EXTRACTION OF URANIUM FROM AQUEOUS SOLUTIONS BY COALS OF DIFFERENT RANK AND PETROGRAPHIC COMPOSITION

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ABSTRACT

A series of laboratory tests was run to test
the uranium extraction capabilities of coals of
different rank and petrographic composition. Coals
of five different ranks, ranging from lignite to
low volatile bituminous, were used and each rank
was represented by a vitrinite-rich and fusinite-
rich fraction. A sample of coke made from low vola-
tile coal also was tested. The samples were crush-
ed and the -70 to +140 mesh fractions were immersed
in solutions of known uranium content for a period
of 32 days. Periodic checks were made to measure
degree of uranium removal and pH. The coke, lig-
nite and subbituminous samples were the most effec-
tive in removing uranium from solution. The fusin-
ite-rich samples were better in this regard than
were the vitrinite-rich samples, especially from
the higher rank coals. However, this influence of
rank and petrographic composition on uranium removal
is closely tied to the acidity of the immersing
solutions; mixtures with lower pH values removed
less uranium from solution than did those which
were more alkaline.

RÉSUMÉ

On a effectué une série d'essais en labora-
toire afin de déterminer les capacités d'extraire
l'uranium à l'aide de charbons de rangs et de com-
positions pétrographiques différentes. On a util-
isé des charbons de cinq rangs différents, s'échel-
onnant du lignite au charbon bitumineux demi-gras;
chaque rang a été représenté par une fraction riche
en vitrinite et une fraction riche en fusinite.
On a également fait l'essai d'un échantillon de
coke obtenu à partir de charbon bitumineux demi-
gras. Les échantillons qui ont été broyés et
criblés de -70 à +140 ont été plongés dans des
solutions dont la teneur en uranium était connue,
pendant une période de 32 jours. Des essais pér-
iodiques ont été effectués afin de mesurer le degré
d'extraction d'uranium et le pH. Les échantillons
de coke, de lignite et de charbon subbitumineux
ont été les plus efficaces pour extraire l'uranium
de la solution. A cet égard les échantillons
riches en fusinite ont été supérieurs aux échantil-
lons riches en vitrinite, surtout ceux qui proven-
aient des charbons de rang plus élevé. Cependant,
cette influence du rang et de la composition pétro-
graphique sur l'extraction de l'uranium est intime-
ment reliée à l'acidité de la solution d'immersion;
les mélanges dont les valeurs du pH etaient plus
basses ont extrait moins d'uranium de la solution
que ceux qui étaient plus alcalins.

EXTRACTION OF URANIUM FROM AQUEOUS SOLUTIONS BY COALS OF DIFFERENT RANK AND PETROGRAPHIC COMPOSITION

INTRODUCTION

The well-known association of uranium with carbonaceous matter has produced economically attractive deposits of uranium in coal seams of the western United States, especially the lignites of the Williston Basin (Denson *et al.*, 1959; Denson and Gill, 1965). To determine the radioactivity in western Canadian coals, the Geological Survey of Canada carried out a number of field measurements (Cameron and Birmingham, 1970) and, as part of this project, it was decided to conduct some laboratory tests relating the petrographic composition of coals to uranium content. Studies on the petrographic composition of uraniferous lignites from the western United States have been described by Schopf and Gray (1954). In other laboratory investigations of uraniferous American coals, Breger *et al.* (1955) reported on the mineralogy and geochemistry of a lignite and a subbituminous coal. Breger and Deul (1956) discussed important aspects of the organic geochemistry of uranium. More recently, Schmidt-Collerus (1969) has investigated further the relationship between uranium and organic matter.

Studies of petrographic composition and uranium content of coal involve the study of geochemical interaction of uranium-bearing solutions with organic material. Laboratory studies indicate that much of the uranium in organic matter is not inherent, but has been extracted from solution by the organic matter (Moore, 1954; Szalay, 1958; Rozhkova *et al.*, 1958). Moore in 1954 investigated the extraction of uranium from aqueous solutions by a variety of substances including a wide spectrum of coaly materials ranging from peat to anthracite and graphite. His experiments were quite simple and consisted of immersing finely ground portions of his sample materials in solutions of known uranium content. At the end of nineteen days, the uranium content of the solutions was measured, and the decrease from the amount originally held was assumed to have been extracted by the test materials. One result of his study was to show that the degree of metamorphism of the coaly material, that is its rank, had a great influence on extracting ability. The low rank lignites and subbituminous coals were much

more effective in retaining uranium than were the higher rank bituminous and anthracite coals.

Because of the simplicity of the experiment and because Moore had not taken petrographic variation into account, it was decided to repeat the experiment with two important changes:

1. Two petrographically different components were hand-picked from the same rank of coal and treated separately in the extracting experiments; and

2. The extracting process was monitored periodically up to the termination point of 32 days.

Twelve samples were selected for testing. These included two fractions, one vitrinite-rich and one fusinite-rich, hand-picked from each of five different ranks of coal. In addition, a sample rich in exinite (coalified spores) was tested along with a sample of coke.

EXPERIMENTAL PROCEDURE

Samples from five different ranks of coal were selected for testing. These ranks are: lignite, subbituminous, high volatile "C" bituminous, high volatile "A" bituminous, and low volatile bituminous. From these samples, vitrinite-rich and fusinite-rich fractions were hand-picked. The exinite-rich fraction was picked from the high volatile "A" coal. The list of samples and their sources are given in Table 1.

