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THE SEPARATION OF VANADIUM FROM CRUDE SODIUM
URANATE AND CONVERSION OF LATTER
INTO URANIUM OXIDE

by

Howard Hill Barker, A. B.

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I - INTRODUCTION

Within the past five years, the extraction of radium has been developed in the United States and radium is now produced in relatively large quantities by the Standard Chemical Company of Pittsburgh, Pennsylvania, and the National Radium Institute of Denver, Colorado. Up to March 1st, 1915,¹⁾ the Standard Chemical Company had produced 18,000 milligrams of radium bromide (9,600 milligrams of radium element), which constitutes practically the entire output of the United States. There are no statistics available upon the output of the National Radium Institute.

In the year 1912-1913, there can be no doubt but what there was twice, and probably three times, as much radium²⁾ obtained from the American ores as from ores mined in the rest of the world put together. In the year 1913, the statistics of³⁾ the United States Geological Survey show that more than one-half of the radium (equivalent to approximately 7.5 g. of hydrous radium bromide) was sent abroad. This exportation of ore was probably due to the fact that there was only one American company preparing radium salts of any degree of purity. The plant of the National Radium Institute has been in operation

for nearly two years, and the monthly output has now nearly reached a half-gram of hydrous radium bromide.

The ore used as a source of radium is a low grade carnotite, containing from two to five percent uranium oxide (U_3O_8), and slightly more vanadium estimated as the oxide, (V_2O_5). Both the vanadium and uranium are valuable by-products and are conserved.

The separation of radium, uranium, and vanadium from carnotite ore is a chemical process ^(a). In the course of treatment of the ore, after filtering, the uranium and vanadium are found in the filtrate along with iron, calcium, and small quantities of other elements. Sodium carbonate is added in excess to this filtrate to precipitate the iron and calcium. The uranium is then precipitated by neutralizing the excess of sodium carbonate, boiling to expel the carbon dioxide, and addition of sodium hydroxide in excess. Sodium uranate and sodium vanadate are formed, and since the latter is soluble in water, we should expect to find the vanadium in solution as sodium vanadate, while the precipitate should consist of sodium ^{di-}uranate ($Na_2U_2O_7$). In practice, however, some of the vanadium is precipitated with the uranium, which is objectionable.

(a) The process used by the National Radium Institute has not been published and we are, therefore, not at liberty to outline the treatment of the ore for the recovery of uranium and vanadium.

By redissolving the precipitate and again precipitating the uranium with sodium hydroxide, the vanadium should be removed. A second precipitation removes about one-half of the vanadium but fails to yield a product of sufficient purity to meet the specifications for the sale of uranium. The National Radium Institute, therefore, was confronted with the additional problem of removing the vanadium from the crude uranate, in connection with the conversion of the product into uranium oxide, the form in which the uranium was to be sold. The market product of uranium need not be entirely free of vanadium but the amount should not exceed one-half percent.

The market price of uranium oxide⁴ is two and one-half dollars per pound; and of vanadium oxide seventy-five cents per pound. However, the recovery of the vanadium from the crude uranate is not as important a factor as the recovery of the uranium, as its percentage in the crude uranate is only about eight percent vanadium oxide (V_2O_5).

In order to get some idea of the magnitude and economic importance of this problem, let us consider for a moment the amount of ore which a plant producing one-half a gram of radium per month would have to treat. Since Lind and⁵⁾ C. F. Whittemore have shown that the ratio of uranium to ~~ma~~ radium in carnotite ore is on the whole normal, the well es-

tablished value for the equilibrium ratio, namely 3.33×10^{-7} , may be used in the calculation, that is, a quantity of ore containing one gram of radium contains 3×10^6 grams of uranium or nearly three and three-tenths tons, equivalent to three and six-tenths tons of the oxide (U_3O_8). Since the low grade carnotities used contain from two to three percent of uranium oxide, it is seen that about one hundred and fifty tons of ore must be treated to obtain one gram of radium. Hence, a plant producing one-half gram of radium per month would have to treat something over 900 tons of ore per year. If the ore averages two and one-half percent uranium oxide, which is a conservative estimate, a total of 22.5 tons would be represented in the by-product annually. Allowing a loss of one-fourth of the uranium in the process of extraction, the market value of the by-product alone at two and one-half dollars per pound would be about \$82,500.

It is thus evident that the separation of vanadium from the crude uranate presents an interesting and valuable problem for investigation.

The first step in the solution of a problem of this kind is to find laboratory methods of accomplishing the result. The next step in the investigation would be to test the successful laboratory methods on a larger scale, in an experimental plant. The experiments that follow are confined to

(5)

a study of laboratory methods for the separation of vanadium in the crude uranate, and the conversion of the latter into uranium oxide.

II - PRELIMINARY WORK

In order to become familiar with the chemical properties of uranium and vanadium, some qualitative tests were performed as outlined in Browning's book, "Chemistry of the Rare Elements"⁶⁾. Following this, an analysis of a carnotite ore was made for uranium and vanadium, and finally a complete quantitative analysis was made of the sample of crude sodium uranate, which was subsequently used in the main experiments.

1. Determination of Uranium and Vanadium

In Carnotite Ore

In the analysis of the ore the method recommended by the Bureau of Mines⁷⁾ was followed. Weighed samples of from four to five grams of the finely pulverized ore were treated with aqua regia to get the uranium and vanadium in solution. However not all of the vanadium yielded to this treatment, so it was necessary to ignite the insoluble residue and treat it with hydrofluoric acid, to render the remain-

ing vanadium soluble. After expelling the excess of hydrofluoric acid, the residue was taken up with dilute hydrochloric acid, and hydrogen sulphide passed into the combined sulphates from the aqua regia, and hydrofluoric acid treatments, to remove any members of the copper-tin group present. The filtrate from the copper-tin group was then concentrated and oxidized with hydrogen peroxide, after which it was neutralized with an excess of sodium carbonate, and boiled until the yellow precipitate of uranium dissolved leaving a brown precipitate consisting principally of iron.

The iron precipitate was dissolved in dilute nitric acid, and again treated as before, with sodium carbonate to remove the last traces of uranium. This iron precipitate was saved to be treated later for the small traces of vanadium which it might contain.

