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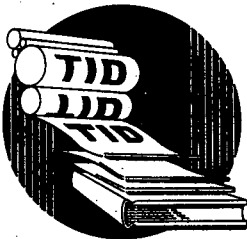
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AND PROTACTINIUM**

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ANALYSIS OF ORE RESIDUES FOR IONIUM AND PROTACTINIUM

By L. I. Katzin, Q. Van Winkle, and J. Sedlet

With the availability of large amounts of pitchblende ore residues, as a result of the processing of uranium for atomic power developments, it has been possible to consider the recovery of long-lived members of the uranium and actinium radioactive decay series in appreciable amount. These materials are of use as radiation sources and sources of other isotopes, in addition to their intrinsic interest. This report deals with analysis of some residue fractions which have not previously been considered as sources for protactinium (Pa^{231}) and ionium (Th^{230}), but which may prove to be convenient sources of these materials.

The isotope Pa^{231} occurs in nature approximately to the extent that radium (Ra^{226}) occurs, which is about 0.15 parts per million in pitchblende ore containing about 60 per cent by weight of U_3O_8 . The sum total of this material which has been extracted and purified, according to literature reports, is probably not significantly more than two grams, considerably less than the amount of radium recovered.

After initial manipulations, pitchblende ores are usually treated with sulfuric acid and sodium nitrate, giving an acidic solution of uranyl salts (and other salts) with an insoluble residue in which is found the radium. Some polonium, ionium, and protactinium dissolve with the uranium. A fraction at least of the protactinium presumably remains with the insoluble gangue; from the fact that protactinium has been obtained from such material. Thus, von Grosse¹ and Graue and Käding² used the ultimate residues following removal of the radium as their sources of protactinium.

The acid solution of uranyl nitrate is treated with excess sodium carbonate to precipitate some of the nonuranium materials appearing in solution, the uranium remaining in solution as the carbonate complex. It is to be expected that the protactinium dissolved in the first step should precipitate with the other hydroxides and carbonates at this point. The behavior of ionium is less definite, since thorium forms a soluble carbonate complex under the proper conditions. It seems likely that there might be at least a partial precipitation at this point. The analytical data bear out this presumption.

The carbonate solution of uranium is then treated with NaOH to precipitate uranium, and the uranium is dissolved in acid and reprecipitated with ammonia. It is to be expected that any protactinium and ionium present in the carbonate solution would follow the uranium through these steps. The ammonium diuranate is next calcined to U_3O_8 , the oxide dissolved in nitric acid, and the concentrated nitrate solution extracted with ether. The ether solution of uranyl nitrate is washed repeatedly with portions of water until no further UX_1 activity (Th^{234}) can be detected. After steps for recovery of additional uranium from the washes and original solution, the residual solutes are combined and saved, together with any insoluble

residue from treatment of the oxide with nitric acid. It is to be expected that this residue, therefore, may be a rich source of ionium, if an appreciable portion survives the carbonate precipitation.

In the classical isolations of protactinium,^{1,3} the starting material was the ultimate residue remaining after extraction of radium, following preliminary removal of uranium. These residues were obtained from the Joachimsthal mine in Czechoslovakia. From the fact that these were residues from extensive chemical treatments, it might be expected that the isolation of protactinium from them might be beset by difficulties in addition to those inherent in the chemical nature of the protactinium. Therefore, it was considered highly worthwhile to investigate a less refractory source. The carbonate precipitates from the uranium process were a logical point of attack, since they represented the probable site of any protactinium that might have dissolved in the original acid treatment, while at the same time the material had already been in solution and should be amenable to redissolution with simple acid treatment. The ionium content of this fraction similarly would be more available than that in the original ore or the radium residues. Another possible source of ionium is the residue of the ether extraction procedure, as already stated.

The analyses of these fractions, to be reported in this paper, show that the carbonate fraction is indeed a relatively rich and readily worked source of both protactinium and ionium, and that the ether extraction residues contain ionium essentially free of protactinium or polonium. Their ionium content is something over 6 parts per million. The data further show that more than half of the protactinium and ionium may be dissolved in the initial acid treatment of the ore, and appear in the carbonate fraction.

EXPERIMENTAL

Several analytical procedures have been reported in the literature for determination of protactinium in ores, which make use of coprecipitation. One procedure, first employed by Hahn and Meitner, and developed further by Wildish,⁴ makes use of tantalic oxide as a carrier for protactinium. Another procedure developed by several workers has involved coprecipitation with titanium, especially by hydrolysis of the hydroxide from salts such as the sulfate. Von Grosse¹ has pointed out the inadequacy of tantalum carrier and has suggested instead the use of zirconium phosphate. Through dissolution of this precipitate in hydrofluoric acid, precipitations of carriers for contaminating radioactivities can be made to give radiochemical purification of the protactinium. A manganese dioxide carrier has also been used.⁵

The principal long-lived alpha activities present in the fractions examined (excluding the uranium isotopes) are radium, polonium, ionium, and protactinium. The polonium, short-lived in comparison to the others, is still of appreciable half-life (140 days) and is supported by its long-lived parent lead isotope RaD (22 years). Radiochemical analytical procedures must therefore be capable of distinguishing these four isotopes where they occur together, and never less than the last three.

The procedures finally adopted depend primarily on the following behavior characteristics of trace concentrations of the activities in question:

1. Barium sulfate will carry radium quantitatively but not protactinium; thorium isotopes are partially carried.
 2. Zirconium phosphate will carry protactinium (and thorium) well under the proper conditions, and will not carry radium.
 3. Manganese dioxide formed in situ from manganous ion and permanganate will carry polonium quantitatively both in the presence and absence of fluoride.
 4. Manganese dioxide will carry protactinium except in the presence of fluoride.
 5. When Th^{232} is added to a detectable concentration, manganese dioxide carries no significant amount of ionium activity.
 6. When thorium is precipitated with hydrofluoric acid (thereby precipitating the isotopic ionium) neither protactinium nor polonium is carried appreciably.
 7. A silver wire will collect polonium from a halogen acid solution.
- Three types of residues have been analyzed so far. These consist of the carbonate fraction discussed earlier (three samples), the ultimate sulfate residue mentioned (one sample) and the residue of ether extraction (one sample).