Each sample was ground by hand with mortar and pestle to pass 70 mesh (210μ). The minus 140 mesh (88μ) material was sieved out in order to

SAMPLE	TYPE OF MATERIAL	SOURCE OF SAMPLE	RANK
1	Vitrinite-rich	Utility Mine, Estevan, Saskatchewan	Lignite
2	Fusinite-rich	Utility Mine, Estevan, Saskatchewan	Lignite
3	Vitrinite-rich	Alfred Fox Mine, Carbon, Alberta	Subbituminous
4	Fusinite-rich	Alfred Fox Mine, Carbon, Alberta	Subbituminous
5	Vitrinite-rich	7-foot seam, Inverness No. 3 Mine, Inverness, N.S.	Bituminous high vol. "C"
6	Fusinite-rich	7-foot seam, Inverness No. 3 Mine, Inverness, N.S.	Bituminous high vol. "C"
7	Vitrinite-rich	Harbour seam, No. 26 Colliery, Glace Bay, N.S.	Bituminous high vol. "A"
8	Fusinite-rich	Harbour seam, No. 26 Colliery, Glace Bay, N.S.	Bituminous high vol. "A"
9	Vitrinite-rich	No. 10 (Balmer) seam, Balmer South Mine, Natal, B.C.	Bituminous low vol.
10	Fusinite-rich	No. 10 (Balmer) seam, Balmer South Mine, Natal, B.C.	Bituminous low vol.
11	Exinite-rich	Band I, Harbour seam, Princess Colliery, Sydney Mines, N.S.	Bituminous high vol. "A"
12	Coke	Coke made from Balmer coal, Natal, B.C.	

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TABLE 1. Samples used for uranium extraction study

eliminate possible centrifuging problems with the extreme fines and, also, to maintain a fairly narrow particle size range within the sample to be tested. The samples were not dried deliberately although undoubtedly a certain amount of moisture was lost during the process of hand-picking and grinding.

The -70 to +140 mesh material from each sample then was divided as follows:

a) 2 to 3 g for microscopic analysis;

b) 15 g for immersion in the uranium-bearing solutions; and

c) the remainder for proximate and ultimate analysis.

Figure 1 is a flowsheet summarizing the disposition and treatment of the samples.

A solution of known uranium content was prepared by dissolving 1.7 g of uranyl sulphate ($UO_2SO_4 \cdot 3H_2O$) in one litre of $0.01N$ H_2SO_4 solution. This was then diluted by the addition of 4 litres of water. The uranium content of this stock solution was determined fluorimetrically and found to be 155 ppm with a pH of 2.65.

Fifteen-gram portions of each sample along with 188 ml of the stock solution were placed in flasks which were then stoppered. At periods of 1, 2, 4, 8, 16 and 32 days, small portions of the mixtures were withdrawn and centrifuged for ten to fifteen minutes. An aliquot (1 ml) of the clear liquid was then taken for uranium analysis, and the remainder of the liquid and solids in the centrifuge tube was returned to the appropriate flask. The standard glass electrode method was used to determine the pH value of each solution at the same time that the samples for uranium analysis were taken. The flasks were shaken vigorously each day during the experiment.

At the end of 32 days, the 15 g samples were removed from solution and split. One half of each sample was air-dried and sent directly for ashing; these sample splits constitute Series G (*see* Fig. 1). The other half of each sample (Series H) was washed in 200 ml of distilled water for three days. At the end of three days, these samples were withdrawn, air-dried and ashed. The solutions of Series H were checked for pH and aliquots withdrawn for fluorimetric analysis. In addition, sample 12 was run a second time, with the conditions exactly the same as in the first run, except that the pH of the solution was maintained at a fairly low value (between 2 and 3) by periodically adding small amounts of acid.

Uranium determinations were carried out on the liquids and on the various ash samples. Thus, for each sample, seven liquids were analyzed for uranium content. These included the aliquots of solution periodically withdrawn along with a sample of the distilled water from Series H in which each coal had been washed at the end of the experiment. In addition, for each sample, there were three subsamples of ash on which uranium determinations were made: (a) the ash of the sample before immersion; (b) the ash of the sample after immersion, but not washed with distilled water; and (c) the ash of the sample after immersion and after washing.

The uranium determinations were made by the fluorimetric method described by Smith and Lynch (1969). According to these authors, the sensitivity of the method for liquids is 0.2 ppb and for solids it is 0.5 ppm.

Sulphate determinations were carried out on the solutions after the experiment was finished, as well as on a sample of the stock solution. The method used was the standard technique of precipitation with barium nitrate. Sulphate contents were expressed in ppm.

COAL SAMPLES

(Hand-picked and crushed to pass the 70 mesh
screen; -70 to +140 mesh fraction used in study)

Pellets for
microscopic
analysis

Fifteen grams immersed in
188 ml of uranyl sulphate
solution

Proximate and
ultimate analysis;
ash analysed for
uranium content

Series A
(Immersion day +1)
pH of solution measured and 1 ml
withdrawn for determination of
uranium content

Series B
(Immersion day +2)
Repeat steps of Series A

Series C
(Immersion day +4)
Repeat steps of Series A

Series D
(Immersion day +8)
Repeat steps of Series A

Series E
(Immersion day +16)
Repeat steps of Series A

Series F
(Immersion day +32)
Repeat steps of Series A

Series G
Half of sample (7.5 g)
dried and ashed; ash
analysed for uranium
content

Series H
Half of sample (7.5 g)
washed in distilled water
for three days; steps of
Series A repeated, then
samples dried and ashed;
ash analysed for uranium
content

