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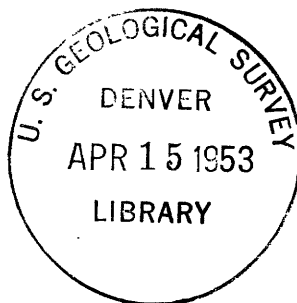
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**NOTES ON THE DIFFERENTIAL LEACHING
OF URANIUM, RADIUM, AND LEAD FROM
PITCHBLEND IN H_2SO_4 SOLUTIONS**

**By
George Phair
Harry Levine**

**This preliminary report is released without editorial and
technical review for conformity with official standards
and nomenclature, to make the information available to
interested organizations and to stimulate the search for
uranium deposits.**

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NOTES ON THE DIFFERENTIAL LEACHING OF URANIUM,
RADIUM, AND LEAD FROM PITCHBLENDE
IN H_2SO_4 SOLUTIONS *

by

George Phair and Harry Levine

ABSTRACT

Two 5-pound samples from the "hot spot" of the pyritic dump of the Wood mine, a past producer of pitchblende near Central City, Colo., showed Ra/U ratios that were abnormally high but nearly constant at about 150 times the equilibrium value for both samples in spite of a sevenfold difference in uranium contents. Analyses of oxidized but still black Katanga pitchblende before and after leaching in very dilute, dilute, and concentrated sulfuric acid solutions showed that: (1) UO_3 is preferentially leached with respect to UO_2 , Ra, and Pb in all three solutions, (2) the resulting residual concentration of both radium and lead effected in the process is proportional to the total amount of uranium leached except in concentrated H_2SO_4 , and (3) after leaching in concentrated H_2SO_4 the resulting residual concentration of radium relative to lead is much lower, as might be expected from data published by Lind, Underwood, and Whittemore in 1918 for the solubility of RaSO_4 . Under similar leaching conditions unaltered pitchblende from Great Bear Lake lost only 1/10 to 1/15 as much uranium as the UO_3 -rich Katanga ore. Both laboratory and field results point to the same conclusion: in an oxidizing, highly acid environment uranium is rapidly leached and both radium and lead tend to be fixed approximately proportionally in the process. These results help

* This report concerns work done on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

to explain (1) why UO_3 -rich uranium minerals tend to give maximal Pb/U ages and (2) why the search for high-grade uranium ore in and around abandoned sulfide mines known to have produced pitchblende in the past has been consistently disappointing.

INTRODUCTION

The complex solutions involved in the leaching of pitchblende in pyritic mines and dumps are characterized by relatively high contents of free H_2SO_4 in these solutions. For example, water from the Idaho Tunnel, 5 miles from Central City, Colo., has been found to contain 0.13 g per liter of hydrogen ion and 18,260 ppm of $\text{SO}_4^{=}$ ion (Clarke, 1924). It is, therefore, a 0.13-normal solution of H_2SO_4 . Bastin and Hill (1917) in describing the pyrite-rich Iron mine, in Russell Gulch near Central City, state, "The waters of this mine are so corrosive that the overalls of miners working in wet places are sometimes eaten to shreds in a day or two, and iron rails, pipes and nails must be frequently replaced." Pitchblende was recently discovered in a newly opened stope in this mine, but none has been found on the leached walls of the older workings.

The results of the redistribution of uranium and radium brought about by such solutions have been recognized by field geologists for some time, but little attention has been given the processes involved. This paper presents quantitative field and laboratory data on the results of sulfuric acid leaching of certain pitchblende ores. The conclusions are believed to have a direct application to the problem of finding uranium in areas of sulfide deposition and to the problem of age determinations by lead-uranium and lead-lead methods.

This study is a part of the U. S. Geological Survey's program of uranium reconnaissance in the Colorado Front Range sponsored by the U. S. Atomic Energy Commission. It is one phase of the writer's continuing study of the geochemical cycle of uranium deposition in the Central City district. Data on the distribution of uranium in the radioactive porphyries and hydrothermal veins of this district have been summarized in Trace Elements Investigations Report 247. Certain aspects of the occurrence of uranium in the pre-Cambrian rocks in the Central City district are now being investigated.

F. S. Grimaldi of the Geological Survey supplied much useful information on chemical matters in the course of this work. J. Bracken and R. Champion also of the Geological Survey made the radium determinations by the radon method, without which these studies would not have been possible.

