sample Number	Cylinder d/gm/sec. x 10^5	Band d/gm/sec. x 10^5	Ring d/gm/sec. x 10^5	B. E. / C. E.	R. E. / B. E.	R. E. / C. E.
1	12.90	23.08	38.70	1.79	1.68	3.00
4	14.80	28.00	45.32	1.89	1.62	3.06
5	12.73	22.08	39.15	1.73	1.77	3.07
8	1.54	2.84	4.94	1.85	1.74	3.20

It will be observed that the ratios deviate less than 4 per cent from the mean value and this variation may be regarded as an index of the precision the method affords. Substitution of a ring electrode for the cylinder in the Curie instrument increases its sensitiveness three-fold, and thus materially shortens the time required for making measurements. The band and ring electrodes were used in all subsequent measurements.

The experimental data obtained, on nine of the ten specimens studied, are summarized in Table XXI.

TABLE XXI.—SAMPLES AND VALUES OBTAINED BY THE USE OF MODIFIED GAMMA-RAY INSTRUMENT.

Sample Number	Wt. of Sample g.	Radium per g. x 10^8			Ratio of rate of discharge RE/BE
		Emanation Method	Band Electrode	Ring Electrode	
1.	67.6	17.4	17.4	17.4	1.52
2.	78.3	62.4	62.8	62.2	1.51
3.	47.4	2.18	2.16	2.22	1.57
4.	50.0	20.9	19.8	20.37	1.57
5.	62.5	16.2	17.1	17.6	1.56
6.	50.5	2.07	1.91	2.04	1.64
7.	113.0	2.69	2.47	2.48	1.53
8.	117.5	1.14	1.28	1.21	1.45
9.	266.6	21.23	16.0	15.9	1.51

The radium content of the samples as determined by the emanation method appear in the third column. The values included in the fourth column are based upon gamma-ray measurements.

Samples 1 and 2 were prepared from concentrates in which the radium was present as carbonate. Samples 3, 4, 5 and 6 represent concentrates where the radium was present as sulfate. Samples 1 to 6 inclusive were practically free from uranium. Samples 7 and 8 were virgin carnotite ore, and sample 9 was high-grade uraninite. Inasmuch as the radium content of all the samples was definitely known, it would have been possible to select any one of the nine specimens as the standard to calculate the value of the others from the experimental data. However, sample 1 was arbitrarily selected. The discharge of the various specimens was calculated in terms of divisions per second per gram of material, and then by a simple proportion, the value of the radium content of the unknown was calcualted. The experimental value for both the ring and band electrodes were calculated in the manner as above described. The ratios of the discharge rates of the two electrodes again give an index of the accuracy of the measurements.

The samples were measured daily over a period of two weeks, and the results recorded are the average of the daily values obtained. It would, of course, be impractical to make measurements over such a prolonged period of time in a commercial laboratory, but as a matter of fact, the readings taken over the first three or four days give results almost identical with those recorded. Inasmuch as all the samples had been sealed for over a month prior to reading, it was not necessary to make any correction for growth of emanation.

The experimental values as determined by the gamma-ray method agree with the true values, within the range of experimental error, in all instances

except that of sample 9. It is thus evident that the method has limitations, for this discrepancy in sample 9 is undoubtedly due to the value of the coefficient of absorption for gamma radiation under the specific conditions of measurement. For the more detailed explanation of this variation, further experiments are in progress.

Sample 9 in Table XXI is worthy of special consideration, inasmuch as it is a sample of high-grade uraninite that has been carefully standardized for use in the calibration of instruments for emanation work. The University purchased about one and one-half pounds of the uraninite practically free from sulfide. The uranium content was carefully determined by: (1) modified Boltwood method (57), (2) Boltwood method (58) and (3) method described by Moore and Kithil (59). The average of not less than triplicate determinations is as follows: By procedure 1: 62.89, 2: 62.37 and 3: 62.13, giving a grand average of 62.46 per cent uranium. This value was then checked by determining the total quantity of radium in the uraninite by the emanation method, utilizing the calibrated instruments described in a previous section of this work. The free emanating power was calculated by determining the quantity of emanation present in a specimen by boiling off directly, accumulating the emanation and measuring. From the difference between the value obtained under this condition and that obtained by determining the total quantity of radium present in the sample, the free emanating power was calculated. The final values accepted for the standard are: 1 g. of unaninite contains .6246 g. of uranium, equivalent to 2.123×10^{-7} g. of radium. The free emanating power is equivalent to 4.32 per cent, and 1 mg. dissolved directly gives 2.031×10^{-7} millicuries of radium.