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FIGURE 1. Flowsheet indicating experimental steps
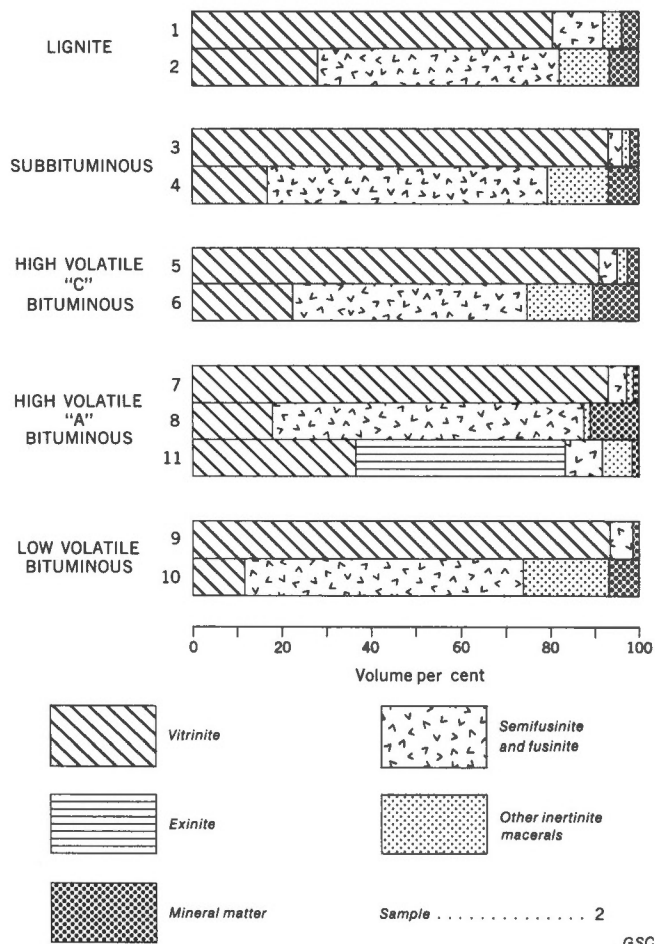
FIGURE 2. Petrographic composition by macerals
of samples treated in extraction study

For the petrographic analysis, maceral determinations were carried out on polished grain mounts prepared from each of the samples tested except the coke. These microscopic analyses were carried out with reflected light and oil immersion at a magnification of x600. Determinations were made by point count; 500 points were counted per sample.

QUANTITATIVE RESULTS

The petrographic compositions of the samples studied are shown in Table 2 and Figure 2. All the vitrinite-rich samples contain more than 91 per cent vitrinite with the exception of the lignite. The fusinite-rich samples contain 64 per cent or more of inertinite macerals with the major part of this amount being fusinite and semifusinite. It was hoped that these samples would be higher in these constituents, but it appears that a relatively large proportion of the fusinite and semifusinite was lost in the minus 140 fraction. The exinite-rich sample is made up largely of exinite (47%) and vitrinite (37%).

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Sample	1	2	3	4	5	6	7	8	9	10	11
Vitrinite	81.4	28.7	92.8	17.2	91.2	22.5	93.2	18.3	94.0	12.2	37.2
Semifusinite and fusinite	9.2	54.0	3.3	61.5	3.8	51.6	4.9	69.0	5.0	62.1	7.8
Other inert macerals	4.7	10.0	1.1	14.2	1.5	15.5	1.3	1.3	-	19.3	6.1
Exinite	-	-	-	-	-	-	-	-	-	-	47.2
Mineral matter [1]	4.7	7.3	2.8	7.1	3.5	10.4	0.6	11.4	1.0	6.4	1.7

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[1] Mineral matter calculated from chemical analysis using Parr's
formula and reduced to volume per cent

TABLE 2. Petrographic composition by macerals of samples used in extraction study

SAMPLE		PROXIMATE ANALYSIS				ULTIMATE ANALYSIS						
		% Moisture	% Ash	% Volatile Matter	% Fixed Carbon (by difference)	% Carbon	% Hydrogen	% Sulphur	% Nitrogen	% Ash	% Oxygen (by difference)	Thermal value BTU/lb. Gross
1	As Rec'd	14.8	7.2	35.0	43.0	55.4	3.7	0.4	0.9	7.2	17.6	9330
	Dry		8.4	41.1	50.5	65.1	4.3	0.5	1.0	8.4	20.7	10950
2	As Rec'd	9.5	11.8	34.2	44.5	57.5	3.4	0.7	0.9	11.8	16.2	9320
	Dry		13.0	37.8	49.2	63.5	3.8	0.8	1.0	13.0	17.9	10310
3	As Rec'd	7.8	4.6	34.6	53.0	63.0	3.7	0.3	1.1	4.6	19.5	10400
	Dry		4.9	37.6	57.5	68.3	4.0	0.3	1.2	4.9	21.2	11282
4	As Rec'd	5.9	12.3	28.2	53.6	62.5	3.1	0.2	0.8	12.3	15.2	10230
	Dry		13.1	30.0	56.9	66.4	3.3	0.2	0.9	13.1	16.1	10860
5	As Rec'd	4.0	4.3	36.2	55.5	66.8	4.2	3.7	1.0	4.3	16.0	11360
	Dry		4.5	37.7	57.8	69.6	4.4	3.8	1.0	4.5	16.7	11830
6	As Rec'd	3.1	14.2	31.3	51.4	58.1	3.0	8.9	0.7	14.1	12.1	9260
	Dry		14.6	32.3	53.1	60.0	3.1	9.1	0.7	14.6	12.5	9550
7	As Rec'd	0.9	0.8	32.6	65.7	83.0	5.3	0.7	1.4	0.8	7.9	14730
	Dry		0.8	32.9	66.3	83.7	5.3	0.7	1.5	0.8	8.0	14870
8	As Rec'd	1.1	18.0	23.4	57.5	67.3	3.2	5.9	0.5	17.9	4.1	11190
	Dry		18.1	23.7	58.2	68.1	3.2	6.0	0.5	18.1	4.1	11320
9	As Rec'd	0.5	1.7	19.8	78.0	87.9	4.8	0.2	1.4	1.8	3.4	15350
	Dry		1.8	19.9	78.3	88.3	4.8	0.2	1.4	1.8	3.5	15430
10	As Rec'd	0.5	11.7	13.9	73.9	73.8	3.4	0.2	0.5	11.7	9.9	13490
	Dry		11.8	14.0	74.2	74.1	3.5	0.2	0.5	11.8	9.9	13550
11	As Rec'd	0.8	2.7	43.7	52.8	82.9	5.7	0.8	1.4	2.7	5.7	14880
	Dry		2.8	44.0	53.2	83.5	5.7	0.8	1.5	2.8	5.7	14990
12	As Rec'd	0.1	10.7	1.6	87.6	87.2	0.4	0.2	1.0	10.7	0.4	12750
	Dry		10.7	1.6	87.7	87.3	0.4	0.2	1.0	10.7	0.4	12770

