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THE EXTRACTION OF URANIUM FROM PITCHBLEND
BY AMMONIUM CARBONATE

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I. INTRODUCTION

When finely ground pitchblende is acted upon by a water solution of a carbonate or bicarbonate, uranium goes into solution. Under suitable conditions, a large part of the uranium present may be extracted in this way. A possible advantage of this procedure over dissolving the mineral in acid is that some of the secondary constituents of the mineral are only slightly soluble in carbonate solutions and are therefore left behind. The reaction involves an oxidation from U_3O_8 to the UO_3 stage, but even the presence of atmospheric oxygen permits it to proceed slowly at room temperature. Higher rates can be obtained by using stronger oxidizers, higher temperature, and stirring.

II. DISCUSSION

A rough comparison of the relative effectiveness of different carbonates was first made by running a number of comparative tests simultaneously. These were made at room temperature in flasks, occasionally shaken by hand; in the earlier experiments, no oxidizer was used, other than the air present in the flasks. On the basis of the amount of uranium dissolved under similar conditions, the bicarbonates of sodium and potassium proved better than the carbonates, the potassium compounds better than the sodium, and ammonium carbonate the best of all. After this result had been obtained, no further experiments on alkali carbonates were carried out.

Addition of a suitable oxidizer accelerated the reaction. Hydrogen peroxide was the one generally employed, simply because it yielded no products which interfered with the analysis. Its instability was a disadvantage, in consequence of which its favorable effect was largely confined to the first few hours. Various other oxidizers, solid or liquid, could have been substituted; Pb_3O_4 , for example, gave satisfactory results with ammonium carbonate. Oxygen, however, is the best choice in all cases where it can be made to give a sufficiently high reaction rate.

At about $60^\circ C.$, in sealed glass tubes, and with agitation by gentle oscillation, the reaction was much faster. This indicated that further improvement would be obtained at still higher temperatures, and with efficient mechanical stirring. Lack of suitable equipment prevented the undertaking of such experiments. It was apparent, however, that a practical carbonate process would have to be carried out at temperatures of the order of $90^\circ C.$ or above, and in a strong metallic digester, into which the gases needed for the reaction, i.e., ammonia, carbon dioxide and oxygen, could be pumped under pressure.

The uranium dissolves with the formation of a soluble complex, which is said to have the composition (Mellor⁽¹⁾) $2(NH_4)_2CO_3 \cdot UO_2CO_3$. The experiments gave some ground for the belief that a liquid containing ammonium

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bicarbonate ($1\text{NH}_3:1\text{CO}_2$) or ammonium sesquicarbonate ($4\text{NH}_3:3\text{CO}_2$) might be better than the normal carbonate.

The solution obtained by ammonium carbonate extraction of high grade pitchblende contained, in addition to uranium, chiefly lead, magnesium, and silica, together with small amounts of nickel, cobalt, and sodium. In connection with the amount of lead dissolved, it was found that up to a point apparently fixed by the solubility of lead carbonate in the carbonate solution employed (such solubility is somewhat greater in ammonium carbonate than in alkali carbonates), the uranium to lead ratio found in solution seemed to correspond roughly to its value in the ore. Beyond that point in the extraction, the uranium concentration in the solution continued to increase while the lead content remained practically constant. It is perhaps permissible to conclude that in such cases a good deal of the lead which remained in the gangue had been converted to the carbonate. If recovery of this lead were desirable, it could be brought into solution by dilute acid. In general the same would apply to the elements of the calcium group, including radium.

The extraction of pitchblende by ammonium carbonate yields a pale yellow liquid from which the uranium could, if desired, be precipitated as uranate by strong alkali, converted into nitrate, and finally purified by ether. (2)

But the procedure proposed, which is apparently much more advantageous, is the following: The carbonate ore extract, drawn off from the gangue, would be filtered and run into an evaporator, where it would be distilled in a closed system, condensing the distillate with its ammonia and carbon dioxide for re-use. At dryness the residue would be chiefly the solid ammonium uranyl complex. The temperature would then be raised to about 400°C ., thus converting the complex into oxide (probably a mixture of UO_3 and U_3O_8). The ammonia and carbon dioxide given off would be pumped into the first distillate and dissolved, thus recovering, except for leakage losses, all of the ammonia and carbon dioxide originally taken. The distillate would be pumped back upon a new charge of ore in the digester, and ammonia and carbon dioxide introduced in amounts sufficient to make up for the leakage losses; oxygen would be added at the partial pressure needed for the reaction (or a solid oxidizing agent if necessary), and the cycle of operation repeated.