The filtrates from the iron precipitates were concentrated to about 200 cc., when 10 cc. of strong nitric acid was added, and the solution boiled to expel all carbon dioxide. Ammonium hydroxide was then added to neutralize the excess of free acid, and to give a slight precipitate of uranium hydroxide, after which 8 cc. of strong nitric acid was added. Ten cc. of a twenty percent solution of lead acetate was then added, and enough of a strong solution of ammonium acetate to neutralize the nitric acid present, and substitute

acetic acid. The object here was to precipitate the vanadium as lead vanadate.

The precipitate was dissolved in dilute nitric acid and reprecipitated in a manner similar to that given above. The filtrates from the two precipitations were combined, while the precipitate of lead vanadate was saved for treatment later. The filtrate from the lead vanadate was concentrated, and 10 cc. of strong sulphuric acid added to precipitate the bulk of the lead. The filtrate from the lead sulfate was neutralized with ammonia, after which a freshly prepared solution of ammonium sulphide, $(\text{NH}_4) \text{HS}$, was added to precipitate the uranium, and what lead was present, as the sulphides. The precipitated sulphides were filtered off, and dissolved in dilute nitric acid, after which concentrated sulphuric acid was added and evaporated until white fumes appeared. The residue was cooled and taken up with water, after which the precipitate of lead vanadate was filtered off.

The filtrate was neutralized with ammonia, and powdered carbonate of ammonia added in excess to precipitate the aluminum. The precipitate of aluminum hydroxide was filtered off, and sulphuric acid added to expel the carbon dioxide. The solution was made slightly alkaline with ammonium hydroxide to precipitate the uranium as ammonium uranate. This precipitate was filtered, ignited and weighed as uranium ox-

ide (U_3O_8).

The ignited precipitate from the iron residue obtained by precipitation with the sodium carbonate in excess, was mixed with sodium carbonate and fused. The fused mass was leached with water, and the filtrate acidulated with sulphuric acid. This was then added to the solution obtained by dissolving the lead vanadate precipitate in nitric acid. To this solution which had been evaporated nearly to dryness with sulphuric acid and taken up with water, 10 cc. of concentrated solution of sulphur dioxide was added, and the mixture boiled to expel the excess of sulphur dioxide. The hot solution was then titrated immediately with a standard potassium permanganate solution, and from the data the percent of vanadium oxide (V_2O_5), was calculated.

The determinations were made in triplicate. The results are given in table I.

Table I
Uranium and Vanadium Content of Carnotite Ore

Number of Sample	Weight of: Sample	Weight of: U_3O_8	Weight of: V_2O_5	Percent of: U_3O_8	Percent of: V_2O_5
1	4.1775	0.1522	0.2330	3.64	5.57
2	4.3924	0.1544	0.2425	3.54	5.52
3	4.6553	0.1540	0.2596	3.31	5.58
			Average	3.49	5.56

2. Complete Analysis of Crude Sodium Uranate

A complete analysis was made of ^{the} crude sodium uranate used in this investigation by very much the same method as was used in determining the uranium and vanadium in a sample of carnotite ore. The analysis consisted in determining the percentages of, hygroscopic water, water of constitution, insoluble matter, members of the copper-tin group ignited as the oxides, ferric oxide, uranium oxide, vanadium oxide, and sodium.

A sample for analysis was prepared by taking the stock supply of crude uranate furnished by the National Radium Institute through the courtesy of Mr. R. B. Moore, and thoroughly grinding it in a pebble mill. The ground material was then quartered until a sample sufficient for the analysis was obtained. Inasmuch as the stock supply of sodium uranate was used in all the subsequent work, the analytical results here obtained prove to be of considerable value in connection with the quantitative experiments undertaken.

The hygroscopic water was determined by heating the material at 120° C. to constant weight. The water of constitution was determined by heating the same sample of material to red heat, and it was assumed that the additional loss represented the water of constitution.

For the determination of the insoluble residue, new samples were boiled with hydrochloric acid. The insoluble material which consisted mostly of silica, was filtered off, ignited, and weighed.

Into the filtrate from the insoluble residue, hydrogen sulphide was passed to precipitate the members of the copper-tin group. The precipitate was ignited and weighed, and the product is designated in table II. as the oxides of the copper-tin group.

From here on, the analysis for the removal and determination of the uranium and vanadium was the same as that used in determining these constituents in carnotite ore.

The iron carbonate residue was ignited and weighed as ferric oxide.

The sodium was determined from samples of the crude uranate, which were treated in the manner given above for the separation of the uranium and vanadium, except that ammonium carbonate was used to precipitate the iron and uranium in place of sodium carbonate. The filtrate from which the vanadium and uranium had been removed was evaporated to dryness in a platinum dish, taken up with hydrochloric acid twice and again evaporated to dryness in order to convert the sodium present to sodium chloride. The sodium chloride was then

ignited to dull red heat, and the amount of sodium calculated from the weight of the sodium chloride.

The analytical results are given in tables II, III, and IV.

Table II gives the percent of hygroscopic water, water of constitution, and sodium on separate samples of the crude uranate. Table III gives the percent of insoluble material, members of the copper-tin group as oxides, ferric oxide, uranium oxide and vanadium oxide, determined on the same samples of crude uranate. Table IV gives a summary of the results.