It has been shown by Kleeman (60) that the ionization produced in a gas is proportional to the density of the gas. Consequently, an attempt was made to further increase the rate of discharge by use of a gas having a density greater than that of air. Accordingly, four samples were measured first with air in the ionization chamber (B, Figure 8) and then with carbon dioxide. The data in Table XXII show the increased ionization thus obtained.

TABLE XXII.—INCREASED IONIZATION DUE TO USE OF A MIXTURE OF AIR WITH A HEAVY GAS, CARBON DIOXIDE.

Sample Number	Discharge in div/sec/g x 10^4		Ratio $\frac{CO_2, \text{ air}}{\text{air}}$	Ratio $\frac{CO_2}{\text{air}}$ *
	Air	CO_2, air		
1.	3.87	5.08	1.31	1.53
2.	13.84	18.45	1.33	
4.	4.53	5.72	1.26	
9.	3.54	4.66	1.31	

*Value obtained by Kleeman[60].

The ratio 1.30 is less than that found by Kleeman (60), for in our apparatus the gamma radiation had to pass through a short distance of air before reaching the ionization chamber which was filled with carbon dioxide.

The effect of greater density can be produced with air by increasing the pressure. Laby and Kaye (61), and Wilson (62) found that the ionization effect due to gamma radiation increases proportionally with pressure until about twenty atmospheres is reached.

The application of the gamma-ray method in the modified form here described, to low-grade specimens of radio-active materials has several advantages: (1) The sample used is from fifty to one thousand times larger than the amounts used in the emanation method; this requirement insures its being more representative of the material tested, (2) the technique of the operation is extremely simple, (3) the introduction of correction factors is reduced to a minimum and (4) a series of determinations may be made on the same sample.

On the other hand, the method has its limitations in that: (1) There has to be a standard available similar to the unknown to be measured, (2) the instrument in its present stage of development is not applicable to material whose radium content is less than 10^{-9} g. per g. with any degree of accuracy.

There seems to be a little doubt but that gamma-ray measurements may be used as a safe substitute for the emanation method in the analysis of a variety of comparatively low-grade products. The data reported show that the method, as here developed, has its limitations as to the grade of material that may be measured with a fair degree of accuracy. For instance, the values obtained on samples 6 and 8, Table XXI, by gamma-ray method, where the radium content is low, show greater deviation from the real values than in the other samples where the radium content is higher.

The Alpha-Ray Method.—No systematic experimental work was conducted on the ores and radio-active products used in these experiments, but several years ago the author made extensive tests on ores from various districts in the American field by the alpha-ray method. For descriptions of the method and instruments used see Moore and Kithil (59). The percent-

TABLE XXIII

Ore No.	Per cent U_3O_8 by Analysis	g. Ra per g. x 10^9 calculated	Alpha-ray activity per g. Ra.	Ore No.	Per cent U_3O_8 by Analysis	g.Ra per g. x 10^9 calculated	Alpha-ray activity per g. Ra
1.	1.69	4.87	1.73	12	1.60	4.61	1.41
2.	1.44	4.15	1.78	13	1.02	2.94	1.79
3.	1.37	3.95	1.57	14a	1.77	5.10	1.60
4a	1.71	4.93	1.54	14b	2.33	6.72	1.62
4b.	2.08	6.00	1.93	15-RK	1.68	4.85	1.74
4c.	2.31	6.66	2.49	15c	2.25	6.49	1.65
5.	2.77	7.99	1.42	15-P	1.97	5.68	1.43
6.	2.16	6.23	1.70	16-D	1.20	3.46	1.52
7.	2.61	7.53	1.54	19-DD	1.06	3.06	1.99
P-13	3.54	10.21	1.74	20-DD	1.78	5.13	1.37
P-14	2.74	7.90	1.70	21-P	2.54	7.32	1.61
8.	2.37	6.83	1.55	22-DD	1.70	4.90	1.61
9a.	1.02	2.94	1.44	23-P	2.12	6.11	1.55
9b.	1.62	4.67	1.65	24	1.79	5.16	1.87
10a.	.86	2.48	1.89	25-DD	1.14	3.29	1.89
10b.	1.63	4.70	1.57	25a.	9.34	26.92	1.61
11.	4.76	4.76	1.65	26b.	.79	2.28	1.48

age of uranium in each sample in the second column of Table XXIII was determined by the ordinary analytical method, and from this value the radium content was calculated, assuming that one gram of uranium is in equilibrium with 3.4 x 10^{-7} g. Ra. The alpha-ray activity in the last column simply represents arbitrary units, in this case, the number of scale divisions fall of the leaf per second, corresponding to 10^{-9} g. Ra in the different ore samples.

