Radium

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PROBABLY no other metal excites as much interest, among both scientific men and the general public, as radium. This is due partly to the high cost of radium salts and partly to the peculiar properties of the element. Since radium-bearing ores were discovered in the United States, the interest of American scientific men has been stimulated and, at the present time, more radium is extracted and refined in this country than in all the rest of the world together.

HISTORY

The property of radioactivity was discovered, partly by accident, by Henri Becquerel, the French physicist, in 1896. He was experimenting with certain fluorescent substances in order to find, if possible, a connection between fluorescence and the recently discovered X-rays. Among other chemicals which possess the property of fluorescence, he was using salts of uranium. His custom was to expose the fluorescent substance to the action of sunlight and then register the effect of possible penetrating radiation on a photographic plate protected from ordinary light. Becquerel's experiments gave positive results at once, and he at first believed that he had discovered a relation between fluorescence and X-rays. Later he exposed a plate to a uranium salt which had not been previously exposed to sunlight. To his surprise, on developing this plate, he found that he had obtained the same effect as he had previously secured when

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the uranium salt had been exposed to sunlight. The pursuit of this partly accidental discovery has given us our whole science of radioactivity. It was found that radium and its salts had the property of ionizing gases, or converting the molecules of gases into charged particles. It is this property which is used almost exclusively in identifying radioactive substances and in making quantitative determinations.

Mme. Curie, wife of the Professor of Physics in the Sorbonne, in Paris, became interested in the work of Professor Becquerel, and examined all the known elements to see whether any of them possessed properties similar to those of uranium. She found that thorium and its salts would also affect a photographic plate, without previous exposure to sunlight, and would also ionize gases. Thorium, as well as uranium, is, therefore, radioactive.

Mme. Curie found that radioactivity was an atomic property. A given weight of uranium metal had the same activity, no matter whether it was combined with chlorine, bromine, the (SO_4) radicle or the (NO_3) radicle. The other elements in combination with the uranium did not affect the activity in any way. She then made a study of radioactive minerals, paying especial attention to pitchblende, which is a natural uranium oxide containing traces of lead, arsenic, bismuth, and other impurities. This was furnished her by the Austrian Government from its mines at St. Joachimsthal. To her surprise, she found that a piece of pitchblende carrying a given weight of uranium had approximately four times greater activity than any pure uranium salt containing the same weight of uranium. This indicated that either her original conclusion that radioactivity is an atomic property was wrong, or the pitchblende contained another element, or elements, which were also radioactive. She proceeded to test these conclusions, and was assisted by the Austrian Government, which sent her a considerable amount of pitchblende for this purpose. The mineral was dissolved, and the different groups of elements were successively precipitated, each precipitate in turn being tested for its radioactivity. The lead group was found to be slightly active, and we know now that this was due to the presence of radium G, or radioactive lead. The copper group was also active, due to the presence of polonium, which, in many of its properties, is allied to bismuth. The activity associated with the iron group was due to actinium, which is allied to some of the rare earths. The majority of the radioactivity, however, was found to be concentrated in the barium, strontium, and calcium group. The separation of the small amount of highly active material found associated with these elements was difficult and tedious. On separating the calcium from strontium, the activity still remained with the barium; and the element, radium, was finally separated by fractional crystallization of its salts, either chloride or bromide, from the corresponding barium salts.

Mme. Curie deserves great credit for the discovery of radium and for a great deal of other scientific work she has carried out with marked success in connection with this element. But those who are not versed in the subject are likely to forget to some extent what has been accomplished by those who entered the field of radioactivity after the actual discovery of radium. On the physical side, science owes an immense debt of gratitude to Sir Ernest Rutherford. It was he who beat out the pioneer path which has given us definite radioactive theories; possessed of a keen mind and a splendid intellect, his insight has been almost uncanny. Sir J. J. Thompson, W. H. Bragg, and other physicists have added to our knowledge of this side of radioactivity; while Sir William Ramsay and Professor Soddy are responsible for a great deal that has been done on the chemical side of the subject. In this country, much has been accomplished by Boltwood, Schlundt, McCoy, and Lind.

WHAT IS RADIOACTIVITY?

Radioactive substances will affect a photographic plate and will ionize gases. This is due to the fact that radium and its salts give off three types of rays, called the alpha, beta, and gamma. The alpha rays travel with a velocity of about 20,000 miles per second and are positively charged. It was early found by Rutherford that their mass was comparable to that of a helium atom; and he definitely made the statement before the proof was actually obtained that the alpha particle was a helium atom with two positive charges on it. This was afterward proved by Sir William Ramsay and Professor Soddy, who dissolved some radium chloride in water and allowed the occluded gases to run into a spectrum tube which had previously been evacuated. On allowing these gases to stand for a day or two, the spectrum of helium gradually appeared.

The beta rays consist of negatively charged electrons, with a mass of about $1/1600$th of a hydrogen atom. During radioactive changes, they are ejected with a velocity of from 100,000 to 186,000 miles per second. While the alpha particle is stopped by an ordinary sheet of note-paper, the beta particle will penetrate a thin piece of glass, but is completely stopped by a millimeter thickness of lead. All evidence points to the fact that the beta particle is similar in its properties to the electron found in a Crooks tube, and gives rise to cathode rays.

