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Topical Report - January, 1947

Contract No. W-38-094-eng-27

**DISTRIBUTION OF URANIUM IN PHOSPHATE
ROCK AND SHALE**

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INTRODUCTION

The purpose of this report is to summarize some of the information obtained to date on the distribution of the uranium in the mineral phases of the phosphate rocks and shale. Virtually no new information is given over that contained in the respective monthly reports beginning September 30, 1946, and what will be included in that for January 31, 1947. An additional purpose is to correlate the ore-dressing and chemical-dissolution studies on uranium distribution in the "ores" being studied.

As this report is a summary of information available elsewhere, details of procedure, etc., are not included. The interested reader is referred to monthly reports for such details.

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SUMMARY

Data are summarized on the distribution of uranium in various phases of one shale and two phosphate rocks. The "ores" were examined by physical means, such as float-and-sink with heavy liquids, and by chemical dissolution studies. The findings of the two methods agree.

The shale and the phosphate rock must be considered separately because the findings were different. A float-and-sink separation of Tennessee shale resulted in 93.4% of the weight under 2.65 sp. gr., with the remainder about equally distributed between 2.65 to 2.95 and over 2.95. The uranium analysis of the under 2.65 product was virtually the same as the head sample. In the minor weight fractions, the uranium content was about half that of the heads in the over 2.95 fraction and about twice the heads in the intermediate fraction.

A magnetic roast followed by a magnetic separation did not disclose concentration of uranium in either the magnetic or the non-magnetic portions.

A froth flotation concentrated the organic matter in the overflow, but uranium was not concentrated in either product.

From the chemical side it was possible to dissolve as high as 67% percent of the uranium from the shale with non-oxidising acids with dissolution of less than 10% percent of the weight of the shale. Oxidising acids were no more efficacious than non-oxidising ones in extracting the

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uranium, but there was slightly more attack on the shale. per se. However, the maximum weight percentage of the shale dissolved even with oxidizing agents was only 13.5.

To effect additional uranium extraction it is necessary to decompose the silicates. (✓)

With Idaho phosphate rock (1090-8) a float-and-sink separation resulted in a weight distribution as follows:

<u>Sp. Gr.</u>	<u>Wt. %</u>
Over 2.71	79.1
2.65 to 2.71	7.0
Under 2.65	9.9

The uranium analysis showed that the over 2.71 sp. gr. portion, which was substantially phosphate contained about the same percentage as the heads sample. The quartz fractions were low in uranium.

With Florida phosphate rock (1090-11), the same findings were true. The high-gravity fraction contained about the same percentage of uranium as the heads whereas the low-gravity portions were substantially lower. The content, however, was higher in both gravity ranges than in the case of Idaho rock.

Pebbles were separated by color into 5 classes; white, brown, black, yellow and red. The first three were largely phosphate and the last two were low in phosphate and high in carbonates. The uranium content of the first three was substantially the same as the overall heads analysis. The last two were low in uranium.

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In the chemical-dissolution studies, with non-oxidizing acids, such as sulphuric acid, the percentage of the uranium dissolved was roughly proportional to the percentage of the total rock dissolved. No trouble was experienced in extracting 85 to 90% per cent or even more of the uranium.

With Idaho phosphate rock the finding was the same, i.e., the percentage of the uranium dissolved was proportional to the percentage of the rock dissolved. Extractions of 98% per cent of the uranium were obtained with non-oxidizing acids.

These studies bear out the conclusion that in the phosphate rock the uranium is directly associated with the phosphate minerals. Other chemical studies not reported in detail here further bear out that when a deficiency of acid is employed the percentage of uranium extracted is still proportional to the percentage of the rock dissolved.

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DESCRIPTION OF THE SAMPLES

Partial chemical analyses including uranium contents determined by chemical and B-count analyses are given in Table 26 for one of the shales and two phosphate rocks described in this report. No. 1090-4 was not analyzed except for uranium but is probably similar to No. 1090-1. For identification of samples, source, etc., see Table 1, page 2, report of September 30, 1946.