The values in the last column should be constant if the method were applicable to all carnotites. It is apparent that this is not even approximately true. However, the method is of service where the ores under examination are of the same origin as the standard used. Consequently, it is necessary that a variety of standards be available when the radium content of an ore is to be determined by the alpha-ray method, and that enough data be available regarding the origin of the unknown to be determined to guide one intelligently in selecting the proper standard for comparison.

The results found check very well those reported by Lind (40). He explains the deviation by three principal causes: (1) Variation in the amount of gaseous diffusion from the ore; the percentage loss is usually referred to as the free emanating power, (2) variability in the radium-uranium ratio (50), (3) the position of the radio-active material in the sand grains.

Concentrates.—Commercial processes involving the disintegration of the ores by means of nitre cake followed by sliming off the values obviously results in a slime or concentrate. It would seem that the concentrates so produced would be far more similar in activities than the ores from which they were produced. Therefore, a series of experiments was conducted to determine if the alpha-ray method could be utilized with any degree of accuracy for estimating the radium content of the slimes or concentrates. Such a method would be very valuable for use in daily checks of plant operation. The results of the experiments conducted are reported in Table XXIV.

TABLE XXIV

Lot. No.	g. Ra per x10^8	Div. discharge per min.	Alpha ray activity per g. Ra x10^8
R-2	15.45	128.6	8.33
R-6	3.90	39.3	10.08
R-7	3.73	37.7	10.19
R-9	5.34	51.9	9.72
R-13	9.67	110.4	11.41
R-15	5.23	46.9	8.97
R-17	11.82	106.0	8.97
R-19	9.12	82.6	9.06
R-20	8.46	73.4	8.68
R-22	4.58	53.3	11.63
R-24	4.76	51.9	10.90
R-28	6.02	58.0	9.63
R-30	5.53	46.9	8.68
R-32	5.02	59.8	9.93
R-36	5.40	53.3	9.87
R-38	9.24	80.0	8.66

Here again the alpha-ray activity per g. Ra x 10^{-8} is a calculated value and should be a constant if the method were reliable. The readings were made on samples that had stood in the open for sufficient time to become in equilibrium, and on samples whose moisture content was practically the same. The data in the last column clearly show that the method is not reliable enough for plant control work, even though the percentage variation is not as large as in the case of virgin ores.

A NEW DEVICE FOR CHARGING ELECTROSCOPES

By Royce LeRoy and Herman Schlundt

In making radium determinations by electroscopic methods it is important that the charging potential applied to the electrode system of the electroscope be always the same to secure uniformly accurate results with a calibrated instrument. When an electroscope is always charged with a constant potential the same degree of saturation of the insulations is insured and it is this factor that makes for a uniform natural leak during the course of measurements. Moreover, by bringing the charged leaf to the same point on the scale of the reading microscope measurements can generally be made a little faster for it will not then be necessary to wait for the leaf to fall from higher positions to the point at which the readings begin.

The ideal charging device for either a commercial or experimental laboratory must (1) function properly over a long period of time, (2) require a minimum of attention and care to keep it in working order, (3) be of comparatively low first cost and be entirely economical in the course of its use and (4) possess the property of flexibility, by which is meant the ready adjustment in securing different voltages required for various electroscopes with a minimum of time required for changing connections to secure that potential. The devices used for securing a potential for charging purposes are (1) wet cell batteries, (2) dry cell batteries, (3) friction devices such as an ebonite rod and a piece of wool, or glass rod and a piece of silk, and (4) electrolytic rectifiers.

Batteries of wet cells, generally of test tube size, and batteries of small dry cells are being used successfully as sources of a potential for charging electroscopes. Short circuiting, however, must be guarded against in using batteries and the cells deteriorate with age. The use of friction devices is not at all satisfactory, it being difficult to charge the leaf system of an electroscope to the required degree each time a measurement is made, and on humid days the devices fail altogether. We have had no experience with electrolytic rectifiers in this laboratory.

During the past year a charging device has been developed in this laboratory that is proving satisfactory in charging electroscopes under all conditions and in securing easily a wide range of potentials either positive or negative. The principles underlying this apparatus are (1) the transforming of an ordinary light circuit of 110 volts A. C. to 3000 volts, (2) rectifying this high tension current by means of a "kenotron" rectifying tube, and (3) using a specially designed high resistance potentiometer to secure any potential that is required to charge the leaf system of an electroscope to the desired degree.

The primary coil of the transformer is connected to the A. C. line by means of a contact switch and points graduated in steps of 2.5 volts, so that the A. C. line voltage used may vary from 102.5 volts to 115 volts. The number of turns on the primary coil varies from 139.5 to 153.5.