The gamma rays are not material in character but are vibrations of very short wave length in the ether. Just as the X-rays are formed in an X-ray tube by the stoppage of the cathode rays by impinging on the target, so the gamma rays are formed during radioactive changes when such changes give rise to beta rays; and these rays are expelled from the atom with the velocity of light. It is evident, therefore, that the gamma rays are practically identical with the X-rays, except that they are of shorter wave length and penetrate matter to a much greater extent.

Anything, therefore, is radioactive which gives out alpha, beta, or gamma rays, or all of them. All radioactive changes are accompanied by at least one of these rays. The elimination is due to the explosion of the radioactive atom, such explosion taking place at a definite rate, so that in the case of radium itself one-half is completely transformed in 1690 years. In the second 1690 years, half of what is left will have been changed. In the third period of 1690 years, half of what is left at the end of the second period will have been changed—and so on. The 1690-year period is called the half-life or half-value period of radium; and it can be readily seen that in 10 times the half-life period, only about 1 per cent. of the element will remain unchanged.

DISINTEGRATION SERIES

The manner in which radioactive elements change is shown in Table 1, giving the uranium series, and Table 2, the thorium series. Uranium 1 changes into uranium X_1 with the elimination of alpha rays; uranium X_1 changes into uranium X_2 with the elimination of beta rays; uranium X_2 changes into uranium 2 with the elimination of both beta and gamma rays—and so on down the list. It is thus plainly seen that the metal uranium is the parent of radium and, indeed, of all the radioactive elements which are found in any uranium mineral, and are shown in Table 1. This will correct what is a somewhat general impression that radium is the only radioactive element found in uranium ores in addition to uranium itself. Indeed, all of the elements of Table 1 are found in any uranium ore, and most of them can actually be separated chemically, and their physical and chemical properties identified.

It has already been stated that an alpha particle is a helium atom which has an atomic weight 4. Theoretically, therefore, whenever a radioactive atom explodes, with the elimination of an alpha particle, the resulting atom, left behind after the expulsion of the alpha particle, should have the atomic weight of the original atom minus 4, the atomic weight of the expelled helium atom. The atomic weight of radium has been determined experimentally as 226. The radium atom, during its change, loses an alpha particle with atomic weight 4 and, therefore, the residual radium emanation atom will have an atomic weight 222. By examining the fourth column of Table 1, it is seen that wherever a change occurs involving an alpha particle, the atomic weight of the resulting element is reduced by 4. As the beta particle is an electron, it has not sufficient mass to affect the resulting atomic weight.

There is some definite experimental proof that the above statements are correct. Sir William Ramsay and Professor Soddy actually deter-

TABLE 1.—*Uranium Radioactive Series**

Uranium Series	Half-value Period	Rays	Atomic Weight
Uranium 1	5×10^9 years	alpha	238
Uranium X_1	24.6 days	beta	234
Uranium X_2	1.15 min.	beta and gamma	234
Uranium 2	2×10^6 years	alpha	234
Ionium	10^5 years	alpha	230
Radium	1690 years	alpha and slow beta	226
Radium emanation	3.86 days	alpha	222
Radium A	3.0 min.	alpha	218
Radium B	26.8 min.	beta and gamma	214
Radium C	19.5 min.	alpha, beta and gamma	214
Radium D	16.5 years	beta and gamma	210
Radium E	5.0 days	beta	210
Radium F	136 days	alpha	210
Radium G (lead)	....	....	206

* The branches of Tables 1 and 2 are omitted for the sake of simplicity.

TABLE 2.—*Thorium Radioactive Series*

Thorium Series	Half-value Period	Rays	Atomic Weight
Thorium	1.5×10^{10} years	alpha	232
Mesothorium 1	5.5 years	beta	228
Mesothorium 2	6.2 hr.	beta and gamma	228
Radiothorium	2 years	alpha	228
Thorium X	3.65 days	alpha	224
Thorium emanation	54 sec.	alpha	220
Thorium A	0.14 sec.	alpha	216
Thorium B	10.6 hr.	beta and gamma	212
Thorium C	60 min.	alpha and beta	212
Thorium D_1	3.1 min.	beta and gamma	208
Thorium D_2 (lead)	10^6 years	beta	208

mined the density of the radium emanation, and the figure obtained as a mean of five determinations was 223. In addition, lead is always found in uranium minerals, and the atomic weight of radium G, or the final disintegration product, according to theory, is 206. This does not coincide with the atomic weight of ordinary lead, which is 207; but some experimental work on the atomic weight of lead obtained from uranium and thorium minerals, by Professor F. W. Richards, O. Hönigschmid and Professor Soddy, has shown that the atomic weight of uranium lead is 206, while that of thorium lead is 208—an exceedingly interesting experimental confirmation of the theory. We have, therefore, actually three forms of lead, the only difference among them being their densities, each one having exactly the same chemical and physical properties. If they were mixed by fusion, no known method could separate them; and the only way of telling one from another would be by making an actual density determination.

There is another radioactive series called the actinium series, which is very similar to the uranium series, but as it is of less importance it is not discussed in this paper.

RADIUM ORE DEPOSITS

The two principal commercial ores of radium are pitchblende and carnotite. The former mineral has no definite composition, consisting of uranium oxides (UO_3, UO_2) with oxides of lead, calcium, iron, bismuth, manganese, copper, silicon, aluminum, and rare earths. Carnotite has a more definite composition, being a potassium uranyl vanadate containing small quantities of barium and calcium. The formula $K_2O.2UO_3.V_2O_5.3H_2O$ expresses its composition fairly well, although not exactly. Of lesser importance are autunite, a hydrated calcium uranium phosphate $Ca(UO_2)_2(PO_4)_2.8H_2O$, and torbernite, a hydrated copper uranium phosphate $Cu(UO_2)_2.P_2O_8.8H_2O$.