Table II

Water and Sodium in Crude Uranate

No. of Sam- Ple	Wt. of Cru- de Uran- ate	Loss in: Water at 120°	Loss in: Water at Red Heat	Percent Hygrosc- opic water	Percent of Wat- er of Constitu- tion.	Total Wat- er.
1	0.2363	0.0069	0.0156	2.91	7.03	9.94
2	0.2583	0.0086	0.0166	3.35	6.40	9.73
		Weight of NaCl	Equiv. Wt. of Sodium	Percent of Sodium		
1	0.9998	0.2119	0.0833	8.33		
2	1.0456	0.2122	0.0835	7.90		

Table III

Insoluble Residue, Cu-Sn Group, Fe_2O_3 , U_3O_8 , V_2O_5

Number of Sample	Wt. of crude Uranate	Wt. of Insol. Material	Wt. of Cu-Sn Gr. as Oxides	Wt. of Fe_2O_3	Wt. of U_3O_8	Wt. of V_2O_5
1	:0.5014	:0.0014	:0.0012	:0.0299	:0.3222	:0.0435
2	:0.5125	:0.0016	:0.0019	:0.0310	:0.3332	:0.0438
		:Percent Insol. Material	:Percent Cu-Sn Gr. as Oxides	:Percent of Fe_2O_3	:Percent of U_3O_8	:Percent of V_2O_5
1		:.28	:.23	:5.96	:64.26	:8.60
2		:.31	:.37	:6.04	:65.00	:8.50

Table IV

Complete Analysis of Uranate, - Percentages

Number of Sample	Water	Insol. Residue	Cu-Sn Gr. as Oxides	Fe_2O_3	U_3O_8	V_2O_5	Sodium	Total
1	:9.94	:0.28	:0.23	:5.96	:64.26	:8.60	:8.33	:
2	:9.73	:0.31	:0.37	:6.04	:65.00	:8.50	:7.90	:
Average	:9.83	:0.29	:0.30	:6.00	:64.63	:8.55	:8.11	: 97.71

This slightly low percentage is due to the fact, that for every three molecules of sodium uranate, there are five atoms of oxygen which are not accounted for in the above

results. If we calculate the amount of oxygen to be added assuming that the crude uranate contains 64.63 percent uranium oxide, the percent of oxygen lost would amount to 3.07 and the total percentage then is 100.78.

III. TREATMENT OF CRUDE URANATE WITH HYDROGENCHLORIDE (GAS)

8)

Edgar F. Smith and Joseph B. Gibbs first showed that vanadic acid can be completely removed from sodium vanadate as a volatile product, by means of hydrochloric acid gas. Later, it was shown by Hillebrand that a part of the vanadium in ores, the vanadous compounds, are not completely removed by this method. Our first experiments were undertaken to ascertain whether the vanadium in the crude uranate can be volatilized by hydrogen chloride. The crude uranate was subjected to the action of hydrochloric acid under varying conditions of temperature. It was found that crude sodium uranate which had been ignited in the free flame to remove moisture present, and then subjected to dry hydrogen chloride, evolves brown fumes, characteristics of the chlorides and oxychlorides of vanadium. The reaction proceeds fully as well at room temperatures as when the uranate is heated. Evidently the reaction produces enough heat to raise the temperature sufficiently to volatilize the chlorides and oxychlorides of vanadium.

During the process, a slight caking is produced as a result of the water formed in the reaction, and this sometimes prevents the hydrogen chloride from interacting with the vanadium in the interior of the uranate..In such cases, it

is necessary to heat the uranate residue to a temperature high enough to expel all the moisture present, then to grind it to a fine consistency. When hydrogen chloride is passed over it a second time, a slight evolution of brown fumes is again observed, showing that only traces of the vanadium are left. Two treatments with hydrogen chloride gave a very complete quantitative separation of the vanadium.

The residue left after the separation of vanadium probably is a mixture of sodium chloride, sodium uranate, and uranyl chloride. This residue is readily soluble in dilute acids from which the uranium can be obtained in the form of oxides. By either precipitation with ammonia and ignition of the uranate, or else by boiling with ammonium chloride, which likewise converts the major part of the sodium uranate into ammonium uranate.

Assuming that the vanadium is present in the crude sodium uranate as a complex salt of vanadium from which vanadic acid can readily be obtained, the brown volatile compound of vanadium may be ascribed to be $2VO_2 \cdot 3H_2O \cdot 4HCl$, which Berzelius obtained when he treated vanadic acid with hydrochloric acid. If this is the case, we may suppose that our reaction proceeds in somewhat the following manner:

I am, however, unable to find that an analysis

of the volatile compound has ever been made, and it is, therefore, doubtful whether the reaction proceeds according to the above equation.

In subjecting the vanadium bearing uranate to the action of hydrogen chloride, the uranate was placed in a long hard glass tube of one centimeter bore. One end of the tube was fitted with a one-hole stopper, carrying a glass tube. A steady stream of hydrogen chloride is passed over the uranate in the tube. The hydrogen chloride was prepared by dropping concentrated hydrochloric acid from a dropping funnel into concentrated sulphuric acid. The other end of the reaction-tube was drawn out and connected with U tubes containing water to collect the volatile vanadium compound and absorb the excess of hydrogen chloride. A current of hydrogen chloride was maintained until the evolution of the brown fumes ceased. The reaction was carried out at different temperatures by placing the glass tubes in a combustion furnace and regulating the temperature.

In order to get some idea of the quantitative separation of the vanadium from the crude uranate by this method, the quantity of vanadium obtained from a weighed sample of uranate was determined by taking the aqueous solution of vanadium and oxidizing it with hydrogen peroxide. After evaporating the solution nearly to dryness with sulphuric acid, it was taken up with water and reduced with sulphur dioxide. The solution was then boiled to expel the excess of sulphur diox-

ide after which the hot solution was titrated with a standard solution of potassium permanganate. The amount of vanadium in the aqueous solution was found to vary from eight to eight and two-tenths percent of V_2O_5 as against eight and fifty-five hundredths percent, the amount actually found in the crude uranate by analysis. (See table IV, page 13) This result shows that the vanadium is nearly removed quantitatively.* The residue showed only a feeble test for vanadium.

Whether this method can be conducted on a commercial scale is an open question. In designing a large form of apparatus, a chemical engineer must consider the following points: (1) The material to be used in the construction of the apparatus- wood, metal, or stonework. Since the reaction proceeds at room temperature, a wooden vat would serve and probably be the most economical. (2) The process should be made continuous. That is, all the hydrogen chloride should be utilized by passing that which is rich in the products of the reaction over fresh crude uranate. (3) The water formed during the reaction is sometimes very objectionable, as it produces caking. The apparatus should, therefore, have a stirring device. (4) Some provision should be made for collecting the volatile vanadium compounds. (5) An efficient hydrogen chloride

* The method used in testing for vanadium in connection with this work is as follows: the substance to be tested is dissolved in nitric acid and cooled, after which a small amount of a dilute solution of hydrogen peroxide is added. The production of a red coloration of the solution under these conditions is considered a characteristic test for vanadium.

generator is an important part of the apparatus.