The transformer has two secondary coils of 8 turns each, supplying a voltage of 10.5 volts and a third secondary coil of 2220 turns supplying 3000 volts. The filament of the "kenotron" rectifier is lighted by the 10.5 volt

current from one of the secondaries and the current of 3000 volts is rectified in the "kenotron" shown in the diagram, Figure 10.

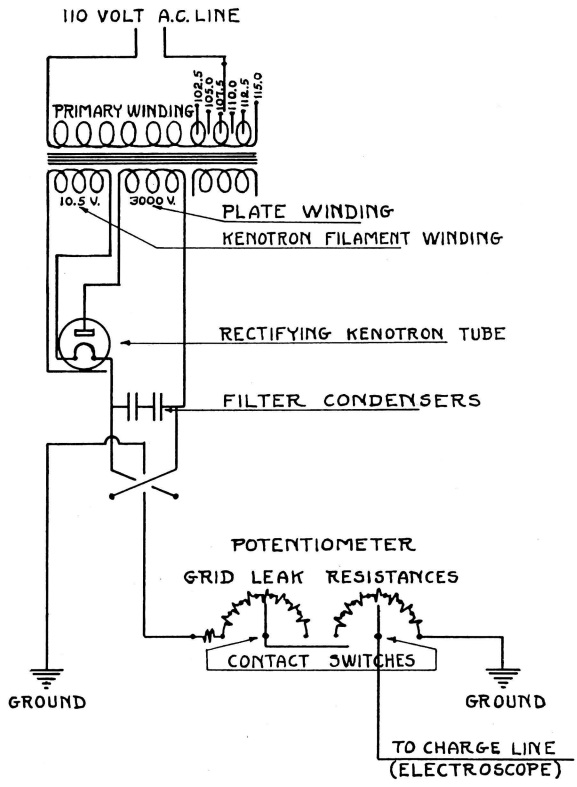


Figure 10. Diagram Showing Wiring Connections for Charging Device

The rectified current is led through a two-way switch from which one wire leads to the ground and the other to the potentiometer. By means of this switch it is possible to change the sign of the potential applied to the leaf system from positive to negative, or vice versa, by throwing the switch in the right direction. The rectified current next passes through the potentiometer, containing a series of high resistances and thence to the ground. The resistances in the potentiometer are the grid leaks so commonly used in radio apparatus and vary in resistance from 0.25 to 3.0 megohms. The total

resistance of the potentiometer is 15.75 megohms. Two contact switches in series are used to plug in between each individual resistance with the lead to the charging line, and afford a high degree of flexibility. It is possible to secure varying potentials desired for the charging line, from more than 2000 volts to a small fraction thereof in steps of approximately 30 volts.

The feature of the apparatus is its extreme flexibility; the desired voltage for charging an electroscope can be had by merely adjusting the contact switches. The A. C. line voltage remaining constant, each contact point will always deliver the same potential to the charging line.

Mention has already been made of the contact switch and points with which the transformer is equipped to make correction for variations in the line voltage. This feature also adds to the flexibility of the device.

In the diagram, Figure 10, two filter condensers are shown of 1 microfarad capacity each. These condensers also serve to eliminate any slight variation in the rectified current due to slight fluctuations of the A. C. line voltage. The condensers are not essential but they do add to the steadiness of the potential applied to the leaf system.

The whole apparatus as it is used in this laboratory is mounted on a portable instrument board, Plate 7. It is only necessary to plug into an

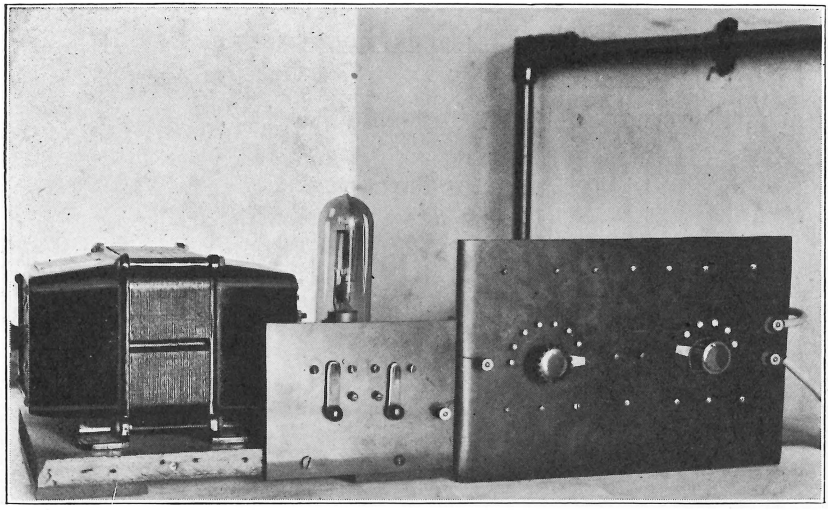


PLATE NO. 7. CHARGING DEVICE.

ordinary light socket to have the apparatus ready for use. All the connecting wires are insulated with either glass or rubber tubing. In the measurements laboratory the charging line has a number of charging connections at any one of which an electroscope can be charged. The voltage obtained from the device is high enough to operate ordinary Geissler tubes.