St. Joachimsthal

The pitchblende deposit at St. Joachimsthal, Austria,[1] is in mica schist interbedded with lime schist and crystalline limestone. Toward the east and northeast the formation is gneiss. The gneiss was intruded by quartz porphyry subsequent to the deposition of the vein material. In the mica schist are fissures filled with volcanic material which cut the mineralized zone at various points and depths. The veins are usually 6 in. to 2 ft. wide, in rare cases widening out to 3 ft. The mode of mineralization varies greatly, the ores occurring in both stringers and pockets. They contain the following metals: Silver, metallic, and as argentite, polybasite, tetrahedrite, etc.; nickel, as nickelin, chloanthite, etc.; cobalt, as smaltite, bismutosmaltite, etc.; bismuth, as metallic bismuth, bismite, etc.; arsenic, as metallic arsenic and arsenopyrite; and uranium, as pitchblende and other alteration products. Galenite, zinc blende, pyrite, marcasite, and copper occur in minor quantities.

The veins show that deposition occurred in three periods: the cobalt and nickel were deposited first, then the uranium, and lastly the silver.

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[1] Richard Beck: "Lehre von den Erzlagerstaetten." 3d Ed., **1**, 408–410. Berlin, Borntraeger, 1909.

Richard Beck: "The Nature of Ore Deposits." Translation by W. H. Weed. 1st Ed., **1**, 284–287. New York and London, *Engineering and Mining Journal*, 1905.

Dolomite spar is aways present, and generally has a white or yellowish-white color, but changes to a brownish-red hue where pitchblende begins to appear, and is a dirty gray where it is actually in contact with the ore. Deep-blue fluorspar is always present.

The mines at Joachimsthal have been worked since 1517. In 1545 the production of silver ores declined considerably, but since then the deposits have been mined for bismuth and cobalt. During the last 25 years the mines have been worked for uranium.

Saxony

In the vicinity of Annaburg, on the Saxony side of the Erzgebirge, the silver-cobalt veins resemble those at Joachimsthal. At Johanngeorgenstadt, the veins contain tin and silver-cobalt ores. Where dolomite spar is found, the silver-cobalt ores contain pitchblende, as at Annaberg. In the Gottessegen mine the pitchblende occurs in the spar in pieces 2 to 3 in. in diameter. These mines are worked principally for bismuth ocher, but also for cobalt and nickel.

In the cobalt-bismuth mines of Schneeberg, are found bismutite and various minerals of nickel, silver, and arsenic. There is also some pitchblende, uranochalcite, uranospinite, galenite, zinc blende, etc.

Cornwall

Pitchblende has also been found in Cornwall, England, in the tin region. As at Joachimsthal and Johanngeorgenstadt, the mineral is found associated with nickel-cobalt veins, although only part of the veins are highly argentiferous. Even though these veins are closely connected with the tin veins, they apparently are not of the same age as the latter, but belong to the same general period of mineralization. According to Ussher, Barrow and MacAllister,[2] the most important uranium producers are the South Terras mine, the Carharrack, Dolcoath, Wheal Unity, Wheal Gorland, Wheal Lovell, and Trenwith. The South Terras mine is situated in the valley of the Fal, southwest of St. Austell. The country rock is slate, intruded by greenstone and granite porphyry dikes.

Pitchblende in the United States

Pitchblende has been found in the following localities in the United States: Feldspar quarry, at Middletown, Conn., in large octahedrons; in Hall's quarry, at Glastonbury, Branchville, Conn., in a pegmatite vein and usually embedded in albite; at Marietta, S. C.; in the Baringer

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[2] The Geology of the Country Around Bodmin and St. Austell. *Memoirs*, Geological Survey of England and Wales (1909), 157.

Hill district, Llano County, Texas; in the Bald Mountain district, Black Hills, S. Dak.; in Mitchell County, N. C.; and in Gilpin County, Colorado. The latter district is the only one of commercial importance.

All of the Gilpin County mines, with one exception, are found on or near Quartz Hill, a few miles from Central City. There are five that have produced pitchblende in quantity: the Kirk, Wood, German, Belcher, and Calhoun. The Kirk, Belcher and German mines are close together on Quartz Hill, the Wood and the Calhoun being in the valley below.

These mines, until recently, have been worked mainly for gold. In this district, gneiss and crystalline schist predominate, with intrusive andesitic dikes and occasionally acid granitic dikes. The rock containing the pitchblende, galena, sphalerite, etc., is a fine-grained aplitic granite which probably once contained an appreciable amount of biotite. The ore deposits are of two general types, one containing pitchblende with pyrite, sphalerite and galena, and sometimes marcasite; the other type contains pyrite, chalcopyrite, sphalerite and galena, with some gold and silver. Generally speaking, the two types are not associated, so that the miner has a choice of mining either for pitchblende, or for gold.