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TABLE 26. COMPOSITION AND URANIUM CONTENT OF SAMPLES

Sample No.		Kind and Origin (1)	Composition, %								U. %	
B.M.I.	U.S.C.S.		CaO	Fe ₂ O ₃	Al ₂ O ₃ (2)	P ₂ O ₅	SiO ₂	P	CO ₂	LOI (3)	Chem.	E-Count
1090-1	BR-154-46W	TS	1.46	10.7	11.6	—	46.0	—	0.2	23.4	0.011	0.0080
1090-4	S100-46W	TS	—	—	—	—	—	—	—	—	0.008	0.0065
1090-8	M-2	IPR	38.3	1.63	2.62	29.7	12.0	2.77	1.57	8.7	0.013	0.012 ₈
1090-11	FP39X	FPR	44.5	1.27	1.49	31.3	7.14	3.46	4.42	7.4	0.020	0.021 ₈

(1) TS = Tennessee shale
 IPR = Idaho phosphate
 FPR = Florida washed phosphate)

(For further details see Table 1, page 2, Sept. 20, 1946 report)

(2) Includes TiO₂, ZrO₂, etc.
 (3) Loss on ignition at 1000° C.

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PHYSICAL SEPARATIONS

Separations of the phases were made by physical means, such as float-and-sink, and the uranium contents were obtained by wet chemical analyses or by the Geiger counter method. The results of various separations with analyses of the products are summarized in Table 27.

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TEHWASSER SHALE

Sample 1090-4 was ground to pass 200 mesh and was separated on heavy liquids to give three products (Numbers 1, 2, and 3 in Table 27). These products, compared with the head sample, had a lower uranium content in the heavy fraction and an increased uranium content in the intermediate fraction while the light fraction was about equivalent to the heads. However, over 90 per cent of the weight was concentrated in ^{the} light-gravity fraction.

A high-iron phase was prepared from Sample 1090-4. An oxidizing roast was employed to eliminate organic matter. This was followed by a reducing roast to make the iron minerals magnetic. The roasted sample was ground to minus 325 mesh and was separated into magnetic and nonmagnetic fractions. The results on Products 4 and 5, Table 27, show that no uranium concentration was obtained with the magnetic separation.

Other work on Sample 1090-4 was designed to obtain a concentration of the organic phase using a froth flotation operation similar to that used for coal concentration. The organic matter was concentrated in the froth. Evaluation of the degree of concentration was by analysis for loss on ignition (L.O.I.). Products 6 and 7, in Table 27, indicate that no concentration of uranium was obtained in the organic phase.

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IDAHO PHOSPHATE ROCK

On Sample 1090-5 a concentration of the quartz phase was desired.

In order to obtain a good heavy-liquid separation between the phosphate and the quartz it was necessary first to give the sample an oxidizing roast to eliminate organic matter. The separation was then made at two gravities. The products were Numbers 8, 9, and 10 in Table 27. The samples enriched in quartz constituting about 17 per cent of the weight were substantially lower in uranium than the samples of high phosphate content. The high-phosphate portion, over 2.71 specific gravity, contained 80 per cent of the weight at a uranium assay of 0.014 per cent, about the same as the original ore.

WASHED FLORIDA PEBBLE PHOSPHATE

On Sample 1090-11 a heavy-liquid separation of a closely sized granular fraction gave a reasonably good quartz concentration, as shown by Products 11 and 12. The quartz-enriched phase was much lower in uranium content than the head sample, but the phosphate phase was about the same.

Color of Pebbles

A separation on Sample 1090-11 was made on the basis of the color of the pebbles. The products are listed in Table 27 as Numbers 13 to 17, inclusive. The white, brown and black phases, all of which are high in phosphate content, have a uranium content about the same as the head sample