We wish to make special acknowledgment to Mr. C. J. Larsen of the Kansas City Telephone Company for valuable advice and suggestions in the development of this device.

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Appendix

Tables of

SOME RADIOACTIVE CONSTANTS

RADIOACTIVE FAMILIES

CONVERSION FACTORS

PROGRESSIVE ACCUMULATION OF RADIUM EMANATION

ENGINEERING EXPERIMENT STATION
UNIVERSITY OF MISSOURI

1923

RADIOACTIVE CONSTANTS

Mass of the electron compared to that of hydrogen atom.	$\frac{1}{1840}$
Number of atoms in one gram of hydrogen	6.06×10^{23}
Mass of an atom of hydrogen	1.66×10^{-24} grams.
Number of molecules per cubic cm. of any gas at S. T. P.	2.71×10^{19}
Value of e Charge carried by hydrogen atom } or	4.77×10^{-10} e. s. units. 1.59×10^{-20} e. m. units.
Value of $\frac{e}{m}$ for alpha particle	4818 e. m. units
Charge carried by alpha particle	9.54×10^{-10} e. s. units.
Number of alpha particles expelled per sec. per gram of radium itself	3.72×10^{10}
Number of alpha particles expelled per sec. per gram of radium in equilibrium with its products, inclusive of RaC	14.88×10^{10}
Total number of pairs of ions produced by one alpha particle from RaC in air by complete absorption.	2.20×10^{5}
Velocity of alpha particle from Ra C'	1.922×10^{9} cm. per sec.
Velocity of alpha particles in miles per sec.	9000 to 12000
Velocity of hard beta rays, about or	2.9×10^{10} cm. per sec. 170000 miles per sec.
Velocity of gamma rays,	180000 miles per sec.
Helium generated per yr. per gram of radium	174 $mm.^3$
Quantity of heat liberated by one gram of radium and its equilibrium products per hr.:	136 cal.
Distributed as follows:-	
alpha rays	125 cal.
beta rays	4.5 cal.
gamma rays	6.5 cal.
Volume of one curie of emanation	0.663 $mm.^3$
Weight of one curie of emanation = 6.56×10^{-6} g. =	6.56 micrograms.
Radium-Uranium Ratio	3.40×10^{-7}

Radioactive Constants of Radium

Atomic weight	226
Half decay period	1580 years
Transformation constant	4.38×10^{-4} per year
Type of radiation emitted	alpha
Range of rays in air S. T. P.	3.21 cms.
Current produced by alpha particles from 1 g. Radium (without equilibrium products)	2.41×10^{6} e. s. units

Radioactive Constants of Radium Emanation

Atomic weight	222
Half decay period	3.81 d.
Transformation constant,	0.18 d^{-1}
or	.0075 $hr.^{-1}$
Type of radiation emitted	alpha
Range of rays in air	3.91 cms.
Current produced by alpha particles from per Curie emanation alone	2.75×10^{6} e. s. units.

Absorption of the various types of rays

Alpha rays	
Completely absorbed by	.006 cms. of Al. foil
Hard beta rays	
Completely absorbed by	2 mm. of lead
Half absorbed by	.1 mm. of lead
Hard gamma rays	
Half absorbed by	14 mm. lead

Ionization due to alpha, beta, and gamma rays is of the relative order of 10,000, 100 and 1.

Velocity of alpha particle $1.0246 \times 10^{9} R_o^{1/3}$

Number of pairs of ions produced in air by any alpha particle $6.25 \times 10^{4} R_o^{2/3}$