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TABLE 3. Chemical analyses of samples used in extraction study

SAMPLE		1	2	3	4	5	6	7	8	9	10	11	12	12A
RANK		Lignite		Subbituminous		High Volatile C		High Volatile A		Low Volatile		High Volatile A	Coke	Coke Rerun
Series A [1] 1 day [1]	pH [2]	7.05	7.10	4.62	5.84	2.05	2.22	2.95	5.48	2.75	5.15	3.02	10.32	9.82
	ppm [3,4]	2	2	99	30	160	120	170	56	120	64	140	<1	2
Series B 2 days	pH	7.05	7.12	4.78	5.98	2.10	2.25	2.84	5.58	2.88	5.46	3.66	10.24	5.42
	ppm	1	1	70	10	140	130	165	32	160	60	130	<1	65
Series C 4 days	pH	7.05	7.20	4.75	6.05	2.12	2.25	3.00	5.80	2.90	5.76	4.20	10.05	3.45
	ppm	1	1	54	8	140	150	165	43	140	47	120	<1	170
Series D 8 days	pH	7.05	7.21	4.74	6.40	2.15	2.25	3.13	6.62	2.82	6.25	4.38	9.90	2.70
	ppm	<1	1	40	2	100	160	160	68	160	13	140	1	170
Series E 16 days	pH	7.18	7.22	4.68	6.38	2.15	2.25	3.20	6.64	2.84	6.56	4.34	9.64	2.65
	ppm	13	1	46	1	120	130	150	68	160	11	140	1	170
Series F 32 days	pH	6.75	7.24	5.32	6.44	2.14	2.22	3.25	6.80	2.80	6.80	4.45	9.00	2.56
	ppm	<1	<1	33	1	125	130	170	80	140	29	120	9	170
Series H	pH	7.90	7.80	6.92	7.00	3.15	3.10	6.30	6.90	6.30	7.71	7.55	8.82	6.50
	ppm	<1	<1	<1	<1	1	1	<1	2	<1	4	1	18	<1
Sulphate Concentrate (in immersing solutions at end of 32 days) ppm [5]		200	240	200	200	2140	7960	290	1380	210	190	270	240	1400

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[1] See Figure 1 for explanation of series
[2] pH of solutions at beginning was 2.74
[3] Uranium content in parts per million (ppm)
[4] Uranium content of solutions at beginning was 155 ppm
[5] Sulphate ion concentration in solutions at beginning was 275 ppm

TABLE 4. Uranium content and acidity of immersing solutions as monitored during experiments

Data from the proximate and ultimate analyses of the samples before testing are presented in Table 3.   These data were obtained according to standard ASTM methods of coal analysis.   Several points should be noted about these chemical data.   The moisture contents of the two lignite samples (samples 1 and 2) seem anomalously low in comparison to freshly mined coal from the Estevan area which, according to Swartzman and Tibbetts (1956), should contain about 35 per cent moisture.   Even though the samples used in the present study were relatively fresh, the time-consuming process of hand-picking and the fine grinding which followed probably resulted in the loss of a considerable proportion of the bed moisture.   Samples 3 and 4, representing the subbituminous rank, also appear to have less moisture than is typical for coals of this rank.   The ash content of the fusinite-rich samples is larger in every case than the ash content of the corresponding vitrinite-rich samples of the same rank.   This is not surprising because fusinite is a porous material and commonly occurs impregnated with a variety of minerals.   A common mineral in fusinite is pyrite and the very large sulphur content of samples 6 and 8 are a reflection of this association.   Also, in parts of a coal seam it is common to find fusinite associated with more attrital organic debris, the whole intimately mixed with a somewhat larger than normal mineral matter content.

The extraction results are shown in Table 4. The data are presented in terms of changing uranium contents with time in the immersing solutions.   The same data for each sample are shown in Figure 3 as curves of time versus uranium concentration in the solutions.