FIELD SAMPLING

The radium-rich dump material of the Wood mine, located in the pitchblende belt near Central City, Colo., provided an excellent starting point for studies of the fractionation of radium with respect to uranium in nature. This long-abandoned mine still ranks second rank among the Nation's mines in total production of pitchblende. More than 150 tons of oxide ore, mostly high grade, was mined between 1872 and 1937. During the field season of 1949 R. U. King of the U. S. Geological Survey pointed out to one of the authors an extremely radioactive hot spot on the weathered dump. From a distance of 18 inches the "hot spot" gave a maximum reading of 12 mR/hr on the 20 mR/hr scale of a beta-gamma survey meter.

The present owners of the Wood mine attempted, by wet tabling methods, to recover the radioactive constituent, believed to be pitchblende, from

several truckloads of heterogeneous dump material, but their attempts were unsuccessful. The writers then obtained negative results on uranium flux tests of radioactive samples from this mine, and these results were confirmed by uranium analyses of radioactive samples collected by Charles Towle, AEC, and R. U. King. The foregoing tests indicated that the very high radioactivity of the dump material was due either to the presence of daughter products of uranium or to the presence of a member of the thorium series.

To provide material for mineralogic and chemical study, two 5-lb samples of the heterogeneous dump material from the Wood mine were collected -- one, P4a, from the surface at the center of the "hot spot"; the other, P5a, from directly below the first at a depth of 18 ft. Together these samples made up at least 10 percent of the material in the "hot spot".

STUDIES OF DUMP SAMPLES

The recognizable fragments in these two 5-lb samples consisted chiefly of more or less decomposed granite wall rock together with a little quartz-rich vein material leached of its pyrite. Most of both 5-lb samples consisted of weathered "clay" or "gouge" produced by the decomposition of both wall rock and vein material. Semiquantitative spectrographic analyses on splits of the crushed samples showed only the constituents typical of granite with, at most, a very small percentage of metallic elements including iron, copper, and lead.

The "clay" was highly radioactive. No uranium minerals were observed under the binocular microscope, but a small amount of fine-grained pitchblende was extracted from both samples in methylene iodide.

The chief metal minerals present in the heavy mineral fractions, in order of decreasing abundances, were chalcopyrite, pyrite, and sphalerite.

To minimize segregation both bulk samples were split with a Jones splitter, crushed to 60 mesh, mixed, and again split. All analyses -- spectrographic, chemical, and radiometric -- were made on the same splits. The equivalent uranium contents determined by laboratory beta-gamma counts averaged about 85 times the amount of uranium determined chemically. A vertical chamber and an end-window counter were used in these measurements; the results are, if anything, low due to the loss of radon by emanation. The same samples were analysed for thorium by the nephelometric method (Grimaldi and Fairchild, 1946), for uranium by the fluorimetric method (Grimaldi and Levine, 1948), and for radium by the radon method (Curtiss and Davis, 1943).

The results of these analyses (table 1) show that:

1. The high radioactivity of both samples is caused largely by concentrations of radium. To satisfy the radium-uranium equilibrium, a uranium content of 13 percent would be required in sample P4a; whereas it contains only 0.085 percent uranium. Thorium was negligible (0.002 by weight percent in both samples).

2. Both samples have radium-uranium ratios which are abnormally high but nearly constant in spite of a 7-fold difference in uranium content. The radium-uranium ratios average 150 times their equilibrium value.

This high but nearly constant radium-uranium ratio suggests that more than 99 percent of the uranium originally present in the "hot spot" of the dump had been leached leaving the "hot spot's" radium content fixed in situ. Such high concentrations of short-lived radium could have

Table 1.--Results of analyses of the two samples of dump material from the "hot spot"
of the Wood mine dump

Sample	Radium (Weight percent)	Percent uranium in equilibrium with Ra (calculated)	Actual uranium in samples (percent)	Percent of original U leached away	Ra/U	Radium enrichment factor
P4a	4.46×10^{-6}	13.1	0.085	99.3	52.5×10^{-6}	154
P5a	5.53×10^{-7}	1.62	0.011	99.3	50.3×10^{-6}	148

been formed only very recently, probably since the high-grade uranium ore was thrown out on the dump. It seems difficult, if not impossible, to conceive of any process which would introduce radium in a constant ratio to the amount of uranium originally present, or introduce both radium and uranium in fixed proportions that exceed their equilibrium ratio by 150-fold.