$R_{15^\circ} = 1.055 R_o$; $R_{20^\circ} = 1.073 R_o$

1 Mache Unit represents 3.64×10^{-10} Curie per liter.

RADIOACTIVE FAMILIES

URANIUM SERIES

Element	A-tomic Wt.	A-tomic No.	Radiation	Half decay Period	Chemical Character (Isotopic with)
Uranium I	238	92	alpha	4.3 billion yr.	Uranium II
Uranium X_1	234	90	beta+gamma	23.8 days	Thorium
Uranium X_2	234	91	beta+gamma	1.14 mins.	Protoactinium
Uranium II	234	92	alpha	About one million yr.	Uranium I
Ionium	230	90	alpha	About 100,000 yrs.	Thorium
Radium	226	88	alpha	1580 yr.	Mesothorium I
Ra-Emanation	222	86	alpha	3.8 d.	Th-Emanation
Radium A	218	84	alpha	3 min.	Polonium
Radium B	214	82	beta+gamma	26.8 min.	Lead
Radium C	214	83	beta+gamma (alpha)	19.5 min.	Bismuth, Ra E
Radium C' (99.96%)	214	84	alpha	1.5×10^{-8} sec.	Polonium
Radium D	210	82	soft beta	16.5 yr.	Lead
Radium E	210	83	soft beta	4.85 d.	Bismuth
Radium F (Polonium)	210	84	alpha	136.5 d.	Ra A
Radium G	206	82	no rays		Lead & Th lead

THORIUM SERIES

Thorium	232-1	90	alpha	16.5 billion yr.	Ionium
Mesothorium I	228	88	soft beta	6.7 yr.	Radium
Mesothorium II	228	89	beta+gamma	6.2 hr.	Actinium
Radiothorium	228	90	alpha	1.90 hr.	Thorium, Ionium
Thorium X	224	88	alpha	3.64 d	Radium, MsTh1
Th-Emanation	220	86	alpha	54.5 sec.	Ra-Emanation
Thorium A	216	84	alpha	0.14 sec.	Polonium, Ra A
Thorium B	212	82	beta	10.6 hr.	Lead, Ra D
Thorium C	212	83	alpha	60.8 min.	Bismuth, Ra E
Thorium C'' (35%)	208	81	beta+gamma	3.20 min.	Thallium
Thorium D (Th lead)	208	81	stable stable		Ra Lead

RADIOACTIVE FAMILIES

BRANCH SERIES

Element	Atomic Wt.	Atomic No.	Radiation	Half Decay Period	Chemical Character (Isotopic with)
At Uranium II the series branches, and 3% of the total number of atoms disintegrating, follow the branch Actinium Series.					
Uranium Y	230	90	beta	24.6 hr.	Thorium
Protoactinium	230	91	alpha	estimated 1.2×10^4 yr.	UX_2
Actinium	226	89	soft beta	About 20 yr.	MsTh 2
Radioactinium	226	90	alpha	18.9 d.	Thorium
Actinium X	222	88	alpha	11.2 d.	Radium, MsTh1
Ac. Emanation	218	86	alpha	3.92 sec.	Ra Em; Th Em.
Actinium A	214	84	alpha	0.002 sec.	Polonium
Actinium B	210	82	beta+gamma	36.1 min.	Lead
Actinium C	210	83	alpha	2.16 min.	Bismuth
Actinium D	206	81	beta+gamma	4.76 min.	Thallium
Actinium lead	206	82	----------	----------	Lead
At Radium-C, 0.04% of the atoms follow the branch series.					
Radium C	214	83	alpha (0.04%)	19.5 min.	Bismuth
Radium C''	210	81	beta+gamma	1.32 min.	Thallium
End Products	210	82	----------		Lead
At Thorium C, 65% of the atoms follow the branch series					
Thorium C	212	83	beta+gamma (65%)	60.8 min.	Bismuth. Ra E
Thorium C' (65%)	212	84	alpha	Estimated 10^{-11} sec.	Polonium
Th lead	207	82	stable		Lead

CONVERSION FACTORS

Radium Salt	Radium Element (Ra)	Anhydrous Radium Bromide ($RaBr_2$)	Hydrous Radium Bromide ($RaBr_2$ $2H_2O$)	Anhydrous Radium Chloride ($RaCl_2$)	Hydrous Radium Chloride ($RaCl_2$ $2H_2O$)	Radium Carbonate ($RaCO_3$)	Radium Sulphate ($RaSO_4$)
1 mg. Radium Element	1.0000	1.7072	1.8667	1.3138	1.4732	1.2655	1.4250
1 mg. Anhydrous Ra Bromide	0.5857	1.0000	1.0934	0.7695	0.8629	0.7412	0.8347
1 mg. Hydrous Ra Bromide	0.5357	0.9146	1.0000	0.7038	0.7892	0.6779	0.7634
1 mg. Anhydrous Ra Chloride	0.7611	1.2995	1.4208	1.0000	1.1213	0.9632	1.0847
1 mg. Hydrous Ra Chloride	0.6788	1.1588	1.2671	0.8919	1.0000	0.8590	0.9673
1 mg. Radium Carbonate	0.7902	1.3491	1.4750	1.0382	1.1641	1.0000	1.1261
1 mg. Radium Sulphate	0.7017	1.1980	1.3099	0.9219	1.0388	0.8880	1.0000