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TABLE 27. PHYSICAL EXAMINATION OF LOW-GRADE URANIUM ORES

Description	Wt., %	Composition, %				Remarks
		U	SiO ₂	Fe	L.O.I.	
<u>No. 1090-4</u>		0.008			25	
(1) Over 2.95 sp.gr.	3.1	0.004(W)				
(2) 2.65-2.95 sp.gr.	3.5	0.013(W)				
(3) Under 2.65 sp.gr.	93.4	0.007(C)				
(4) Roasted-magnetic	6.4	0.009(C)		37.0		
(5) Roasted nonmagnetic	93.6	0.010(C)		6.6		
(6) Flotation froth	6.0	0.006(C)			40	
(7) Flotation under-flow	10.6	0.007(C)			12	
<u>No. 1090-8</u>		0.013	12.0			
(8) Over 2.71 sp.gr.	79.1	0.014(C)				Phosphate, low in quartz.
(9) 2.65-2.71 sp.gr.	7.0	0.003(C)	81.6			Mostly quartz.
(10) Under 2.65 sp.gr.	9.9	0.004(C)	77.9			" "
<u>No. 1090-11</u>		0.021	7.1			
(11) Over 2.71 sp.gr.	96.8	0.020	2.5			Phosphate, low in quartz.
(12) Under 2.71 sp.gr.	3.2	0.008	62.9			Quartz predominates.
(13) White	70	0.021(C)				Phosphate.
(14) Brown	< 5	0.022(C)				"
(15) Black	20	0.021(C)				"
(16) Yellow	5	0.005(C)				Carbonates, some calcite, little phosphate.
(17) Red	< 1	0.005(C)				Carbonates, some iron oxides, little phosphate.

L.O.I. - Loss on ignition.

(W) Designates wet analysis.

(C) Designates analysis by Geiger Counter.

If no designating mark is given the analysis shown is a check by both wet and counter methods.

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while the yellow and red phases, which are low in phosphate and high in carbonate content, are low in uranium.

CHEMICAL TREATMENTS

The chemical treatments consisted of leaching them with various reagents and, in the case of the phosphate rock, making superphosphate and leaching this with water. Except where otherwise noted all analysis were chemical. Because chemical analysis were only for the major constituents the amounts given under Reagent, % of Theoretical is only approximate. It is based on the best estimate of total basis in the sample.

TENNESSEE SHALE

The results of leaching two similar Tennessee shales with various solutions are shown in Table 28.

A feature of the tests is the relatively large amount of uranium that was dissolved with relatively small dissolution of the shale itself. The greatest amount of shale dissolved, without a strong oxidizing agent such as nitric acid, was 9.6 per cent with 1:4 sulphuric acid on-1090-k. About 30 per cent of the uranium was dissolved. With 1:1 hydrochloric acid the rock dissolved was 6.25 and 8.6 per cent for Samples 1090-1 and 1090-4, respectively, and the corresponding uranium extractions were 57 and 67 per cent respectively.

Nitric acid dissolved more shale, probably because of oxidation of organic matter, but dissolved no more uranium. Mild oxidizing mixtures or alkali carbonates were least effective.

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TABLE 28. DISSOLUTION OF TENNESSEE SHALE AND CONTAINED URANIUM; TEMP. 150°F., TIME, 3 HOURS

Expt. No.	Name and Concen- tration	Reagent		% of Theor- etical (1)	Dissolved		Ratio U/Ore
		Amt./ 100 g. Ore, cc.			Ore, %	U, %	
<u>No. 1090-1 ground to minus 20 mesh</u>							
30	10% FeCl ₃ ·6H ₂ O	300	-	4.25	23	5.3	
65	2% H ₂ SO ₄ -1% Fe ₂ (SO ₄) ₃	200	27	3.6	26	7.2	
64	2% HCl-1% FeCl ₃	200	36	4.3	27	6.4	
63	1:1 HNO ₃	200	103	12.3	37	3.0	
34	36.5% H ₂ SO ₄ -20% H ₃ PO ₄	176	186	-	39	-	
37	35% H ₂ SO ₄	208	114	3.0	41	13.7	
32	1:1 HCl	300	117	6.25	57	9.1	
31	1:1 HNO ₃	300	156	13.5	60	4.4	
<u>No. 1090-4 ground to minus 100 mesh</u>							
62	2N Na ₂ CO ₃	200	-	1.6	20	12.5	
61	1:4 H ₂ SO ₄	200	144	9.6	30	3.1	
60	1:1 HCl	200	78	8.6	67	7.8	

(1) Based on total bases present.
Approximate.