The Kirk mine has probably been the most important producer of the five mentioned although reliable data on the output of pitchblende from this mine, up to a few years ago, has been difficult to obtain. During the last 12 years, about 20 tons of ore, with an average content of 35 per cent. U_3O_8, and over 100 tons with a content of 3 to 4 per cent. U_3O_8, have been mined. The mine has been shut down for some time. More recent operations of the German and Belcher mines produced 120 tons of low-grade ore, averaging about 1 per cent. U_3O_8, and 6 tons of high grade. Smaller quantities of ore have been produced at various times from these mines and from the Wood and the Calhoun.

Australia

Uranium ores are found in certain localities in Australia. One of these deposits is 80 miles east of Farina, a railroad station on the Great Northern line in South Australia, and lies between Mount Painter and Mount Pitt. H. L. Y. Brown[3] states that the rocks of the district consist of coarse and fine feldspathic, siliceous, and micaceous granite, gneiss, quartzite and mica schist. The rocks are contorted in places and penetrated by dikes of coarse, pink-colored eruptive granite.

Two of the prospect pits are on outcrops of iron oxide with cellular quartz and gossan, the whole having the appearance of an irregular lode. The uranium minerals, torbernite and autunite, are disseminated through the ore, and are also crystallized on the walls of the fissures and

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[3] Occurrence of Uranium Ores and other Rare Minerals near Mount Painter, in the Flinders Range of South Australia. South Australia, Mines Dept., 1911.

cavities in it. Uranophane and gummite occur sparingly; fergusonite and some monazite are also present. Another uranium deposit lies southeast of the one just described, about 20 miles southeast of Olary, on the railroad line from Petersburg to Broken Hill, South Australia. The ore occurs as a yellow and greenish yellow incrustation and powder on the faces, joints and cavities of a lode, which consists of titaniferous magnetite, magnetite, etc., and quartz in association with black mica.

Portugal

Autunite is found in commercial quantities in Portugal in the district between the towns of Guarda and Sabugal. An excellent description is given by Segaud and Humery.[4] Apart from the uranium, the rocks of the region are much mineralized, showing deposits of galena, arsenopyrite, chalcopyrite, tungsten and cassiterite.

All of the deposits referred to above are important and have been developed as commercial sources of radium; in fact, until about 7 years ago, they were the only sources from which radium ores were obtained.

Carnotite Deposits of Colorado and Utah

About 1910, the carnotite deposits of southwestern Colorado and eastern Utah began to receive attention. They were known as far back as 1881, but the composition of the ore was unknown until 1897. In 1899, an analysis showed that the ore not only contained uranium, but was a potassium uranyl vanadate.

In 1900, a small plant was erected in the McIntyre district, south of the Paradox Valley, Colo., for the extraction and recovery of uranium oxide from carnotite ore. Only moderate success was achieved, and the plant was shortly shut down. Operations were also started by other concerns, notably the Western Refining Co. and the Dolores Refining Co.; these plants extracted uranium and vanadium only. None of these operations was of importance, and it was not until 1909 to 1910 that any interest was shown in the carnotite deposits as a source of radium. At that time, the ore was almost exclusively shipped abroad.

In the fall of 1912, representatives of the U. S. Bureau of Mines made a thorough survey of the carnotite fields and announced the fact[5] that the carnotite deposits of Colorado and Utah constituted by far the largest source of radium-bearing ores in the world. Developments since that time have proved this statement to be correct, as the larger part of the radium that has been produced in the world has been derived from American carnotite ore.

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[4] Segaud et Humery: Les Gisements d'Uranium du Portugal. *Annales des Mines, Mémoires,* Ser. 11 (1913) **3,** 111–118.

[5] Richard B. Moore and Karl L. Kithil: A Preliminary Report on Uranium, Radium and Vanadium. U. S. Bureau of Mines, *Bulletin* No. 70 (1913).

The deposits are found mainly in Dolores, San Miguel, and Montrose Counties, Colorado, and extend over a belt about 60 miles long by 20 miles wide. The ore is also found to the west of the La Sal Mountains in Utah, and along the San Rafael Swell, southwest of Green River, Utah. Small patches of ore are found scattered between these points and extend as far north as Meeker, Colorado.

The most usual ore is a sandstone so impregnated with yellow carnotite that the color is decidedly noticeable, and contains small kidneys of brown sandy clay. The kidneys constitute a considerable part of some of the ore; in many cases they are thinly scattered through the sandstone. Although ore of the character mentioned is widely distributed in the Paradox and adjacent districts, and constitutes a large part of the ore shipped, it is by no means the only ore of commercial importance. Indeed, the variety of the types of ore here and in Utah is one of the interesting features of the uranium and vanadium deposits. There are dark blue, brown, and black vanadium ores, the dark blue ores being lustrous when first mined and usually carrying uranium; high-grade carnotite in vug holes so soft that it can be molded in the fingers; and the same kind of ore crystallized with gypsum. Red calcium vanadate is found alone and mixed with carnotite. The ores of the Paradox district differ in many respects from those in Utah, but chiefly in carrying larger proportions of carnotite, and as a rule are more yellow. Not only do they carry more uranium but also, on the average, more vanadium, although individual shipments from Utah, particularly from Temple Mountain, might seem higher in vanadium than the average ore from the Paradox district.