PROGRESSIVE ACCUMULATION OF RADIUM EMANATION

$I_t = I_o(1-e^{-\lambda t})$; $\lambda = 0 \cdot 1801$ days^{-1}; $I_o = 1$

hours	0 days	△	1 day	△	2 days	△	3 days	△	4 days	△	5 days	△	6 days	△	7 days	△
0	.0000	75	.1648	63	.3025	52	.4175	44	.5136	36	.5937	31	.6607	25	.7166	22
1	.0075	74	.1711	62	.3077	52	.4219	43	.5172	36	.5968	30	.6632	26	.7188	20
2	.0149	74	.1773	61	.3129	52	.4262	43	.5208	36	.5998	30	.6658	24	.7208	21
3	.0223	73	.1834	62	.3181	51	.4305	42	.5244	35	.6028	29	.6682	25	.7229	21
4	.0296	72	.1896	60	.3232	50	.4347	42	.5279	35	.6057	30	.6707	25	.7250	21
5	.0368	72	.1956	60	.3282	50	.4390	42	.5314	36	.6087	29	.6732	24	.7271	20
6	.0440	72	.2016	60	.3332	50	.4432	41	.5350	34	.6116	29	.6756	25	.7291	21
7	.0512	71	.2076	59	.3382	50	.4473	41	.5384	35	.6145	29	.6781	24	.7311	20
8	.0583	70	.2135	59	.3432	49	.4514	42	.5419	34	.6174	29	.6805	24	.7332	19
9	.0653	70	.2194	58	.3481	49	.4556	40	.5453	34	.6203	28	.6829	23	.7351	20
10	.0723	69	.2252	58	.3530	48	.4596	41	.5487	34	.6231	28	.6852	24	.7371	20
11	.0792	69	.2310	58	.3578	48	.4637	40	.5521	33	.6259	28	.6876	23	.7391	20
12	.0861	69	.2368	57	.3626	48	.4677	40	.5554	34	.6287	28	.6899	23	.7410	20
13	.0930	68	.2425	57	.3674	47	.4717	39	.5588	33	.6315	27	.6922	23	.7430	19
14	.0998	67	.2482	56	.3721	47	.4756	39	.5621	32	.6342	28	.6945	23	.7449	19
15	.1065	67	.2538	56	.3768	46	.4795	39	.5653	33	.6370	27	.6968	23	.7468	19
16	.1132	66	.2594	55	.3814	47	.4834	39	.5686	32	.6397	27	.6991	23	.7487	19
17	.1198	66	.2649	55	.3861	46	.4873	38	.5718	32	.6424	27	.7014	22	.7506	18
18	.1264	65	.2704	54	.3907	45	.4911	38	.5750	32	.6451	26	.7036	22	.7524	19
19	.1329	65	.2758	55	.3952	46	.4949	38	.5782	31	.6477	27	.7058	22	.7543	18
20	.1394	64	.2813	53	.3998	44	.4987	37	.5813	32	.6504	26	.7080	22	.7561	19
21	.1458	64	.2866	54	.4042	45	.5024	38	.5845	31	.6530	26	.7102	22	.7580	18
22	.1522	64	.2920	53	.4087	44	.5062	37	.5876	31	.6556	25	.7124	21	.7598	18
23	.1586	62	.2973	52	.4131	44	.5099	37	.5907	30	.6581	26	.7145	21	.7616	18