After removal of the vanadium by this method, the next step is the conversion of the uranium compounds into urano-uranic oxide (U_3O_8). The usual commercial method of conversion consists in boiling the sodium uranate with a concentrated solution of ammonium chloride. Ammonium uranate is produced, but the conversion is not complete. Upon ignition, the ammonium uranate is decomposed, yielding uranium oxide. A mixture of uranium oxide and sodium uranate is thus obtained, from which the sodium uranate is removed by digesting with dilute sulphuric or hydrochloric acids. From ten to fifteen percent of the uranium oxide, however, is also dissolved. Hence the recovery of uranium oxide is only partial. In this connection, some experiments conducted by Dr. Herman Schlundt in the United States Bureau of Mines during the summer of 1914 will show the percentage of uranium that is converted into the oxide by boiling sodium uranate with ammonium chloride, followed by ignition of the mixed uranates, and extraction of the sodium uranate in the residue by treatment with dilute sulphuric acid. In one case, Dr. Schlundt used samples of both dry and moist sodium uranate, and dissolved them in concentrated sulphuric acid, then precipitated the uranate with an excess of ammonia, and ignited the precipitate of ammonium uranate to obtain uranium oxide. In the case of the dry sodium uranate, fifty-nine percent of the uranium was recovered as pure oxide (U_3O_8);

and in the case of moist sodium uranate, the recovery was sixty-four percent. This process resolves itself into virtually treating the sodium uranate with ammonium sulphate. The other method studied by Dr. Schlundt consisted in boiling both dry and moist sodium uranate in concentrated solutions of ammonium chloride, filtering off the precipitates, igniting and treating the residue with dilute sulphuric acid. In the experiments with the dry sodium uranates by this method, the recovery of uranium oxide was found to be sixty-four percent; and in the case of moist sodium uranate, a recovery of sixty-one percent was obtained.

These experiments show that in the usual commercial methods of converting sodium uranate into oxide, approximately sixty-four percent of the uranium is recovered, and, assuming that fifteen percent of the uranium oxide is dissolved by the acid used in extracting the sodium uranate, it is seen that seventy^{five} percent of the sodium uranate is converted into ammonium uranate.

2. Treatment of Carnotite Ore With Hydrogen Chloride (gas) to Remove Vanadium

Since hydrogen chloride removed vanadium completely from crude sodium uranate, the idea suggested itself of trying the effect of the gas on the vanadium in the original ore, with a view of developing a quantitative method of

determining the vanadium in carnotite ores.

A few charges were run at room temperature, but it was found that the removal of the vanadium was far from complete, thus confirming the conclusions of Hillebrand.⁹⁾ Experiments were next tried by heating the ore while the hydrogen chloride was passing over it. It was found that the yield of chlorides and oxychlorides was much greater, but even in this case, only about one-half of the vanadium was removed. The ore caked rather badly, due to the water formed in the first part of the operation, so it was necessary to remove it from the tube, pulverize it, and treat it again with hydrogen chloride(gas).

The apparatus used in these experiments was practically the same as that used in the removal of the vanadium from crude sodium uranate. Only in one case, was there a reasonably good separation of vanadium.

The experiments which yielded the best results were conducted as follows; the sample of the ore was placed between plugs of glass wool in the hard glass tube, and hydrogen chloride(gas) passed over it until no more brown fumes were given off. The hydrogen chloride generator was disconnected then and the ore heated to drive off all moisture present. After this, it was removed from the tube, thoroughly ground and mixed with powdered glass, in order to let the

gas have an opportunity to come in direct contact with each particle of the ore. The sample was replaced in the tube and hydrogen chloride(gas) passed over it for about two and one-half hours, at as high a temperature as could be obtained in a combustion furnace. The residue that remained in the tube was brown and sandy like in appearance and gave only a very slight test for vanadium. Other experiments conducted under nearly the same conditions failed to give as satisfactory results as the above one did, showing that it is rather difficult to remove the vanadium by this method.

These experiments, however, suggested the possibility of a new and rapid method for the determination of vanadium in carnotite ores,⁹ notwithstanding Hillebrand states that this method cannot be applied to the determination of vanadium in such ores.

The treatment of the ore by hydrogen chloride for the removal of vanadium has a very direct bearing on the problem at hand. If the vanadium could be removed from the ore by this treatment, at the beginning of the process a uranate would be obtained free from vanadium. Moreover, the removal of the vanadium before treatment of the ore for the extraction of radium would very materially simplify the entire process.

3. Treatment of the Crude Uranate With Chlorine Gas

In connection with the experiments of hydrogen chloride for the removal of vanadium, chlorine gas suggested

itself as a possibility. Experiments were tried substituting chlorine gas for hydrogen chloride, but the results were negative. Chlorine gas does not react with the vanadium present in the crude sodium uranate, and only ~~the~~ minutest traces of the tetrachloride and oxychloride of vanadium were observed.

III SEPARATION OF VANADIUM BY MEANS OF

AMMONIUM CHLORIDE

Inasmuch as hydrogen chloride readily removes vanadium from crude sodium uranate as a volatile product, it seemed worth while to conduct some experiments with mixtures of ammonium chloride and sodium uranate at somewhat elevated temperatures. Under these conditions, the partial dissociation of ammonium chloride into ammonia and hydrogen chloride would furnish the constituent to react with the vanadium, and at the same time the ammonia and excess of ammonium chloride furnish ~~at~~ favorable conditions for the conversion of some of the uranate into the oxide.

A number of preliminary experiments were conducted to ascertain; (1) quantity of water to have present in the mixture of uranate and ammonium chloride, (2) the temperature at which the reaction should proceed, (3) the amount of ammonium chloride required, (4) the kind of a vessel best adapted for the experiments, (5) the effect of other ammonium salts when added as partial substitutes for ammonium chloride.