Table 4 also shows the pH values determined on the solutions when the samples were withdrawn. The last column in Table 4 gives the sulphate ion
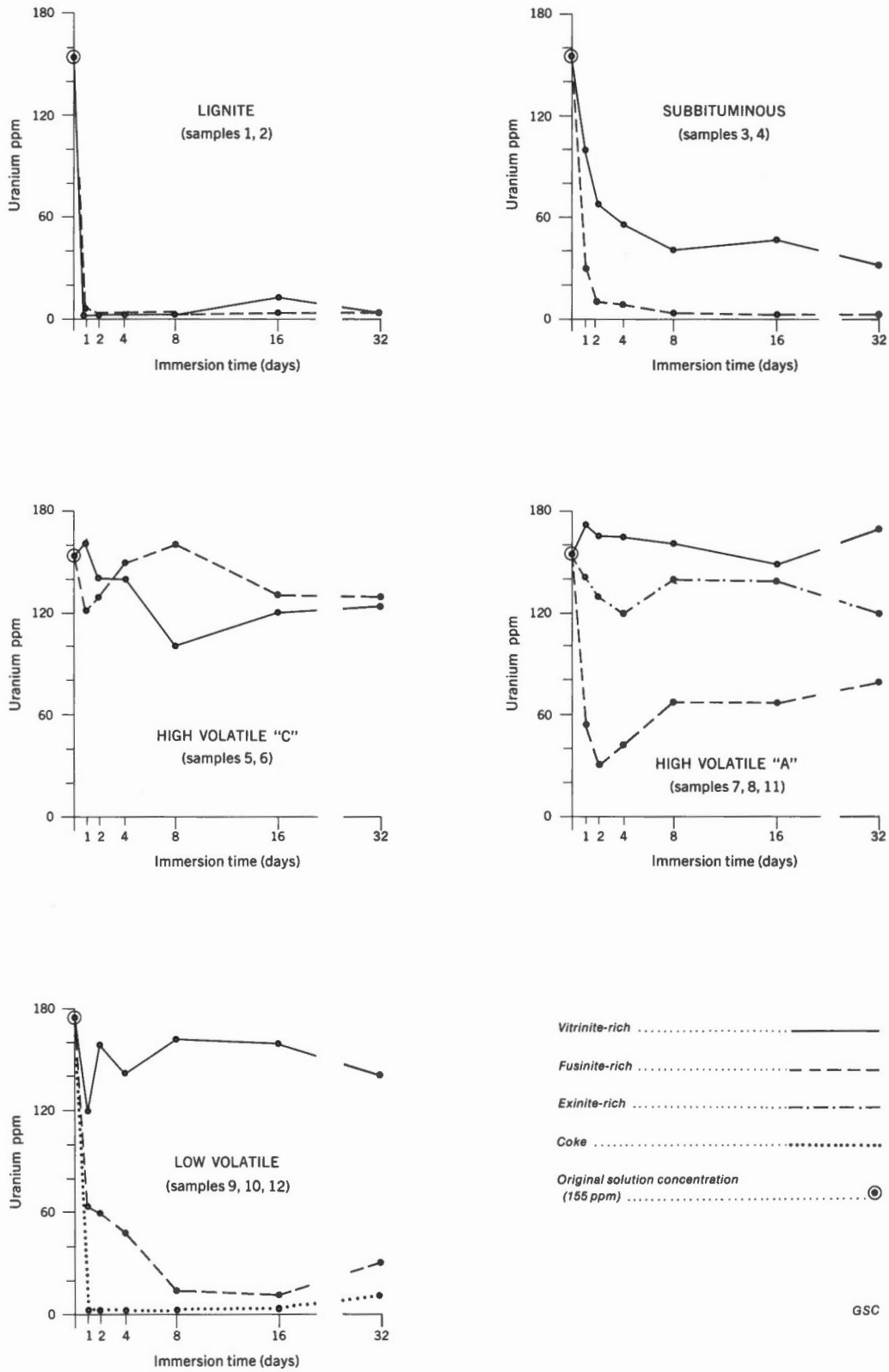
FIGURE 3. Uranium extraction profiles for various samples tested.
Uranium ppm left in solution

SAMPLE	Samples Before Experiment			Samples After Experiment					
				Unwashed in distilled water (Series G)			Washed in distilled water (Series H)		
	Ash[1] content as received	Uranium ppm		Ash content as received	Uranium ppm		Ash content as received	Uranium ppm	
		Ash	Total coal		Ash	Total coal		Ash	Total coal
1	7.2	24	2	7.9	26000	2031	7.5	30000	2259
2	11.8	18	2	11.4	20000	2288	10.1	24000	2424
3	4.6	18	1	4.6	32000	1456	4.3	34000	1445
4	12.3	6	1	12.7	15200	1932	12.4	16000	1981
5	4.3	4	<1	2.7	10400	278	2.4	8000	192
6	14.2	2	<1	8.5	1400	119	7.6	1000	76
7	0.8	21	<1	0.6	2800	17	0.6	1080	6
8	17.9	1	<1	14.6	5760	842	12.1	8200	992
9	1.8	67	1	1.7	8200	139	1.5	850	12
10	11.7	3	<1	10.7	16000	1712	10.7	12000	1282
11	2.8	10	<1	2.5	1900	47	2.3	1388	33
12	10.7	4	<1	10.4	14000	1456	9.4	9000	850
12A				9.8	360	26	9.7	390	38

[1] Ash contents in weight per cent

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TABLE 5. Ash and uranium contents of coal samples
before and after immersion experiments

concentration in the solutions at the end of the experiment. The values obtained may be compared with the value of about 275 ppm present in the original stock solution. This is made up of the sulphate from the uranium salt plus that contributed by the H_2SO_4 solution.