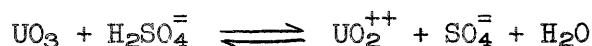
As both samples were closely associated one above the other on the dump, it seems logical to assume that both steeped in the same supergene solutions, and as a result the leaching of uranium from each sample was proportional to the amount originally present. The simultaneous fixing of the radium content is to be expected in view of the extreme insolubility of RaSO_4 in dilute acids containing the common ion SO_4^{2-} . The experimental results to be described confirm the residual concentration of both radium and lead and show that the amount of such concentration is approximately proportional to the amount of uranium leached in dilute H_2SO_4 solutions.

These particular quantitative results of the field sampling apply only to the material in the "hot spot" of the dump. Considerable lateral variation across the dump is to be anticipated in view of the large differences in amount and composition of the leaching solutions formed at widely separated points. The process, however, probably operates throughout the dump area, and the differences are ones of degree of leaching.

LABORATORY LEACHING STUDIES

Available data on which to base a prediction as to the relative solubilities of mechanical mixtures of UO_2 and UO_3 in H_2SO_4 include, for example, the fact that UO_3 forms uranyl salts in acid solution according to the

relation:



and that these uranyl salts are very soluble in aqueous solutions. On the other hand, UO_2 is relatively insoluble in nonoxidizing acids, including HF, and in their aqueous solutions.

The mixtures of UO_2 and UO_3 in the variable mineral pitchblende, however, are not mechanical mixtures but show the predominant face-centered cubic structure of UO_2 , in spite of the presence of a minimum of 15 percent UO_3 which is generally interpreted as the result of auto-oxidation. Supergene oxidation of pitchblende results in greatly increased U^{+6}/U ratios with corresponding decrease in specific gravity and hardness, but the uraninite structure is retained until an advanced stage.

According to Brooker and Nuffield (1951) "~~Specimens~~ [of pitchblende] relatively low in U^{+6} gave sharp X-ray powder photographs. With increasing U^{+6}/U , back reflections became weak and diffuse, then low-angle reflections became diffuse, and finally with $\text{U}^{+6}/\text{U} = 85.0\%$ no pattern was obtained. The corresponding cell edges decreased from 5.45 kx for $\text{U}^{+6}/\text{U} = 17.4\%$ as compared to 5.46 for synthetic UO_2 , to 5.39 for $\text{U}^{+6}/\text{U} = 78.5\%$. Therefore in the 6 specimens the quality of the X-ray pattern and the cell sizes are related to the degree of oxidation."

In view of the predominance of the UO_2 structure it seems logical that the UO_3 in the pitchblende would be less readily available for leaching than the same amount in a comparable mechanical mixture. Accordingly a series of experiments was designed to test the relative leachability of the various components of pitchblende in H_2SO_4 solutions. Like the pitchblende found on the dumps and exposed on the walls of the abandoned mines the material selected had undergone partial supergene oxidation.

Katanga pitchblende ore was handpicked to provide 10 g of high-grade concentrate containing 67.31 percent uranium. This concentrate consisted of nearly pure pitchblende with less than an estimated 2 percent of not easily removable yellow secondary uranium minerals. Analysis showed that the pitchblende contained more UO_3 than UO_2 although it was black. The 10-g sample was ground fine in a mortar and five 2-g splits were taken.

One of the splits was leached in concentrated H_2SO_4 , one in 1.84N H_2SO_4 , and one in 0.17N H_2SO_4 . Over a three-day period a total of 31 ml of acid (at room temperature) was used for each. The solutions were shaken for a few minutes daily, but otherwise no attempt was made to keep them stirred. Each sample was leached for 144 hours. At the end of 24, 48, and 72 hours, 2 ml of each solution were removed for U analysis, an equal quantity of fresh acid being added after each removal to keep the volume constant at 25 ml. All solutions were analyzed for uranium after 144 hours.