The oxide so obtained would be treated with nitric acid in such amount and concentration as would give the proper concentration and pH for the ether purification, and the silica which had been rendered insoluble by heating filtered off. The remaining impurities are not such as would be likely to interfere in the ether extraction.

It has been suggested in objections to the proposed procedure that the solid uranyl complex carbonate would form troublesome hard crusts on the heat exchange surfaces of the evaporator. The properties of the substance itself answer this objection. It is entirely non-hygroscopic, and when deposited by evaporation shows exceptionally little tendency to adhere to smooth surfaces, whether of glass or metal, either falling off spontaneously, or being easily wiped off. The flakes are soft and brittle, rather than

hard and tough. This is true so long as the material is essentially carbonate, and does not contain any considerable proportion of nitrate or sulfate which might be introduced in reworking recovered material containing these ions. Such contamination could easily be avoided.

Since most of the ammonia and carbon dioxide is recovered for repeated use, the cost of materials for the extraction of uranium from the mineral and the conversion to nitrate, would be of the same order of magnitude as for the direct extraction of the mineral with nitric acid.⁽²⁾ However, the nitrate solution obtained by the carbonate process would have the advantage of less contamination by unwanted constituents. No attempt was made to work out a procedure for the recovery of the other values in the ore, but there is no apparent reason why this should be more difficult with the carbonate than with the direct nitric acid extraction of the ore.

For treatment of high grade pitchblende, the ammonium carbonate extraction would probably be more expensive than the nitric acid process, but it seems worthy of further study for low grade pitchblende, where the cost of the nitric acid treatment is increased by the relatively larger proportions of acid used in dissolving undesired constituents of the mineral.

III. EXPERIMENTAL

All ore samples used were taken from a single 100 lb. specimen of the ore, received in pulverized condition, and said to have been previously treated by the cyanide process for removal of the noble metals. In the air-dried condition, in which it was always weighed out for experiments, this material contained uranium equivalent to 67.3% U_3O_8 and lead equivalent to 6.1% PbO . All calculations were based on these figures. It also contained about 10% SiO_2 ; about 2% each of CaO and MgO ; about 1% each of Na_2O , SO_3 , NiO , Fe_2O_3 and Al_2O_3 ; and various other constituents in smaller amounts.

Experiments at Room Temperature

The results which proved the superiority of ammonium carbonate over the normal and acid carbonates of sodium and potassium are given in Table 1. In each case 1.00 g. of ore (through 100 mesh) was placed in a half-liter rubber-stoppered conical flask, and treated with 200 ml. of the solution to be tested. The flask was then closed, thoroughly shaken by hand, and allowed to stand at room temperature. A number of experiments with different solutions were started in this way at the same time; Experiments A-J were carried out simultaneously in the first group, and Experiments K-N in the second. Once in every twenty-four hours the stopper of each flask was lifted for a few moments to admit new air, then replaced, and the flask briskly shaken by hand for two minutes. Except for the air so admitted, no oxidizing agent was employed in the experiments recorded in Table 1, all of which were conducted in the manner just described.

After a number of days, a sample for analysis was taken from each flask with a pipette. Each sample was treated with an excess of strong

nitric acid, evaporated to dryness, and the silica removed by filtration. The residue was then analyzed for uranium, and occasionally for lead if the amount of the latter warranted it. When the experiment was to be continued, the liquid removed in sampling was replaced by an equal volume of the liquid which had been placed in that flask at the start, and the same procedure followed as before. Samples taken for analysis were 50 ml. in all cases except in Experiments A to J of Table 1, where the samples at the end of seven days were 20 ml. in volume.

Two methods for determining uranium were employed: (a) Removal of interfering elements and precipitation as ammonium uranate, followed by drying at 115°C . and weighing as $(\text{NH}_4)_2\text{U}_2\text{O}_7$; (b) Isolation of uranyl nitrate by ether extraction in a continuous extractor, conversion to U_3O_8 and weighing as such. Method (b) was used in all the analyses of Table 3, and in Experiments K-N in Table 1. The data for lead were subject to rather large errors, since they were based in many cases on weighings of very small precipitates of lead chromate. Silica was weighed as SiO_2 .