Experiments were first conducted by mixing the crude uranate and dry ammonium chloride and subjecting this

mixture to heat in a test tube. The ammonium chloride was readily volatilized but apparently no vanadium was volatilized. A part of the uranate, however, was converted into the oxide. Experiments were then tried with the mixtures of ammonium chloride and crude uranate made up to a thick paste by the addition of water. When the paste is subjected to heat, the water is gradually expelled, and then as the temperature is increased, copious fumes of ammonium chloride are given off, and just as the volume of chloride vapor diminishes the characteristic brown vapor of the volatile vanadium compounds make their appearance and continue to be evolved copiously until the molten mass in the crucible becomes solid. Upon testing the residue obtained in this treatment, it was found to contain only a trace of vanadium.

The experiment was here tried of pouring the molten liquid from the crucible into a beaker containing water, to ascertain whether mere fusion with ammonium chloride would render the vanadium soluble. The melt dissolves almost completely in the water. The solution has a decided green color, and gave tests for both uranium and vanadium. Evidently this procedure must be included in the list of negative experiments.

Experiments were next conducted to determine the minimum quantity of ammonium chloride required for the nearly complete separation of vanadium by the above procedure.

Mixtures of uranate and ammonium chloride in the following proportions were heated: (1) ten parts by weight of ammonium chloride to ten parts by weight of crude uranate, (2) fifteen parts by weight of ammonium chloride to ten parts by weight of crude uranate, (3) twenty parts by weight of ammonium chloride to ten parts by weight of crude uranate. The vanadium was satisfactorily separated only in the case where twice as much ammonium chloride was used as crude sodium uranate.

The experiments were first conducted in iron crucibles, but it was noted that a crucible would not stand more than two charges before it showed holes. Nickel crucibles were attacked fully as badly. Iron test tubes made out of $1\frac{3}{4}$ in. steam pipe capped at one end only withstood two charges. Alundum and porcelain crucibles, however, served the purpose very well, and in the experiments that followed, porcelain crucibles were used.

In a few experiments, ammonium nitrate was substituted for a part of the ammonium chloride usually used. This modification did not yield very satisfactory results. While it was possible to remove the vanadium by using a mixture of fifteen grams of ammonium chloride, five grams of ammonium nitrate and ten grams of sodium uranate, the percentage conversion of uranium into oxide in the residue was thereby reduced, as shown in the tabulated data that follows.

As a result of these preliminary experiments the following procedure was adopted:- A known weight of sod-

ium uranate, ten grams in most cases, is taken and twice that weight of ammonium chloride added. The mixture^{is} placed in a mortar and pulverized, which at the same time mixes it. The pulverized mixture is then placed in a porcelain crucible and water added until a stiff paste is obtained. Heat is then applied slowly at first with constant stirring to drive off the excess of moisture. Strong fumes of ammonia are noted at this point. As the mass becomes dry, it has a tendency to cake, but with vigorous stirring this can be prevented to a large extent. After the water has been expelled the mass begins to fuse, and continues to do so until there is a green molten liquid in the crucible. This liquid boils freely with the expulsion of ammonium chloride fumes until the large excess of ammonium chloride is driven off, and then the brown fumes of the chloride and oxychloride of vanadium begin to make their appearance. They were given off very copiously toward the end of the process, and especially as the molten mass became solid. Sometimes these brown fumes make their appearance before solidification begins, but usually not. As soon as the volatile products cease to be given off, the crucibles are removed from the flame because further heating of the residue greatly increases the percentage of sodium uranate in the residue.

The black residue from this treatment gives a slight test for vanadium. The percentage of vanadium may be estimated colormetrically by comparison with standard solutions

of vanadium. In this way, it was found that the vanadium content of the uranate is reduced from 8.55 percent vanadium oxide to less than 0.5 percent.

To ascertain to what extent the uranium is converted into the oxide by treatment with ammonium oxide, several quantitative experiments were conducted. The weight of the residue after treatment with ammonium chloride was first determined by introducing the ammonium chloride and a weighed quantity of uranate mixture into a tared crucible and making a run. From the weight of the residue thus obtained, the ratio of uranate to residue may be calculated. This ratio is required for subsequent calculations.

Table V

No. of Sample	Wt. of Crude Uranate	Wt. of Residue	Ratio
1	10.00	9.60	.96
2	10.00	9.55	.955

To ascertain the percentage conversion and the percentage of recovery of uranium, analyses were made of the residues obtained in several experiments. The residue from the crude uranate obtained by treatment with ammonium chloride must consist of a mixture of uranium oxide, sodium uranate, sodium chloride, iron oxide, and impurities from the am-

monium chloride. This residue was shaken with dilute (1:40) sulphuric acid in excess, which dissolves out the sodium salts of uranium, and chlorides, and a small percentage of uranium oxide, leaving a black residue consisting of uranium oxide with a small amount of iron oxide. For commercial use the iron present is usually not objectionable.

Samples of pure uranium oxide were prepared from two different samples of uranium nitrate in the following way: (1) by dissolving uranyl nitrate in water, precipitating with ammonia, and igniting the precipitate, (2) by evaporating some of the aqueous solution to dryness and igniting. The uranium oxide thus prepared was treated with dilute (1:40) sulphuric acid. The percentage solubility found varies from nine percent, in the case of the oxide prepared, by evaporating and igniting, to about twenty-five percent in the case of that which was precipitated. Dr. Schlundt (p.19) did some work on this point, during the summer of 1914 at the Bureau of Mines using 1:20 sulphuric acid and boiling. He found that the solubility ranged from ten to fifteen percent. In the calculations which will follow, fifteen percent is considered as having dissolved.

Table VI

Recovery Of Uranium Oxide

No. of Sam- ple	Wt. of Resi- due	Crude Ur- anate Eq- ivalent	Total U as Oxide	Wt. of Pu- re U_3O_8	Total Conver- sion	Percent Recov- ery	Percent Conver- sion
				a- 0.2840:			
1	:0.5918:	0.6184	:0.3995:	b- 0.2698:	0.3174:	67.5	: 79.4
2	:0.6082:	0.6355	:0.4105:	a- 0.2930:	0.3724:	67.7	: 79.9
				b- 0.2783:			

Table VI shows the results of a quantitative determination made on the residue, obtained by treating a given weight of crude uranate with twice its weight of ammonium chloride, to determine the percentage of recovery of uranium oxide, and the percentage conversion.