The results are more variable than was desired, but they indicate that in the more concentrated solutions almost all the soluble uranium went into solution within 24 hours and that thereafter the uranium content of the solution remained fairly constant. Only in the dilute (0.17N) solutions does the uranium content of the solution show a steady increase with time. The data are as follows:

Uranium contents of H_2SO_4 solutions in g/ml

<u>Time</u>	<u>Conc. H_2SO_4</u>	<u>1.84N H_2SO_4</u>	<u>0.17N H_2SO_4</u>
24 hours	0.013	0.020	0.008
48 hours	0.013	0.022	0.010
72 hours	0.013	0.034 (?)	0.012
144 hours	0.014	0.016	0.014

The leached samples were filtered at the end of 144 hours; that leached in concentrated H_2SO_4 was washed with about 30 ml of distilled water. The wash water was found to contain almost as much uranium (0.013 g/ml) as was in the concentrated acid which fact suggests the formation of a uranium sulfate relatively insoluble in concentrated H_2SO_4 but soluble in H_2O . Because of this loss of uranium in washing, the results of the uranium analyses of the concentrated H_2SO_4 solutions cannot be used to compute the actual amount of uranium leached from the 2-g sample. The results with the other two solutions are satisfactory and permit such calculations to be made.

Amount of uranium leached from 2-g samples
of Katanga pitchblende

1.84N H_2SO_4					0.17N H_2SO_4				
ml		U content (g/ml)		Total	ml		U content (g/ml)		Total
2	x	0.020	=	0.040	2	x	0.008	=	0.016
2	x	0.022	=	0.044	2	x	0.010	=	0.020
2	x	0.034	=	0.068	2	x	0.012	=	0.024
25	x	0.016	=	0.400	25	x	0.014	=	0.350
Total U leached				= 0.552 g/2-g sample	Total U leached				= 0.410 g/2-g sample
				or 0.276 g/g sample					or 0.205 g/g sample
Percent of original U leached:				<u>41.00</u>	Percent of original U leached:				<u>30.46</u>

The leached and unleached splits were analyzed for U, UO_2 , UO_3 , PbO , and Ra with the following results:

	Percent by weight				Ra (Curies/g)
	U	UO_2	UO_3	PbO	
Unleached	67.31	33.19	45.72	7.68	1.96×10^{-7}
Leached					
In conc. H_2SO_4	63.9	46.48	27.60	10.86	1.99×10^{-7}
In 1.84N H_2SO_4	68.16	45.06	28.46	10.19	2.67×10^{-7}
In 0.17N H_2SO_4	68.58	41.64	38.30	9.51	2.37×10^{-7}

Hillebrand's method (1929) was used in the UO_2 analyses. The unleached sample was found to contain only 0.013 percent by weight ThO_2 .

Effect of the H_2SO_4 leach on the UO_2/UO_3 ratio

The selective leaching of UO_3 from the pitchblende in all three concentrations of H_2SO_4 is clearly shown by the following data:

	UO_2/UO_3	$\frac{\text{UO}_2/\text{UO}_3 \text{ (leached)} \times 100}{\text{UO}_2/\text{UO}_3 \text{ (unleached)}}$
Unleached	0.727	--
Leached		
In conc. H_2SO_4	1.68	231
In 1.84N H_2SO_4	1.61	221
In 0.17N H_2SO_4	1.25	171

If all the uranium leached were in the form of UO_3 , the resulting UO_2/UO_3 ratio would be higher. We infer that some UO_2 was also leached in the process but the amount was relatively small compared to the change in UO_3 .

Effect of the H_2SO_4 leach on the Pb/U ratio

Because of the relative insolubility of lead compared to UO_3 in H_2SO_4 solutions, the pitchblende shows an increase in lead content after leaching in all three solutions. The amount of this increase is roughly proportional to the amount of uranium leached indicating that the greater part of the lead contained in the soluble uranium is fixed, probably as the sulfate. The resulting increase in the Pb/U ratio was sufficient to change the uncorrected apparent ages from approximately 760 million years to as much as 1,100 million years.

Except in the concentrated H_2SO_4 the relative increase in the Ra/U ratio after leaching is similar to the relative increase in the Pb/U ratio.

	<u>Relative Pb/U ratio</u>	<u>Relative Ra/U ratio</u>
Unleached pitchblende	1	1
Leached pitchblende		
Conc. H_2SO_4	1.48	1.07
1.84N H_2SO_4	1.30	1.34
0.17N H_2SO_4	1.21	1.18

The large difference between the relative Pb/U ratio and the relative Ra/U ratio after leaching in concentrated H_2SO_4 probably results from the greatly increased solubility of RaSO_4 in concentrated H_2SO_4 . According to Ellsworth (1932) "... though the presence of 50 percent sulfuric acid has no appreciable effect on the solubility (of RaSO_4), at higher acid concentrations the solubility increases rapidly." The relative increase in solubility of PbSO_4 in concentrated H_2SO_4 is much less than the change in solubility of RaSO_4 . Lind, Underwood, and Whittemore (1918) measured by the

emanation method an extremely rapid increase in solubility of RaSO_4 with increase in concentration of H_2SO_4 above 65 percent. This is shown as follows:

Solubility of RaSO_4 at room temp.