Nearly all of the samples tested show a common trend of a rapid increase in pH on the first day and, thereafter, gradual increases in pH until the end of the experiment. This did not hold for samples 5 and 6. With these two samples, the solutions maintained their original acidity and, in fact, became slightly more acidic; that is, the pH dropped from the original value of 2.74 to 2.20 and 2.10. In sample 9, the pH was virtually unchanged to the end of the experiment. The fusinite-rich samples (Nos. 4, 8 and 10) of the subbituminous, high volatile A and low volatile coals tended to change the original acidity of the solutions to a greater degree than did their vitrinite-rich counterparts. Extraction proceeded with great rapidity in some of the samples. In the two lignite samples (samples 1 and 2) and in the coke sample (sample 12), the uranium content of the solution dropped from 155 ppm to 2 ppm or less after one day of immersion; that is, virtually all of the uranium was removed from solution in a period of 24 hours or less.

Several of the samples show maximum extraction after an immersion of 2 to 8 days, and then an apparent gradual return of uranium to solution after immersion for longer periods of time. This is especially prominent in the extraction pattern of sample 8. With this sample, maximum extraction was achieved on the second day of immersion as indicated by the value of 32 ppm measured on the solution. After this, the concentration in the solution slowly increased to 80 ppm by the 32nd day. Because there is no real change in pH, this increase probably reflects a lack of equilibrium.

Table 5 gives the ash and uranium contents of the samples before and after immersion in the uranium-rich solution. The "after immersion" contents are divided into two groups labelled "unwashed" (Series G) and "washed" (Series H). Figure 4 shows graphically the amounts of uranium in ppm that were extracted by the samples of Series G.

Table 5 shows that all of the samples before testing contained only trace quantities of uranium. Table 5 and Figure 4 also show the differences in the amounts of uranium removed between the low rank and high rank coals as well as between the vitrinite-rich and fusinite-rich samples of the same rank.

The ash columns in Table 5 indicate that immersion in solution has altered the mineral matter content of the samples, in some cases to a considerable extent. Thus samples 5, 6 and 8 have had their ash contents reduced by 1.6, 5.6 and 3.2 per cent, respectively. Such reduction indicates that some of the mineral constituents, such as sulphates, have been dissolved in the extraction process. This is substantiated by the high sulphate concentrations reported for these samples in Table 4.
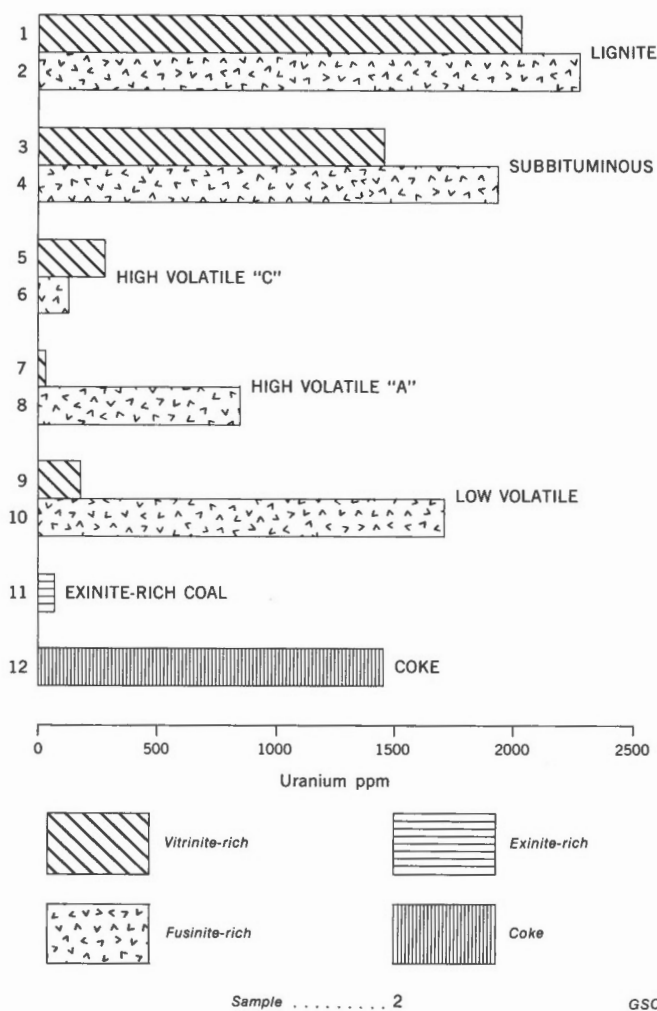
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FIGURE 4. Uranium contents of samples at end of extraction experiments

the basis of this framework for the disposition of uranium and utilizing data in Tables 4 and 5, material balances were worked out for each sample and are presented in Table 6. Some of the disparities between the uranium originally present and that accounted for at the end likely are due to the fact that the calculations involving the ash were on the as-received basis. Moisture contents were not determined on the sample splits of Series G and H submitted at the end of the experiment.

The data in Tables 4 and 5 would seem to indicate the greater effectiveness of the low rank coal as extracting agents when compared to the higher rank bituminous coals. In this respect, the results are in keeping with those obtained by Moore (1954) and Szalay (1958). Our data also seem to suggest that the fusinite-rich samples are the best extractors. However, these relationships may be deceiving.