The deposits are invariably pockets, many of which, however, are of considerable size. A few individual claims have produced as high as 500 tons of shipping ore, which, however, is exceptional. The ore is found in a light-colored sandstone overlain in places with shale and conglomerate; according to Hillebrand and Ransome, this is the McElmo formation.[6]

METALLURGICAL TREATMENT

The average commercial ore from which radium is extracted contains from 5 to 10 milligrams of radium element per ton of ore. Allowing for losses in extraction and recovery, it takes about 5000 or 6000 tons of ore to give an ounce of radium element. It can be seen, therefore, that the metallurgical processes involved in the extraction of radium are entirely different from those connected with any other element. There are two general steps which must be carried out: first, to obtain

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[6] W. F. Hillebrand and F. L. Ransome: On Carnotite and Associated Vanadiferous Minerals in Western Colorado. U. S. Geological Survey, *Bulletin* No. 262 (1905), **11.**

a radium concentrate from the ore; and second, the re-treatment of this concentrate in order to extract a high-grade product. The first step is necessarily carried out on a large scale, while the major part of the second step is done in the laboratory.

The different methods of treating radium-bearing ores to obtain a concentrate may be classed under three general heads: (1) an alkaline leach, followed by an acid leach; (2) fusing the ore with some material that will disintegrate it and make the extraction of the valuable contents possible; (3) an acid leach.

1. *Alkaline Leach Methods*

It is probable that some of the early experimental work on extracting radium from carnotite ore involved boiling the ore with a solution of sodium-carbonate, thus getting rid of the uranium and vanadium, which go into solution. Since radium has properties similar to those of barium, any radium in the ore would be converted into radium carbonate, and on treating the residue with dilute c. p. hydrochloric acid, the radium would be dissolved with any other acid-soluble products.

The radium concentrate always obtained is radium-barium sulfate. By adding barium chloride and sulfuric acid, or sodium sulfate, to the slightly acid solution carrying the radium, barium sulfate is formed in the solution and drags down radium sulfate with it. The radium is almost always precipitated in this manner in a liquor sufficient in volume to hold it actually in solution. Undoubtedly adsorption has something to do with the precipitation of the radium along with the barium sulfate, but this does not fully explain the small losses that accompany such precipitation. The term "pseudo-isotopy" has been given to this property by Dr. S. C. Lind.[7]

The general principles outlined above are included in the Haynes-Engle process, which involves boiling the ore with an alkaline carbonate solution. The object of this process was to recover uranium and vanadium only, and did not attempt to obtain the radium in any form. A patent taken out by Warren F. Bleeker involved the extra step which the Haynes-Engle process did not cover, namely, the leaching of the residues with hydrochloric acid in order to obtain the radium in solution, after the ore had been boiled with an alkaline carbonate solution.

The alkaline leach method has many advantages and some disadvantages. It separates the uranium and vanadium from the ore during the first stage of the process. It eliminates sulfates by converting the metallic sulfates in the ore into metallic carbonates and soluble sulfates, which go into the filtrate with the uranium and vanadium. The radium,

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[7] S. C. Lind, J. E. Underwood, and C. F. Whittemore: The Solubility of Pure Radium Sulfate. *Journal*, American Chemical Society (March, 1918) **40**, 465–472.

therefore, is left behind in the residue as carbonate, practically free from sulfates. This prevents the re-precipitation of the radium as sulfate, on treating with acid, until after the acid solution is filtered from the tailings. On the other hand, it has the following disadvantages: It converts some of the silica in the ore into sodium silicate, which makes filtration very difficult—in fact, most of the filtering and washing has to be done by decantation. It is difficult to treat concentrates obtained by this process, as these are almost invariably of very fine mesh, which adds to the filtration difficulties. The treatment with alkaline carbonate converts most of the iron and a good part of the aluminum in the ore into an acid-soluble form, so that the acid consumption is high. The method, however, can be used with success for the treatment of certain uranium ores, particularly carnotite, autunite, and torbernite.

2. *Fusion Methods*

The first method used for the extraction of radium was fusing pitchblende ores with sodium sulfate. This method was originally used by the Austrian Government in connection with the treatment of pitchblende ores from its mines in St. Joachimsthal. By this fusion, the uranium in the ore is changed to sodium uranate, which can be dissolved from the insoluble residue, after leaching out the excess of sodium sulfate with water, by dilute sulfuric acid. The radium remains behind with the residue and, before the discovery of radium, was discarded. Afterward, the residue was boiled with sodium carbonate, which converted a portion of the radium sulfate into radium carbonate, and this was leached out with dilute hydrochloric acid. After repeating this process several times, practically all of the radium was leached from the residue, and the acid leaches were combined. Barium sulfate was then precipitated in the acid solution in the ordinary manner, and in this way the radium was obtained as a concentrate with the barium sulfate.

A somewhat similar treatment is given to the ores from Olary, South Australia, by the Radcliffe process. The main uranium mineral is carnotite, but this is associated with considerable quantities of ilmenite and other rare-earth minerals that are not found in American carnotite. The concentrates are mixed with three times their weight of salt-cake, and fused in a reverberatory furnace; the fused product is then crushed and agitated in wooden vats, with water. By suitable adjustments it is possible to separate on the bottom of the vats a considerable amount of comparatively coarse material that is almost free from radium and uranium. The turbid overflow carries in suspension the radium, lead, and barium, as sulfates, together with a considerable amount of finely divided silica. The overflow is pumped to large lead-lined tanks and allowed to stand all night. This is nothing but a sliming process and has the advantage that the radium in the form of sulfate always remains with the fine material. The slimes settle completely in 12 hr. and are collected periodically and treated for the recovery of radium.