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The remaining 30 to 40 per cent of the uranium did not seem amenable to extraction without more drastic attack on silicates.

The fineness of grinding within the narrow range studied seemed to have little effect.

IDAHO PHOSPHATE ROCK

The results on Idaho phosphate rock ground to minus 100 mesh are shown in Table 29.

The two most striking feature of these data are that (1) the amount of uranium dissolved was roughly proportional to the amount of rock dissolved and (2) nearly all, 85 to 90 per cent, of the total uranium was soluble in nonoxidizing acid solutions. These results indicate two things: (1) the uranium is uniformly disseminated through that part of the rock mass dissolved by the reagents and (2) the uranium probably is almost entirely in the hexavalent condition.

The extent of total dissolution of the ore was uncertain in some instances where sulphuric acid was used, because of formation of gypsum. The amount of residual phosphate was used as a tentative index.

WASHED FLORIDA PEBBLE PHOSPHATE

The data obtained with Florida rock are given in Table 30.

The remarks made about Idaho phosphate apply to this rock. The percentage extraction of uranium was in proportion to the percentage of the rock dissolved and the uranium was almost wholly, 98 per cent, soluble in a non-oxidizing acid.

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TABLE 29. DISSOLUTION OF IDAHO PHOSPHATE ROCK 1090-S AND
CONTAINED URANIUM

Expt. No.	Name and Concen- tration	Reagent		Conditions		Dissolved		
		Ant./ 100 g. Ore, cc.	% of Theor- etical (1)	Temp., °F.	Time, Hours	Ore, %	U, %	Ratio U/Ore
44	0.75 N HNO ₃	2300	93	Room	2	79	86	1.1
45	0.95 N HCl	1935	95	"	"	79	86	1.1
58	1.2 N HCl	100	6.5	"	1	8	21	2.7
38	35% H ₂ SO ₄	208	100	150	3	99(2)	95(3)	-
57	5 vol. % H ₂ SO ₄	100	10	150	3	-	20	-
87	24% H ₂ SO ₄	243(4)	73	Room	24	(5)	65(6)	-
10	36.5% H ₂ SO ₄ -20% H ₃ PO ₄	176	152	150	2	99(2)	62	-
35	36.5% H ₂ SO ₄ -20% H ₃ PO ₄	176	152	150	3	97(2)	59	-
88	22% H ₂ SO ₄ -16% H ₃ PO ₄	245	151	Room	24	(5)	71(6)	-
12	N citric acid	200	11	150	2	3.7	12.3	3.3
Superphosphate from 100 g. ore extracted with 500 cc. water								
67	224 g. 78% H ₃ PO ₄	-	143	Room	24	65	87(6)	-
70	168 g. "	-	107	"	24	74	75(6)	-
71	112 g. "	-	71	"	24	72	39(6)	-
73	80 g. 63% H ₂ SO ₄	-	82	"	24	(5)	34(6)	-
76	40 g. "	-	41	"	24	(5)	24(6)	-

- (1) Based on total bases. Approximate.
(2) Based on residual phosphate after leaching.
(3) Being rechecked.
(4) Calcined ore - 91.2 grams.
(5) Not yet available.
(6) Analysis by B-count.

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TABLE 30. DISSOLUTION OF FLORIDA PHOSPHATE ROCK 1090-11 AND
CONTAINED URANIUM; TEMP., 150°F., TIME,
3 HOURS

Expt. No.	Name and Concen- tration	Reagent		% of Theor- etical (1)	Dissolved		Ratio U/Ore
		Amt./ 100 g. Ore, cc.			Ore, %	U, %	
33	10% $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	300	-	-	-	9	-
36	36.5% H_2SO_4 -20% H_3PO_4	176	147	76 ⁽²⁾	76	38	-
39	35% H_2SO_4	208	96.5	73 ⁽²⁾	73	44	-
28	1:1 HCl	300	92.5	90	90	98	1.1
29	1:1 HNO_3	300	121	95	95	99	1.05

(1) Based on total bases present. Approximate.

(2) Based on analysis for residual phosphate.

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