Of the factors governing the removal of uranium from solution in the present study, pH is probably the most important. In Figure 5, the uranium present in the coal after the immersion experiments is plotted against the final pH of the solutions. The figure shows two groupings of points. One group represents those samples that removed relatively small amounts of uranium from solution. These include samples 5, 6, 7, 9, 11 and 12A, and are associated with solution pH values below 5. All showed a uranium content of less than 300 ppm after immersion. The second group includes samples 1, 2, 3, 4, 8, 10 and 12. These showed uranium contents of 1500 ppm or more with one exception, sample 8, which had a uranium content of 842 ppm. This second group is associated with pH values above 5. The influence of pH is shown clearly by the pair of samples 12 and 12A. These are splits of the same original sample and the experimental conditions differ only in that, for 12A, the solution was maintained at a low pH throughout the immersion phase by the periodic addition of acid.

In order to test the influence of pH on the removal of uranium from solution, a series of experiments was run using only splits of a stock

The analyses of the distilled water solutions used in washing splits of each of the samples after immersion showed that very little uranium had returned to solution during the washing. The uranium is probably fixed in the coal by the neutralizing effect of the distilled water.

At the beginning of the experiment, the uranium in the system for each sample consisted of that in solution plus whatever amount of uranium was in the coal originally. The latter was negligible for all samples (see Table 5). The former amounted to 29.14 mg calculated from 188 ml of solution with a uranium content of 155 ppm. At the end of the experiment, the uranium was distributed as follows: (a) in the coal of Series G; (b) in the coal of Series H; (c) in the residue of the original solution; and (d) in the distilled water used for washing the samples of Series H. In addition, it was estimated that about 10 ml of the original solution were lost or removed in the periodic withdrawal of the small sub-samples of solution; these losses and removals would account also for a small amount of the original uranium. On
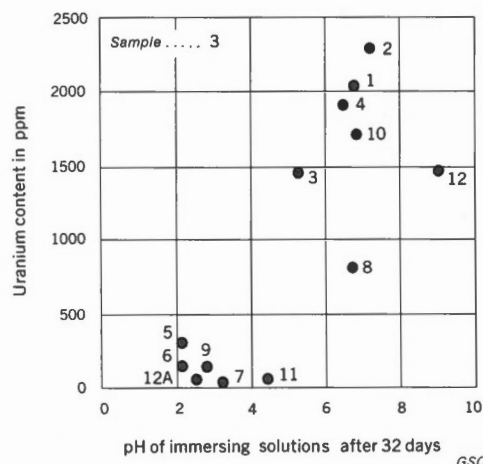

FIGURE 5. Plot of uranium content of samples after 32 days immersion versus pH values of immersing solutions

SAMPLE	Uranium in original solution	Uranium in coal before immersion	Total uranium before experiment	Uranium in coal of series H	Uranium in coal of series G	Uranium in residue of original solution after experiments	Uranium in distilled water wash	Uranium lost in removing periodic subsamples	Total uranium accounted for at end of experiment
1	29.14	0.03	29.17	15.28	16.94	0.05	0.02	0.03	32.32
2	29.14	0.03	29.17	17.16	18.18	0.05	0.02	0.01	35.42
3	29.14	0.01	29.15	10.92	10.84	5.87	0.04	0.68	28.35
4	29.14	0.01	29.15	14.49	14.86	0.09	0.02	0.10	29.56
5	29.14	0.002	29.14	2.08	1.44	22.25	0.12	1.57	27.46
6	29.14	0.0004	29.14	0.89	0.57	23.14	0.10	1.64	26.34
7	29.14	0.002	29.14	0.13	0.05	30.26	0.02	1.96	32.42
8	29.14	0.001	29.14	6.32	7.44	14.24	0.36	0.69	29.05
9	29.14	0.02	29.16	1.04	0.09	24.92	0.02	1.48	27.55
10	29.14	0.004	29.14	12.84	9.61	5.16	0.86	0.39	28.86
11	29.14	0.004	29.14	0.35	0.24	21.36	0.12	1.34	23.41
12	29.14	0.006	29.15	10.92	6.37	1.64	3.60	0.0038	22.53
12A	29.14	0.006	29.15	0.27	0.29	30.26	0.02	1.15	31.99

GSC

TABLE 6. Material balances for uranium extraction experiments (all data in mg)

SAMPLE	A		B		C		D		E		F	
	pH	conduc[1]	pH	conduc	pH	conduc	pH	conduc	pH	conduc	pH	conduc
1 (+1 day)	2.74	890	3.00	680	4.05	380	5.03[2]	410	6.16[2]	440	7.05[2]	450
2 (+2 days)	2.74	920	2.98	670	3.87	380	4.80	410	6.07	440	6.24[3]	440
3 (+6 days)	2.75	940	3.00	680	4.06	380	5.05	400	5.45[4]	430	6.24[4]	450
4 (+14 days)	2.78	940	3.03	670	4.07	380	4.94	410	5.22	430	6.15[4]	450
Amount of 0.1 N NaOH required to adjust pH	0 ml		2.8 ml		6.1 ml		8.2 ml		9.3 ml		10.2 ml	

GSC

[1] Conductivity measured in $\mu mho/cm^2$
[2] Bright yellow crystals on bottom of flask
[3] Opaque due to pale yellow suspension
[4] Clear liquid with a bottom layer of pale yellow precipitate

TABLE 7. Experimental data on solutions run to check effect of pH on uranium precipitation

solution prepared by dissolving 1.7 g of uranyl sulphate in one litre of 0.01N H_2SO_4 and then diluting by the addition of 4 litres of distilled water. No coal was added in this test and the only variable introduced was a change in pH. Six 500 ml portions of this stock solution were placed in flasks and the pH changed by the addition of calculated amounts of NaOH. The pH was then checked after 1, 2, 6 and 14 days and 5 ml aliquots of centrifuged supernatant liquid withdrawn for fluorimetric analyses. The conductivity of the solutions also was measured at the same time. The pH and conductivity data for each of the six solutions are given in Table 7 along with amounts of NaOH solution required to bring about changes in pH. The uranium-bearing solutions are identified as A, B, C, etc. The fluorimetric data on uranium content of the solutions are given in Table 8 and are shown graphically in Figure 6.