Column 2 represents the weight of the residue obtained from a charge which was taken for analysis. Column 3 represents the equivalent weight of crude uranate calculated from the ratio 0.957 of table V. Considering the crude uranate contains 64.6 (table II) percent uranium oxide, column 4 represents the total amount of uranium oxide present in the residue. Column 5-a represents the weight of uranium oxide found after treating the residue with dilute (1:40) sulphuric acid. However, it was found as will be shown later that this residue is only ninety-five percent pure, and thus b represents the weight of uranium oxide actually recovered on this basis. Column 6 represents the amount of uranium oxide present

in the residue before treatment with dilute sulphuric acid. Assuming that fifteen percent of the uranium dissolved in the dilute acid used to remove the remaining sodium uranate. Column 7 represents the percentage recovery, figured from the weight of uranium oxide given in column 5. Column 8 represents the percentage conversion based upon the values of column 6.

The purity of the uranium oxide removed was determined by dissolving two samples of the uranium oxide residue after treatment with dilute sulphuric acid in nitric acid. The insoluble material was filtered off, and the iron precipitated with ammonium carbonate in excess. The iron was filtered off and the ammonium carbonate solution boiled to expel the excess of ammonia and precipitate the uranium compound, which was then converted to uranium oxide by ignition.

Table VII

Purity of Uranium Oxide

Number of Sample	Wt. of U_3O_8	Wt. of Pure U_3O_8	Percent Purity
1	0.2555	0.2396	93.9
2	0.2432	0.2328	95.6

To ascertain the effect of temperature on the percentage recovery of uranium, an experiment was run in which the final temperature was raised much higher than in preceding case.

Table VIII

Effect of Temperature on Conversion

No. of Sam- ple	Wt. of Resi- due	Crude Ur- :anate Eq- :ivalent	Total U as :Oxide:	Wt. of pu- :re U_3O_8	Total : :Conversion	Percent : :Recovery	Percent : :Conversion
1	:0.6182	:0.6460	:0.4151	a- 0.2555 b- 0.2427	:0.2855	:58.5	:68.7
2	:0.5936	:0.6192	:0.4000	a- 0.2432 b- 0.2310	:0.2717	:57.5	:67.9

A comparison of the percentage of conversion with those of table VI shows that the further heating, after the evolution of volatile vanadium compounds ceases, materially reduces the yield of uranium oxide.

To confirm this conclusion a third series of experiments was conducted in which the volatile products were vaporized at still lower temperatures than obtained in the first experiment. The results obtained are given in table IX. It will be noted here that the percentage recovery of uranium oxide is higher than in either of the preceding experiments, which shows that the lowest temperature possible to remove the vanadium gives the most efficient recovery of uranium oxide.

Table IX

Effect of Temperature on Recovery of Uranium

No. of Sam- ple	Wt. of Resi- due	Wt. of Crude Ur- anate eq- ivalent	Total U as Oxide	Wt. of pu- re U_3O_8	Total Conver- sion	Percent Recov- ery	Percent Conver- sion
1	:0.6976:	0.7310	:0.4722:	a- 0.3916 b- 0.7320	:0.4376:	78.7	: 92.6
2	:0.6694:	0.6994	0.4519	a- 0.3726 b- 0.3540	:0.4164:	78.3	: 92.1

A quantitative determination was made on the residue obtained by treating ten grams of crude uranate with a mixture of fifteen grams of ammonium chloride and five grams of ammonium nitrate. The vanadium here was removed to less than half a percent, but the results of the experiment clearly show that the percentage recovery of uranium oxide is very materially decreased. While the addition of the ammonium nitrate reduces somewhat the temperature at which the mixture fuses, it is evident from the data of table X that its presence materially reduces the yield of uranium oxide.

(See page 34 for table X)

Table X

Effect of Ammonium Nitrate

No. of Sam- ple	Wt. of Resi- due	Crude Ur- anate eq- ivalent	Total U as Oxide	Wt. of pu- re U_3O_8	Total Conver- sion	Percent Recov- ery	Percent Conver- sion
1	:0.5120:	0.5350	:0.3456:	a- 0.1768 b- 0.1680	:0.1976:	48.6	: 57.1
2	:0.5316:	0.5555	:0.3589:	a- 0.1850 b- 0.1758	:0.2068:	48.9	: 57.6

V. SEPARATION OF VANADIUM BY MEANS OF NITRIC ACID

10) Hillebrand refers to the work of Friedel and
11) Cummenge on the separation of vanadic acid from carnotite ore by rendering the oxide insoluble in water by evaporating the nitric acid solution to dryness. This method of separating the vanadium from crude sodium uranate was tried, but it did not work very successfully, as a large part of the uranium was rendered insoluble as well as the vanadium, and then, too the vanadium was not completely removed from the uranate. Some modifications of this method were then tried, which finally furnished a quantitative method of separating vanadium from the crude uranate. In connection with some qualitative experiments upon the action of nitric acid on sodium uranate, we found that when the vanadium bearing uranate was dissolved in dilute nitric acid and the solution then boiled that the vanadium was precipitated quantitatively. Quantitative experiments were then conducted to determine the following factors: (1) the proper amount of nitric acid necessary to dissolve the crude uranate, (2) the recovery of uranium from the solution of uranium oxide and its purity, (3) the amount of uranium in the precipitate containing the vanadium.

1. The Quantity of Nitric Acid. By taking weighed samples of uranate and dissolving them in nitric acid of different concentrations and then boiling this solution to precipitate the vanadium, it was found that acids ranging in concentration from N/20 to N/50 completely removed the uranium. Boiling of concentrated nitric acid solutions of the uranate results in only partial precipitation of the vanadium. The quantity of pure nitric acid necessary for a given weight of crude uranate is given in the table below. It might be stated here that it is only necessary to boil the nitric acid solution for two or three minutes to precipitate the vanadium. It should also be stated that the quantity of nitric acid required is less than shown by the equation,