The process of Schlundt, which is being used by one company in the United States in connection with carnotite, is very similar to the Radcliffe process. The ore is fused with acid sodium sulfate, leached and washed with water to extract the uranium, vanadium, and other soluble products, and the residue is slimed in order to obtain a crude concentration of the radium, which stays with the fine material.

The U. S. Bureau of Mines has found that if a radium-barium sulfate high in silica is fused with caustic soda containing a small quantity of sodium carbonate, the silica can be easily washed out as sodium silicate, while the barium and radium remain behind as radium-barium carbonates, which can be readily dissolved in hydrochloric acid. Usually the commercial caustic soda contains enough carbonate without the addition of an extra amount. This method has been applied commercially to the treatment of crude concentrates, such as are obtained by the Schlundt process.

One firm has used a sodium carbonate fusion. The ore is fused with soda ash, usually about 2½ times the weight of the ore being required. This is done in a reverberatory furnace, lined with magnesite brick, and the fused mass is run directly into vats, in which it is leached. The silica is thus converted into sodium silicate and so passes into solution, together with the uranium and vanadium. The iron, calcium, barium, radium, etc., remain as the insoluble residue, which is washed in filter presses. This material is then treated with dilute sulfate-free hydrochloric acid, which dissolves the carbonates, and the radium and barium are precipitated by the addition of the requisite amount of sulfuric acid, or sodium sulfate. The whole is allowed to stand in settling tanks and the clear liquid is drawn off, leaving the barium-radium sulfates, mixed with a considerable amount of silica and other impurities, as a sludge at the bottom of the tank. This is taken off without previous filtration, and dried, forming a crude radium-barium sulfate, which is then refined.

The main advantages of this method are that it will treat an ore containing considerable quantities of sulfates, as the process removes the sulfates as soluble sodium sulfate in a similar manner to the alkaline leach method. In addition, it is applicable to the treatment of concentrates, as fineness of material is really an advantage instead of a disadvantage, as it does not involve any "sliming." The main disadvantage is the cost, both for the chemicals and the labor required. The concentrate obtained is also low-grade, which involves additional refining costs.

3. *Acid Leach Methods*

Leaching with hydrochloric acid gives an excellent extraction, provided the ore is comparatively free from sulfates. As a considerable proportion of such ores contain traces of gypsum, it is a method which must be used on selected ores. A hydrochloric acid leach has been used successfully on Cornish pitchblende, which is practically free from pyrite, but is not applicable in any way to American pitchblende, which contains considerable quantities of pyrite. It has also been used on Portugese autunite. In general, the hydrochloric method is applicable to certain ores, but has a limited use.

Leaching with nitric acid has been used more successfully. This is the method originated by the U. S. Bureau of Mines[8] and used in the plant of the National Radium Institute. As is generally known, barium sulfate is much more soluble in nitric acid than in hydrochloric acid, and this is especially true when the nitric acid is concentrated and hot. For this reason, ores containing sulfates can be successfully treated by a nitric acid leach, and the method has been successfully applied to ores carrying as much as 1 per cent. gypsum. On ores carrying small quantities of sulfates, the extraction obtained is very high, frequently going, on a commercial scale, to 93 and even to 95 per cent. Boiling, 40-per cent. nitric acid is used, and filtration is obtained on either a vacuum or a pressure filter. Filtration must be done rapidly, because, as the acid cools, the radium has a tendency to precipitate out, especially in the presence of sulfates. During the process of recovering uranium and vanadium by this method, practically nothing but sodium hydroxide and sodium carbonate are added to the nitric acid. Consequently, sodium nitrate is obtained as the final product after the precipitation of the radium, uranium, and vanadium; and this sodium nitrate is recovered by evaporation and crystallization and used over again for the manufacture of nitric acid in the ordinary way. The average losses of nitric acid were about 15 per cent., so that 85 per cent. of the acid used was recovered as sodium nitrate. This actually reduced the cost of the nitric acid below that of hydrochloric, and this, together with the high extraction of the radium obtained, was largely responsible for the low cost of the recovered radium and the success of the method.

The process cannot treat successfully ores carrying as large quantities of gypsum as can be treated by some of the other methods, such as the sodium carbonate fusion, but it is applicable to a very large percentage of the carnotite ore produced. Difficulty was experienced in treating concentrates, most of which are below 150 mesh. As already stated, it has been necessary to filter rapidly in order to get a good extraction; and the problem of filtering a 40-per cent., boiling nitric solution, containing fine material in suspension, was found to be difficult. It was finally overcome by the development and use of a pressure filter instead of a

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[8] Charles L. Parsons, R. B. Moore, S. C. Lind, and O. C. Schaefer: Extraction and Recovery of Radium, Uranium, and Vanadium from Carnotite. U. S. Bureau of Mines, *Bulletin* No. 104 (1915).

suction filter; this consisted of a steel shell containing an earthenware filter set in concrete. The earthenware filter had at its bottom, as filtering medium, a plate of either filtros or alundum. The steel top was made tight with swing bolts, and a pressure of 100 lb. was applied.