Carbonate Residues

The carbonate fraction consisted of two samples from one process, and a third sample from a process operated by a different producer. Treatment with concentrated nitric acid yielded a gelatinous residuum composed mainly of silica; the readily soluble portion and the residue were analyzed separately.

Following separation by centrifugation, the gel was treated with HF and perchloric acid, the perchloric acid eventually fumed off, and the remaining solid matter fused with alkali carbonate. The carbonate melt was leached with hot KOH solution (0.05M) to remove any tantalum present, and the leaches discarded. The remaining solid was dissolved by fusing it with KHSO_4 and dissolving in normal HCl. After the addition of some Pa^{233} to act as tracer for the protactinium, radiochemical analysis was carried out.

Sulfate Residues

The solid material was fused with NaOH and the melt leached with dilute hydrochloric acid, dissolving about 18 per cent of the solids. This solution was analyzed separately. The remaining solids were fused with carbonate and the melt leached with water which was discarded. The solid carbonates then dissolved completely in dilute hydrochloric acid. Following addition of Pa^{233} tracer, the two solutions were analyzed separately.

Ether Residues

A uniform sample was dried, then fused with carbonate. A water leach of the melt was discarded. The residue was treated with HF and HNO_3 several times, and was evaporated each time to dryness. Following a final evaporation, the material was dissolved in nitric acid, leaving a white granular residue insoluble in nitric acid or HF (probably alkaline earth fluoride). The acid solution was analyzed further. Unfortunately the fluoride residue,

which may have been composed in part of thorium fluorides, was discarded. Another analysis, carried out subsequently by Mr. C. C. Bard, gave complete solution. The value from this analysis is found in Table 1.

Analytical Results

A summary of the analytical findings for the residue samples investigated is found in Table 1. The exact values of the analyses are not significant, and should be considered only as an indication of relative orders of magnitude. This is necessitated in part by analytical uncertainties, and in part by the inhomogeneity of the material itself. The variability from the latter standpoint is necessarily quite large. Decay of polonium is another source of variability. Material balances are not complete, as can be seen; this is in part due to analytical failures, but in part due to radioactivities other than those being reported (short-lived activities and, in the case of sample 5, radium and its daughters).

The carbonate fractions are seen to contain about 0.3 to 0.35 parts per million of protactinium, which is mainly bound with the acid-insoluble silicious portion of this fraction. The ionium, present to the extent of some 15 to 20 parts per million, is found in the readily soluble portion of the fraction. Information furnished about the carbonate fraction,⁷ is that it is 215 parts by weight for 580 parts by weight of the crude ore, i.e., 37 per cent. For pitchblende which is 65 per cent by weight U₃O₈, this indicates that on the order of two-thirds the original protactinium content of the ore was dissolved in the sulfuric-nitric acid treatment, and precipitated by the carbonate treatment, with more than three-fourths of the ionium content following the same path. The apparent high level of ionium in the sulfate residues is in part at least a reflection of the fact that much of the soluble portion of the ore has been removed, giving a bulk concentration. For example, removal of the uranium alone gives a concentration of about threefold. It is interesting to note that the radioactivity surviving in the ether residues is practically entirely ionium (together with a certain amount of uranium). It is difficult to assign a concentration factor for this material, but it must be rather large due to the previous treatments.

On the basis of the results obtained, a number of milligrams of protactinium and approximately one-half gram of ionium (with three times as much Th²³²) have been obtained in pure state, from a carbonate fraction.⁶⁻⁸ The yields obtained for the protactinium corresponded to 50 to 60 per cent of the material indicated by preliminary analysis. No attempt was made to obtain complete recovery of ionium.

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Table 1--Radioactive Analyses of Uranium Process Residues

Sample origin	Fraction	Total alpha (c/m/g at 50%)	Analysis					
			Protactinium		Thorium		Polonium	
			per cent of act.	ppm	per cent of act.	ppm	per cent of act.	µc/g
1. Carbonate ppt from 65% pitch- blende (African) No. 3-1	HNO ₃ sol.	4.5 x 10 ⁵	<0.3	<0.03	78	16	20	0.08
	Silicious residue	3.5 x 10 ⁴	40	0.27	<20	<0.3	25	0.008
2. As above, but another ship- ment. No. 3-2	HNO ₃ sol.	2.2 x 10 ⁴	<1	<0.04	--	---	--	----
	Silicious residue	2.4 x 10 ⁴	75	0.35	<5	<0.05	20	0.004
3. As above, but from another processor No. 7	HNO ₃ sol.	4.4 x 10 ⁵	-	-	94	<19	4-6	0.02
	Gelatinous residue	7 x 10 ⁴	25	0.38	10	0.3	>50	>0.03
4. Sulfate resi- due, 65% Afri- can pitch- blende. No. 1	Sol. HCl af- ter NaOH	6.0 x 10 ⁵	<3.6	<0.4	90	24	0-5	0-0.03
	Sol. HCl af- ter Na ₂ CO ₃	2 x 10 ⁶	<0.2	<0.08	5-10	5-9	0-5	0-0.1
5. Residue of ether extrac- tion of ura- nium. No. 8	HNO ₃ -HF soluble	1.4 x 10 ⁵	<0.05	<0.01	~100	6	--	----
	Insoluble fluoride		Not Analyzed					

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