The percentage composition of the carbonate solutions is given in grams of solute per 100 grams of water. In a few cases, the carbonate solution contained an added nitrate. Columns headed "% Extracted" give the value calculated from the weight actually found in the liquid, plus the weights, if any, which had been removed in taking samples for previous analyses.

Table 2. shows the effect of adding hydrogen peroxide as an oxidizing agent. In Experiment 2, one ml. of 28% H_2O_2 was added at the start, and again after four and six days. None was added thereafter.

One experiment, not recorded in the tables, deserves mention. For the first six days it was an exact duplicate of Experiment 2 of Table 2. On the seventh day, the undissolved ore was very carefully collected on a small hardened filter paper, washed into another flask, and extracted for another week under exactly the same conditions as before. It was then filtered off again and extracted in the same way for a third week. After this triple extraction with 10% ammonium carbonate solution the gangue weighed 0.1888 g. and yielded on analysis 0.0195 g. of U_3O_8 , or only 2.9% of the amount present in the ore taken. With liberal allowance for the small amounts of gangue lost in the double transfer, this means an extraction of about 97% of the uranium in the ore. Practically the same percentage extraction was found for lead, a result several times larger than that found in any other experiment. This was probably due to the fact that the volume of liquid in this case was three times the normal.

Experiments at High Temperature

Since no special apparatus suitable for a study of the reaction at high temperatures was available, the experiments had to be carried out under rather unsatisfactory conditions as regards both temperature and stirring.

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TABLE 1EXPERIMENTS AT ROOM TEMPERATURE USING ONLY AIR AS OXIDIZER

(1,000 g. of ore / 200 ml. of carbonate solution)

<u>Exp. No.</u>	<u>Carbonate Solution</u>	<u>g. U₃O₈ in Solution</u>		<u>% U₃O₈ Extracted</u>	
		<u>After 7 days</u>	<u>After 22 days</u>	<u>After 7 days</u>	<u>After 22 days</u>
A	1% Na ₂ CO ₃	0.036	0.0349	5.4	5.7
B	10% "	.078	.1345	11.4	21.1
C	1% (NH ₄) ₂ CO ₃	.120	.1290	17.8	21.0
D	10% "	.246	.4475	36.6	70.3
E	10% NaHCO ₃	.102	.2180	15.2	34.0
F	5% NaHCO ₃ , 5% NaNO ₃	.141	.2196	20.8	34.7
G	5% " , 5% NH ₄ NO ₃	.173	.2438	25.8	38.8
H	5% Na ₂ CO ₃ , 5% NaNO ₃	.038	.0945	5.7	14.6
J	1% " , 10% "	.025	.0342	3.7	5.5
		<u>After 21 days</u>		<u>After 21 days</u>	
K	2.5% K ₂ CO ₃		0.0584		8.5
L	10% "		.2216		32.9
M	2.5% KHCO ₃		.1828		27.2
N	10% "		.3264		48.6
		<u>After 38 days</u>		<u>After 38 days</u>	
D	(Cont.) 10% (NH ₄) ₂ CO ₃		0.5715		85.0

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TABLE 2

ACTION OF 10% AMMONIUM CARBONATE SOLUTION AT ROOM TEMPERATURE WITH AND WITHOUT HYDROGEN PEROXIDE

(1.000 g. of ore / 200 ml. of carbonate solution)

Exp. No.	g. U_3O_8 in soln.	g. PbO in soln.	g. SiO_2 in soln.	% U_3O_8 Extracted	% PbO Extracted	g. of Gangue	Max. Conc. U_3O_8 g./l.
<u>After 4 days</u>							
1 (no H_2O_2)	0.1790	0.0063	-	26.7	10	-	-
2 (with H_2O_2)	.3150	.0138	-	46.8	22.6	-	-
<u>After 21 days</u>							
1(cont.)	0.4020	0.0135	0.013	65.3	25	0.423	2.01
2 "	.4450	.0112	.013	77.8	24	.263	1.98

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The ore and solution were sealed in heavy glass tubes, leaving a gas space equal to about one-fourth the volume of the solution. Each tube, enclosed in a casing of iron pipe, was attached in a horizontal position to a motor driven oscillating frame, submerged in a water thermostat, which produced a backward and forward flow of the solution in the sealed tube, at a rate of about twelve cycles per minute. The stirring effect was hardly adequate, and some caking of the ore on the inner surface of the tube occurred in most cases. Moreover, in the absence of any definite knowledge of the pressures to be expected, the temperatures used were probably unnecessarily low, for no tube was burst. Data for the higher temperature experiments are given in Table 3.