Refining

The radium-barium sulfate concentrate obtained in a satisfactory metallurgical process should carry about 1 mg. of radium element per kilogram of concentrate, a ratio of one to a million. The next step is to get this concentrate back into solution. The most successful method is to reduce the sulfate with about one-sixth its weight of pulverized charcoal in a furnace at a temperature from 800° to 900° C. In the presence of silica, the reduction takes place slowly and is not complete; but if the sulfate does not contain more than from 5 to 10 per cent. silica, the reduction may reach 90 per cent. or more. The radium-barium sulfides are then dissolved in sulfate-free hydrochloric acid, and filtered. From this stage on, the refining process is simply one of fractional crystallization. Radium chloride and bromide are less soluble than the corresponding barium salts; the crystals first obtained on evaporation are therefore richer in radium than the mother liquor from which they are obtained. The difference in solubility of the bromides is considerably greater than that of chlorides; at some stage in the process, all of the chloride salts are converted into bromides, after which fractionation is continued as bromide, in hydrobromic acid solution. The factor of separation is higher in acid than in neutral solution; it is customary, therefore, to fractionate both chlorides and bromides in acid solution. Full details of the methods of fractionation are given in U. S. Bureau of Mines *Bulletin* No. 104.[9]

METHODS OF ORE CONCENTRATION

Both wet and dry methods of concentration may be used for carnotite ores. The wet method simply involves crushing the ore and agitating with water in a manner that will best separate the fine-grained particles of carnotite from the coarser silica particles. After allowing to settle, the fine material can be slimed off and run into settling tanks, while the coarser tailings are re-treated with water. The only successful method of dry concentration that has so far been used has involved the Raymond pulverizer and dust collecting system. The National Radium Institute built a small plant near the claims it was working in Long Park, Colo., and gave the method a thorough testing, with excellent results.[10] The

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[9] *Op. cit.*

[10] Karl L. Kithil and John A. Davis: Mining and Concentration of Carnotite Ores. U. S. Bureau of Mines, *Bulletin* No. 103 (1917).

capacity of the mill was a little over one ton of milling ore an hour; and the average output was 365 lb. of concentrate an hour. The milling ore had an average content of 0.85 per cent. U_3O_8; the average of all concentrates was 2.92 per cent. U_3O_8; the tailings averaged 0.3 per cent.; the ratio of concentration was about 6 to 1. As much as 63.7 per cent. of the carnotite contained in the milling ore was extracted, and 60 per cent. of all the carnotite in this ore was actually recovered in the concentrates.

FUTURE SUPPLY OF ORE

It is difficult to estimate the exact amount of radium in existence at the present time; probably it is somewhere around 3 oz. of radium element. On account of the great scientific interest attached to radium, and on account of its use in the war and in medicine, the permanency of the ore supply is an important question. Considerably more than half the amount of radium now in existence has come from Colorado and Utah carnotite ores. Six years ago, the engineers of the Bureau of Mines estimated that, at the current rate of production, the deposits might last, commercially, 10 or 12 years. At the present time, it is very difficult to obtain ore. Most of the deposits are owned by five operating radium companies. The production has increased very greatly during the war; and the author is very doubtful whether we can depend upon our carnotite deposits to yield commercial quantities of ore for more than 6 or 7 years longer. It is his judgment that the fields will not produce more than 100 additional grams of radium element at the most—if that much. This would about double the world's present supply; but, on account of the large use of radium in cancer treatment, such an amount, although large scientifically, would be small in proportion to the probable demand.

TABLE 3.—*Radium Production from American Carnotite*

Year	Tons U_3O_8	Tons U	Grams Ra Contained	Grams Ra Recovered, (75% Basis)
1912	28.8	24.4	7.4	5.5
1913	41.0	34.8	10.5	7.9
1914	87.2	74.0	22.5	16.9
1915	23.5	19.9	6.0	4.5
1916 (*a*)				
1917	70.0	59.3	18.0	13.5

(*a*) Official statistics are not available for 1916.

USES OF RADIUM

The use of radium in cancer research has extended over a period of several years. Some very remarkable results have been obtained, especially recently in the treatment of certain forms of cancer. A large number of permanent cures have been effected; and whereas the medical fraternity was skeptical at first, a great deal of the opposition has been overcome, and several of the largest and most prominent hospitals in the country are now supplied with considerable quantities of radium for cancer treatment. A word of warning must be given in this connection. The successful use of radioactive waters and low-grade radium preparations is doubtful and should be carefully distinguished from the successful results obtained with considerable quantities of high-grade radium salts. Naturally, there have been some attempts to foist on the public, at a high price, low-grade preparations, the value of which is, to say the least, very uncertain.

The chief technical use for radium is in connection with permanently luminous paint. If radium salts are mixed with phosphorescent zinc sulfide, a product is obtained which is permanently luminous in the dark without previous exposure to light. The zinc sulfide must be specially prepared and usually contains traces of impurities, such as copper, manganese, etc. Just what relation exists between these impurities and the peculiar properties of the zinc sulfide is not known, although experimental work is now being done to determine it. The luminous paint usually carries from 0.1 to 0.25 mg. of radium element to 1 gm. of zinc sulfide, depending upon the particular use of the paint.

This material is now being largely used on the faces of watches and clocks; to coat electric light push-buttons and the chains attached to electric globes; and for various other purposes. It is a great pity that our supply of radium is being disseminated in this manner. But as the physicians and surgeons of the country are not purchasing enough radium to make the industry a financial success, it is natural that the manufacturers should take other means of creating a demand. The day is not far distant, in the judgment of the writer, when we shall greatly regret the radium that has been lost in this way.

Radium has a most decided war use at the present time; nine instruments used on airplanes have dials made luminous with radium paint; it is employed in the same manner for compasses and gunsights. The efficiency of night firing, with both machine guns and artillery, has been greatly increased by the use of these luminous sights. Other uses cannot be specified, at the present time, in a public paper.