hours	8 days	△	9 days	△	10 days	△	11 days	△	12 days	△	13 days	△	14 days	△	15 days	△
0	.7634	17	.8024	14	.8349	13	.8622	10	.8849	8	.9038	8	.9197	6	.9329	5
1	.7651	18	.8038	15	.8362	12	.8632	10	.8857	9	.9046	7	.9203	6	.9334	5
2	.7669	17	.8053	15	.8374	12	.8642	10	.8866	8	.9053	7	.9209	6	.9339	5
3	.7686	18	.8068	14	.8386	12	.8652	10	.8874	9	.9060	7	.9215	6	.9344	5
4	.7704	17	.8082	14	.8398	12	.8662	10	.8883	8	.9067	7	.9221	6	.9349	5
5	.7721	17	.8096	15	.8410	12	.8672	10	.8891	8	.9074	7	.9227	5	.9354	5
6	.7738	17	.8111	14	.8422	12	.8682	10	.8899	9	.9081	7	.9232	6	.9359	5
7	.7755	16	.8125	15	.8434	12	.8692	10	.8908	8	.9088	7	.9238	6	.9364	4
8	.7771	17	.8139	14	.8446	11	.8702	10	.8916	8	.9095	6	.9244	6	.9368	5
9	.7788	17	.8153	13	.8457	12	.8712	9	.8924	8	.9101	7	.9250	5	.9373	5
10	.7805	16	.8166	14	.8469	11	.8721	10	.8932	8	.9108	7	.9255	6	.9378	4
11	.7821	16	.8180	14	.8480	12	.8731	9	.8940	8	.9115	6	.9261	5	.9382	5
12	.7837	17	.8194	13	.8492	11	.8740	10	.8948	8	.9121	7	.9266	6	.9387	5
13	.7854	16	.8207	14	.8503	11	.8750	9	.8956	8	.9128	6	.9272	5	.9392	4
14	.7870	16	.8221	13	.8514	11	.8759	9	.8964	7	.9134	7	.9277	5	.9396	5
15	.7886	15	.8234	13	.8525	11	.8768	9	.8971	8	.9141	6	.9282	6	.9401	4
16	.7901	16	.8247	13	.8536	11	.8777	10	.8979	8	.9147	7	.9288	5	.9405	5
17	.7917	15	.8260	13	.8547	11	.8787	9	.8987	7	.9154	6	.9293	5	.9410	4
18	.7932	16	.8273	13	.8558	11	.8796	9	.8994	8	.9160	6	.9298	6	.9414	4
19	.7948	15	.8286	13	.8569	11	.8805	9	.9002	7	.9166	7	.9304	5	.9418	5
20	.7963	16	.8299	13	.8580	10	.8814	8	.9009	8	.9173	6	.9309	5	.9423	4
21	.7979	15	.8312	12	.8590	11	.8822	9	.9017	7	.9179	6	.9314	5	.9427	5
22	.7994	15	.8324	13	.8601	10	.8831	9	.9024	7	.9185	6	.9319	5	.9432	4
23	.8009	15	.8337	12	.8611	11	.8840	9	.9031	7	.9191	6	.9324	5	.9436	4

hours	16 days	△	17 days	△	18 days	△	19 days	△	20 days	△	21 days	△	22 days	△	23 days	△
0	.9440	9	.9533	7	.9610	6	.9674	5	.9728	4	.9773	3	.9810	3	.9842	2
2	.9449	8	.9540	6	.9616	5	.9679	5	.9732	4	.9776	4	.9813	3	.9844	2
4	.9457	8	.9546	7	.9621	6	.9684	5	.9736	4	.9780	3	.9816	3	.9846	3
6	.9465	8	.9553	7	.9627	6	.9689	4	.9740	4	.9783	3	.9819	3	.9849	2
8	.9473	8	.9560	6	.9633	5	.9693	5	.9744	4	.9786	3	.9822	2	.9851	2
10	.9481	8	.9566	7	.9638	5	.9698	4	.9748	4	.9789	3	.9824	3	.9853	2
12	.9489	7	.9573	6	.9643	6	.9702	5	.9752	3	.9792	4	.9827	2	.9855	2
14	.9496	8	.9579	7	.9649	5	.9707	4	.9755	4	.9796	3	.9829	3	.9857	2
16	.9504	7	.9586	6	.9654	5	.9711	4	.9759	3	.9799	3	.9832	2	.9859	2
18	.9511	7	.9592	6	.9659	5	.9715	5	.9762	4	.9802	3	.9834	3	.9861	2
20	.9518	8	.9598	6	.9664	5	.9720	4	.9766	3	.9805	3	.9837	2	.9863	2
22	.9526	7	.9604	6	.9669	5	.9724	4	.9769	4	.9808	2	.9839	3	.9865	2

hours	24 days	△	25 days	△	26 days	△	27 days	△	28 days	△	29 days	△	30 days	△	31 days	△
0	.9867	4	.9889	4	.9908	2	.9923	2	.9936	1	.9947	1	.9955	2	.9963	1
4	.9871	4	.9893	3	.9910	3	.9925	2	.9937	2	.9948	2	.9957	1	.9964	1
8	.9875	4	.9896	3	.9913	3	.9927	2	.9939	2	.9950	1	.9958	1	.9965	1
12	.9879	3	.9899	3	.9916	2	.9929	3	.9941	2	.9951	2	.9959	1	.9966	1
16	.9882	4	.9902	3	.9918	2	.9932	2	.9943	2	.9953	1	.9960	2	.9967	1
20	.9886	3	.9905	3	.9920	3	.9934	2	.9945	2	.9954	1	.9962	1	.9968	1

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