As shown in the table, uranium peroxide, lead dioxide, and red lead were tried as oxidizers. The latter would seem to be a suitable solid for use on a commercial scale, if oxygen under pressure failed to give a sufficiently high reaction rate.

In Experiments 48 and 49, ammonium bicarbonate was treated for the first time. On account of the difference in the temperatures employed, no satisfactory comparison of its effectiveness with that of the normal carbonate is possible, but it appears to be fully as good.

The quantity designated in the table as "Ratio to Theory" is the ratio of the number of moles of carbonate or bicarbonate present to the minimum number which would theoretically suffice to convert all the uranium in the ore taken, after its oxidation to the hexavalent state, into the soluble complex $2(\text{NH}_4)_2\text{CO}_3 \cdot \text{UO}_2\text{CO}_3$. Based on this composition, the minimum per gram atom of uranium would be 3 moles of carbonate or 4 moles of bicarbonate. Thus the value of 3.3 for the Ratio to Theory in Experiment 48 means that 3.3×4 or 13.2 moles of bicarbonate were present per gram atom of uranium.

IV. SUMMARY

1. It has been found that the uranium in pitchblende can be extracted by carbonate solutions, preferably ammonium carbonate, in the presence of a suitable oxidizing agent. Oxygen, hydrogen peroxide, and red lead have been used effectively as oxidizers.

2. The use of a pressure digester operating at 90° C, or above has been suggested.

3. Procedures for recovering the ammonium carbonate and for obtaining uranyl nitrate have been proposed.

4. The ammonium carbonate process has been recommended for study as to its possibilities for treatment of low grade uranium oxide minerals.

TABLE 3

EXPERIMENTS IN SEALED TUBES

Exp. No.	Ore Sample, g.	Carb. Sol. %	Ratio to Theory	Oxidizer	Temp., °C.	Time, hrs.
Ammonium Carbonate Solutions. Volume of Liquid 35 ml.						
36	2.000	22	6	PbO ₂ , 1 g.	50-60	23
37	"	"	6	UO ₄ 2H ₂ O, 0.75 g.	52-60	18
38	1.000	"	12	H ₂ O ₂ , 28%, 0.6 ml.	"	"
41	2.000	"	6	Pb ₃ O ₄ , 2.0 g.	60-65	27
42	1.000	7.2	3.8	H ₂ O ₂ , 28%, 0.6 ml.	"	"
46	"	5.3	2.7	Pb ₃ O ₄ , 1.5 g.	60-65	25
47	"	"	"	H ₂ O ₂ , 28%, 0.5 ml.	"	"

Ammonium Bicarbonate Solutions. Volume of Liquid 80 ml.

48	1.000	3.1	3.3	H ₂ O ₂ , 28%, 0.5 ml.	30-35	30
49	"	"	"	Pb ₃ O ₄ , 1.5 g.	"	"

Total U ₃ O ₈ in liq., g.	U ₃ O ₈ conc. g./l.	% U ₃ O ₈ Extracted	Total PbO in liq., g.	Total SiO ₂ in liq., g.	Wt. of gangue, g.
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Ammonium Carbonate Solutions. Volume of Liquid 35 ml.

36(cont.)	0.915	26.1	68.0	-	-	-
37	"	(0.59) ^(a)	(17.0) ^(a)	(43.0) ^(a)	-	0.0135
38	"	.460	13.2	68.3	-	.0123
41	"	1.115	31.8	82.8	< 0.002	-
42	"	.518	14.8	77.0	< 0.002	.008
46	"	.417	11.9	62.0	.0004	.0085
47	"	.476	13.6	70.7	.0007	.0076

Ammonium Bicarbonate Solutions. Volume of Liquid 80 ml.

48	"	0.3885	4.9	57.8	< 0.001	0.0062
49	"	.2977	3.7	44.3	.0005	.0067

(.73)^(b)

(a) Rough estimate, corrected for uranium in oxidizer. (b) Rough estimate,

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(1) Mellor, J. W. "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. XII, pp. 113-114, Longmans, Green and Co., London (1932).

(2) Reference to a contribution in this series from the Sterling Chemistry Laboratory, Yale University entitled "Continuous Countercurrent Ether Extration of Uranyl Nitrate from Solutions Prepared by Nitric Acid Attack of Pitchblende."