MESOTHORIUM AS A SUBSTITUTE FOR RADIUM

One way of preventing the dissemination and loss of radium is to provide a substitute. Mesothorium (see Table 2) is an excellent substitute in many ways. Its half-life period is much shorter than that of radium. When first prepared, it gradually increases in activity, comes to a maximum, and then begins to lose its activity. After "ripening" for about a year after being prepared, it can be used for luminous paint just as efficiently as radium. Its usefulness for such purpose will last for 4 or 5 years, which is as long as is required for cheap watches, push-buttons, etc. Mesothorium can be obtained as a byproduct in the treatment of monazite sand for the manufacture of thorium nitrate used in incandescent mantles. During the last year, the U. S. Bureau of Mines has been experimenting along these lines and has developed a process which is being put into the largest thorium plant in the country at the present time, and it is hoped that before long mesothorium can be substituted for some of the radium that is now being used in luminous products. Mesothorium can also be used for cancer treatment, although its short life makes it much less desirable for this purpose than radium.

DISCUSSION

W. A. Schlesinger,* Denver, Colo.—Two problems are of great interest to the radium manufacturer at the present time: The first is to perfect a process, more efficient and more economical, which is capable of treating a greater variety of ores. Practically all the radium now manufactured in the United States is extracted from carnotite ores and these vary a great deal according to their location. The amount of sulfates contained in the ore is of particular importance, and any straight acid-leaching method, such as developed by the Bureau of Mines, becomes prohibitive when the ore contains more than 0.5 per cent. of sulfates, as the sulfates go into solution and naturally precipitate the radium as insoluble radium sulfate. Since the amount of ore obtained from any one claim is usually comparatively small, it is necessary to work a number of claims in different localities, and a process, in order to be commercially satisfactory, should handle all of these ores. In other words, it would be entirely unprofitable for radium manufacturers to employ any process which cannot treat any but sulfate-free ores. He must deal with carnotite containing appreciable amounts of sulfates, and must be able to work this in with the other ores. Carbonaceous ores from certain sections in Utah, which are known to contain as much as 10 per cent. and more of volatile matters, are prone to a nitric acid-leaching process.

The second problem relates to the treatment of concentrates. There is no doubt that a very large amount of low-grade ore, containing less than 0.75 per cent. uranium oxide, is available. It has been demonstrated that these ores can be concentrated, but there is still room for research work to develop a process that will efficiently handle such concentrates. The straight acid-leaching method, if used with concentrates, is con-

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* The Radium Company of Colorado, Inc. (Formerly The Schlesinger Radium Co.)

fronted by difficulties in filtering. The concentrates are naturally very fine, and when leached with acid will easily clog the filtering medium.

It was suggested that, by mixing concentrates with straight ore ground to 20 mesh, one could overcome the filtering difficulties, with a straight acid-leaching method on sulfate-free ores, by the use of pressure filters, and obtain an extraction of approximately 75 per cent. If, however, this method gives an extraction of 95 per cent. on the straight ore alone, and if by mixing with 25 per cent. of concentrates the combined extraction is reduced to 75 per cent., no advantage is gained by this procedure.

A considerable amount of radium has lately been used in the manufacture of self-luminous compounds, consisting of specially prepared zinc sulfide mixed with varying amounts of radium. The powder is then, with the help of a suitable varnish, made into a paint and applied with a brush. The character of the varnish varies according to the use to which one wishes to put the paint, and whether or not the paint has to withstand the action of alcohol, glycerine, or water. We have applied self-luminous radium preparations to over half a million Government instruments since the outbreak of the war. Units for luminosity measurements have also been developed, and the luminosity of these paints is now being measured in micro-lamberts, which are a fraction of a candle power.

The suggested use of mesothorium is very interesting, but little has been published and few experiments have been made in this country to show whether mesothorium is as efficient as radium when mixed with zinc sulfide for luminous paint. Experimental data should be collected to show the rate of deterioration of zinc sulfide when mixed with mesothorium.

I do not think a shortage of radium will occur for years to come, especially in view of the low-grade deposits. The amount of radium used for luminous paints, even now, is comparatively small; probably 500 milligrams is being used every month for the manufacture of luminous paint for war purposes in this country.

R. B. MOORE.—It would, of course, be an excellent thing if we could have one process, as suggested by Dr. Schlesinger, that would be equally efficient in connection with all types of carnotite ore. This, however, is almost too much to ask as the radium ores are just as varied in character as are copper ores, and we do not expect any process for the recovery of copper to be equally efficient on all types of ore.

I have been asked to say a few words about Dr. Douglas in his connection with radium. The radium I have showed you was some which was produced by the National Radium Institute, in which Dr. Douglas was greatly interested; in fact, he was one of those who financed that organization. He did this mainly for two reasons: first, as a philanthropic object for the alleviation of suffering from cancer, and secondly, because of his interest in scientific and technical progress of all kinds.

At that time the extraction of radium from ores had been only slightly investigated; practically nothing was known about it in this country. All of the radium he obtained as his share in the operations went to the Memorial Hospital, in New York, and is still there as a gift to the Hospital. Dr. Douglas, therefore, accomplished the two objects he had in mind—he helped to make possible a study of the technical methods of extraction and at the same time gave his share of the radium obtained for research work in cancer treatment.