2. Recovery of Uranium and Its Purity. The recovery of the uranium from the filtrate of the nitric acid solution is best accomplished by precipitating it with ammonium hydroxide and then igniting the precipitate of ammonium uranate. Some sodium uranate is probably precipitated out with the ammonium uranate, which, upon ignition gives us a mixture of uranium oxide and sodium uranate, along with a small quantity of iron. The sodium uranate can be easily removed by agitating the ignited residue with cold dilute(1:40) sulphuric acid. The oxide of uranium thus obtained is free from vanadium,

and sodium uranate. I

In this connection, reference should be made to the work of Metzger and Heidelberger on the analysis of sodium uranate. These investigators precipitated the uranium from the nitric acid solution of sodium uranate as ammonium uranate, which they ignited. They assumed that the residue was pure uranium oxide. That this conclusion is not correct is shown by the following experiment:- If no sodium uranate is present in the ignited residue obtained by the first precipitation of uranium from the acid solution of sodium uranate with ammonia, then, by redissolving some of the first residue in nitric acid and reprecipitating with ammonia, the quantity of oxide by ignition should equal the first weight. The weight of oxide from the second precipitation is less, by at least one and one-half percent as will be seen from table XI. The data of table XIV also confirms this conclusion. The percentage of uranium oxide recovered by the treatment of sulphuric acid, plus the amount obtained from the filtrate, should equal the amount of the original uranium oxide residue, if it were pure. But here, again, there is discrepancy of about two percent.

Table XI

No. of Sam- ple	Wt. of cru- de Uran- ate	Total :U as :Oxide	Wt. U ₃ O ₈ : 1st : pp't.	Wt. U ₃ O ₈ : 2nd : pp't.	Percent :U ₃ O ₈ : 1st : pp't.	Percent :U ₃ O ₈ : 2nd : pp't.	Percent :Discrep- :ancy
1	2.000	1.292	1.1755	1.1209	90.8	88.0	2.8
2	3.000	1.938	1.7308	1.6393	85.9	84.5	1.4

It was found on analysis of the uranium oxide obtained after treatment with dilute sulphuric acid that it was about ninety-five percent pure. The impurity here is undoubtedly due to iron present, which is not objectionable for commercial purposes.

3. Uranium Present in Precipitate Containing Vanadium. The amount of uranium present in the vanadium precipitate was determined in a manner similar to that used in determining the uranium in the sample of carnotite ore. Inasmuch as the precipitate is not soluble in aqua regia, the method of analysis given in Bulletin 70 U. S. Bureau of Mines, required modification. The precipitate was, therefore, fused with potassium acid sulphate, and then leached with water. The usual method for a uranium determination in carnotite ore was then followed, except that it was necessary to add a large excess of lead acetate to precipitate the vanadium as lead vanadate, due to the sulphate present from the potassium acid sulphate. The analytical data obtained are summarized in table XII.

Table XII

Analysis of Vanadium Precipitate

No. of Sam- ple	Wt. of Uran- ate	Total U: as Oxide	Wt. of V ₂ O ₅ Residue	Wt. of U ₃ O ₈	Percent U ₃ O ₈ in Residue	Percent U ₃ O ₈ of Total
1	2.8270	1.826 g	0.5728	0.2406	43.7	13.1
2	2.9383	1.898	0.5590	0.2733	48.8	14.4

Next a series of determinations was run to find the weight of pure nitric acid required to react with a given weight of crude uranate, the percentage recovery of uranium oxide and the weight of the vanadium residue. Four determinations were made and the results obtained are given in table XIII.

Table XIII

No. of Char-ge	Wt. of Crude Uranate	Total :U as Oxide	Wt. of Pure HNO_3 per g. of uranate	Wt. of U_3O_8 by ppt	Wt. of U_3O_8 obtained from H_2SO_4 acid residue	Wt. of V_2O_5 residue
1	3.6197	2.3383		2.1320	1.8530	
2	2.8270	1.8262	0.6048	1.5986	1.0354	0.5728
3	2.9383	1.8980	0.5738	1.6173	1.2997	0.5590
4	10.5883	6.8440	0.5719	5.9026	4.0116	2.2349
					Percent V_2O_5 Residue	Percent U_3O_8 Obtained
1						79.2
2					20.2	56.6
3					19.0	68.4
4					21.1	58.6

It will be noted from this table that the recovery of uranium dropped considerable in the cases of samples 2 and 4. This result is readily accounted for when the sulphuric acid filtrate was taken and analysed for uranium oxide. In the case of sample 2, 22.5 percent of the total uranium oxide was found in the filtrate. That would bring the recovery up to 79.1 percent. In the case of sample 4, 25 percent of the total uran-

ium content was found in the dilute sulphuric acid filtrate, thus bringing the percentage recovery up to 83 percent. Thus, we see that the recovery is very nearly the same in all cases. It will also be noted that the weight of vanadium residue bears an almost uniform ratio to the weight of the crude uranate treated. This method of treatment still leaves approximately 13.5 percent of the total uranium (table XII) in combination with the vanadium, but the vanadium is completely removed and fully 75 percent of the uranium is recovered as pure oxide. This result compares favorably with the recovery of uranium by the previous method, namely, the treatment with ammonium chloride, where the recovery of uranium is only 68 percent.

VI. SEPARATION OF VANADIUM BY MEANS OF (1) HYDROCHLORIC
ACID AND (2) SULPHURIC ACID

After obtaining a good separation of vanadium from crude uranate with dilute nitric acid, the investigation was extended to hydrochloric acid. Experiments were conducted very similar to those used in the case of nitric acid, and it was found that here, again, the vanadium could be removed quantitative.

Two samples of the crude uranate of approximately five grams were dissolved in the least possible amount of hydrochloric acid, which had been standardized. The solutions were then brought to a boil and boiled for a few minutes to precipitate the vanadium which settled out very readily. The vanadium residue was filtered off, and ammonia added to precipitate the uranium. The precipitate of ammonium uranate was filtered off, ignited to uranium oxide and the residue treated with dilute (1:40) sulphuric acid to extract the sodium uranate present in the ignited residue.

Table XIV gives a summary of the results obtained in these experiments.