The effect of pH on the precipitation of uranium is shown clearly by these data and the

SAMPLE	A [1]	B	C	D	E	F
1	140	132	120	132	36	11
2	165	147	148	147	18	2
3	153	152	147	144	22	4
4	127	106	137	116	30	1

[1] Uranium content in ppm   GSC

TABLE 8. Uranium content of solutions
run to check effect of pH

critical pH appears to be between 5.03 and 5.22.
All solutions with pH values of 5.22 or higher re-
tained a maximum of only 38 ppm uranium in solution
while those with 5.03 or less retained at least 106
ppm in solution (sample B4) to a maximum of 165 ppm
(sample A2). This compared favourably with the data
shown in Figure 5 where those samples with pH values
above 5 are associated with large-scale removal of
uranium from solution while those with pH values
below 5 removed relatively small amounts of uranium.

Examination of the data in Figure 5 relative
to determining the influence of petrographic compo-
sition suggests that this influence is secondary,
at least within the limits of this experiment. In
Figure 5, the group of points with pH values above
5 represents samples associated with the removal of
relatively large amounts of uranium from solution.
Four of the five fusinite-rich samples are repre-
sented in this group. The association of fusinite-
rich samples with higher pH values may be related
to the leaching of mineral matter such as alkalis
from the generally more mineral-rich fusinite. The
mechanism of uranium removal in this instance may
be the precipitation of hydrated oxides as suggested
by Breger (pers. com.). Thus, the petrographic com-
position seems to have some relationship to the pH
and the pH appears to control uranium removal.
There may be also a relationship with the porous
character of the fusinite enabling the mineral mat-
ter to be leached out more easily and perhaps also
providing sites for the retention of precipitated
uranium compounds.

As regards rank, there is an apparent decrease
in effectiveness of uranium removal with increase in
rank. However, this parallels a general change in
the acidity of the immersing solutions and it was
suggested earlier that pH value was probably the
more important control. That this is not clear cut
is indicated by the following example. If one com-
pares the two fusinite-rich samples 4 and 8, it can
be seen that the solutions at the end had about the
same pH. The lower rank sample 4 was more effect-
ive in removing uranium. On the other hand, sample
10, whose solution also showed about the same pH at
the end, removed more uranium than did sample 8 even
though 10 had the higher rank. The experiments
would have to be re-run maintaining a constant or
near constant pH value in order to resolve more
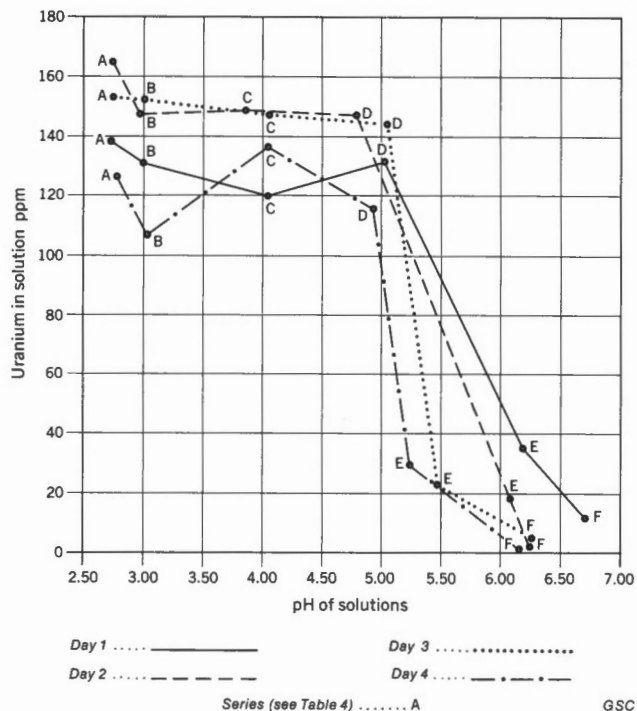exactly the controls exerted by rank and petrographic
variation.

FIGURE 6. Effect of pH change on precipitation
of uranium from solution

CONCLUSIONS

The results of the experiment showed differ-
ences between fusinite-rich and vitrinite-rich
samples in relation to the removal of uranium from
solution. These differences, however, appear to
be due mainly to differences in the acidity of the
immersing solutions. Most of the uranium was re-
moved from solution with those samples where the
pH was above 5. This group included 4 of the 5
fusinite-rich samples. With samples where the pH
was below 5, most of the uranium remained in solu-
tion. Thus the fusinite-rich samples, possibly
because of the leaching out of alkaline mineral
matter from the organic material, tended to raise
the pH of the solutions in which they were immersed,
and thus brought about the removal of larger amounts
of uranium. It is suggested that the mechanism of
removal is by the precipitation of hydrated oxides
of uranium and is, therefore, not true extraction
in which the uranium becomes attached to the or-
ganic matter.

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