Table XIV

Separation of Vanadium With Hydrochloric Acid

No. of Char-ge	Wt. of Crude Uranate	Wt. of U as Oxide	Total :HCl per g. of uranate	Wt. of Pure :U ₃ O ₈ by pp't	Wt. of U ₃ O ₈ :from H ₂ SO ₄ acid resd.	Wt. of U ₃ O ₈ :from H ₂ SO ₄ Fil.	Wt. of V ₂ O ₅ :Resid.
1	5.7852	3.7383	0.3422	3.3586	2.3864	0.8884	1.0360
2	5.4948	3.5496	0.3712	3.2353	2.4673	0.7078	1.2520
				Per-cent ↑	Per-cent ↑	Per-cent ↑	Per-cent ↑
1				89.8	63.3	23.8	18.4
2				91.1	69.5	19.9	22.7

Comparing the percentage of vanadium oxide residues here obtained with those obtained by the nitric acid treatment, it appears that the percentage weight of the vanadium bearing residues averages 20.5 percent, which is in good agreement with the percentage obtained by the nitric acid treatment. Hence, we assume that the vanadium oxide residue is the same in both cases.

It will also be seen, from the table, that the percentage of pure uranium oxide in sample 2 is less than in sample 1, but, on the other hand, the amount of uranium oxide recovered from the sulphuric acid treatment is larger, which accounts for the difference. Since the two acids serve equally

well, and the choice for a commercial method would be determined by their cost.

2. Sulphuric Acid

A few qualitative experiments were conducted on the removal of vanadium from crude sodium uranate by boiling a dilute sulphuric acid solution. The vanadium is removed here fully as effectively as in either of the preceding cases, and the indications are that the quantity of acid required is no greater than when nitric and hydrochloric acids are used. A more complete investigation of the sulphuric acid method is in progress.

This method looks promising from a commercial standpoint, on account of the lower cost of sulphuric acid.

VII. SUMMARY OF RESULTS

The experiments here described have resulted in at least four methods that have proven successful for removal of vanadium from the crude uranate, which is obtained on a large scale in the plant of the National Radium Institute.

1. By the action of hydrogen chloride gas, it has been shown that in time the vanadium is completely removed, leaving a residue consisting of sodium uranate, sodium chloride, uranyl chloride, and the other impurities in the crude uranate. The uranium may be removed from this residue by either of two methods: (1) by boiling with excess of ammonium chloride, which converts the uranium into ammonium uranate, which may be ignited to uranium oxide; (2) by dissolving the residue in a dilute mineral acid and precipitating the uranium with ammonia, as ammonium uranate, which may be converted into uranium oxide by ignition. The percentage recovery of uranium oxide, free from vanadium, but containing a small percentage of iron, which is not objectionable for its sale, varies from fifty-nine to sixty-four percent.

2. By mixing the vanadium bearing uranate with twice its weight of ammonium chloride and enough water to make a thick paste, the vanadium may be nearly completely volatilized.

zed by heating in a porcelain crucible. When subjected to proper conditions of temperature, it is possible to reduce the quantity of vanadium present in the crude uranate from eight and five-tenths percent to less than one-half of one percent. The ammonium chloride serves the double purpose of converting a part of the uranium present to ammonium uranate, which, upon ignition, yields uranium oxide, as well as removing the vanadium. The percentage of uranium recovered may be regulated very materially by the heat treatment to which the mixture is subjected. Where the residue, after volatilization of the ammonium chloride, is heated to a high temperature, the percentage recovery of the uranium oxide (U_3O_8) is reduced very materially, due to the fact that some of the uranium oxide formed in the operation is converted back to sodium uranate. The highest percentage recovery was obtained where the temperature was not raised any higher than necessary to volatilize the ammonium chloride and vanadium compounds. In this connection, it was found that a mixture of fifteen grams of ammonium chloride and five grams of ammonium nitrate to every ten grams of crude uranate served the purpose of removing the vanadium from the crude uranate just as well as the ammonium chloride alone. However, the percentage recovery of uranium oxide is reduced very materially, as it is only possible to get a recovery of about fifty-eight percent under the most favorable conditions of temperature. This reduction in the percentage recovery more than

counterbalances any advantage that the use of ammonium nitrate might have as a partial substitute for ammonium chloride.

3. The vanadium can be completely precipitated by dissolving the crude uranate in the least possible amount of dilute nitric, hydrochloric, or sulphuric acid, and then boiling the solution. Approximately thirteen percent of the uranium is precipitated out with the vanadium, but the amount is small as compared to that which remains in solution. The uranium may be recovered by adding ammonia to the solution containing the uranium, free from vanadium, to precipitate it as ammonium uranate, which may be converted into uranium oxide by ignition.

The percentage recovery of uranium oxide in the case of nitric and hydrochloric acid treatments is found to vary from fifty-eight to seventy-nine percent. No quantitative determinations have been made on the sulphuric treatment. Some uranium is lost in the dilute sulphuric acid treatment of the residue for the removal of the sodium uranate, but this uranium may be recovered from the acid solution by precipitation with ammonia.

Only by one of the above methods is the removal of the vanadium and the conversion of the uranium oxide accomplished in one step. That is the case of the ammonium chloride treatment. In all of the other processes the vanadium is re-

moved by one step and the uranium recovered by another operation. However, it will be noted that the percentage recovery of uranium oxide in all the methods was practically the same.

Probably hydrogen chloride (gas) may also be utilized to remove the vanadium from carnotite ores quantitatively, by proper regulation of temperature. Further experiments in this direction must be conducted before a positive statement can be made in contradiction to the findings of Hillebrand that vanadium cannot be determined quantitatively in ores by treatment with hydrogen chloride.

As a result of our experiments on the precipitation of uranium from a nitric acid solution of sodium uranate with ammonia, a doubt has arisen with regard to the experimental procedure of Metzger and Heidelberger in the analysis of sodium uranate. Our experiments indicate that the oxide of uranium obtained still contains nearly two percent of sodium uranate.

In connection with the determination of the vanadium in the precipitate obtained by boiling a dilute mineral acid solution of the uranate, it was found that the method of analysis of uranium-vanadium compounds outlined by the Bureau of Mines requires some modification at the beginning of the analysis. The residue containing vanadium is insoluble in hydrochloric acid, nitric acid, and aqua regia. It is, therefore,

necessary to fuse it with potassium acid sulphate and leach the fused mass, thereby effecting solution of the residue, after which the regular course of analysis outlined in Bulletin No. 70 of the Bureau of Mines for the determination of uranium and vanadium may be followed.

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University of Missouri
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Approved:

Herman Schlundt

May 15, 1915

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