0.10N H_2SO_4	2.2×10^{-8} g/25 ml solution
1.0N H_2SO_4	2.2 "
10.0 percent H_2SO_4	2.4 "
60 percent H_2SO_4	6.3 "
65 percent H_2SO_4	6.4 "
70 percent H_2SO_4	> 79.0 " (solution not saturated)

The data are as follows:

	<u>In 1.84N H_2SO_4</u> (g/g sample)	<u>In 0.17N H_2SO_4</u> (g/g sample)
U leached	0.275	0.205
Calculated Pb in U leached	0.029	0.022
Apparent increase in Pb	0.023	0.017

	<u>Pb/U ratio</u>	<u>Uncorrected apparent age (M.Y.)</u>
Unleached	0.106	0.760
Leached		
Conc. H_2SO_4	0.157	1100
1.84N H_2SO_4	0.138	975
0.17N H_2SO_4	0.129	910

The apparent ages were interpolated from Wickman's graphs (1939).

Effect of the H_2SO_4 leach on the Ra/U ratio

The average Ra/U ratio in the unleached oxidized pitchblende was slightly low, 2.91×10^{-7} g Ra/g U as compared to 3.4×10^{-7} g Ra/g U

at equilibrium, the figure generally accepted at present for unaltered uranium minerals (Ellsworth, 1932). A definite increase in the Ra/U ratio took place after leaching in all three H_2SO_4 solutions. The apparent increase in radium content of the two samples leached in dilute solutions is roughly proportional to the amount of uranium leached. The increase in the Ra/U ratio is as follows:

	<u>Ra/U $\times 10^{-7}$</u>
Unleached	2.91
Leached	
Conc. H_2SO_4	3.114
1.84N H_2SO_4	3.917
0.17N H_2SO_4	3.455

APPLICATIONS TO THE PROBLEM OF AGE DETERMINATION

These experiments are believed to have a direct application to the problem of apparent age determinations by lead-uranium and lead-lead methods. The leaching of uranium minerals rich in UO_3 as compared to UO_2 by natural H_2SO_4 solutions may be expected to lead to an enrichment in both total lead and radium relative to uranium. Where considerable importance is to be attached to age determinations on a few samples, and a high degree of accuracy in the final results is desired, not only should the samples be collected with special care, but their geological environment should be fully described. So-called "sooty" pitchblende -- the soft, earthy variety having very low specific gravity -- seems particularly susceptible to solution in H_2SO_4 , and for the present, apparent ages based on such material should be regarded with some skepticism particularly when based on single samples. These conclusions agree

with the generalization of Ellsworth (1932) to the effect that uranium minerals with very high UO_3/UO_2 ratios, including altered uraninites and most secondary uranium minerals, tend to have misleadingly high Pb/U ratios.

The total lead extracted from uranium minerals differs from "normal common lead" in that it contains relatively greater proportions of the uranium daughters, Pb^{206} and Pb^{207} , as compared to the nonradiogenic Pb^{204} . For the present discussion the thorium-lead, Pb^{208} , may be neglected. To obtain corrected lead-uranium and lead-lead ratios, Pb^{204} is generally used as the common lead index and appropriate amounts of Pb^{206} and Pb^{207} are deducted from the total lead in the proportion in which these isotopes are found in so-called "common lead". The excess Pb^{206} and Pb^{207} represent the contribution of the U^{238} and U^{235} originally present in the sample. It follows that, where uranium has been leached, the corrected amounts of Pb^{206} and Pb^{207} will be too high, and, depending upon the extent of the leaching, the apparent ages based upon the $\text{Pb}^{206}/\text{U}^{238}$ and $\text{Pb}^{207}/\text{U}^{235}$ ratios will be increased accordingly. In general, the effect upon the $\text{Pb}^{207}/\text{U}^{235}$ age will be greater than that upon the $\text{Pb}^{206}/\text{U}^{238}$ age, but both will be increased. The relative change in a Tertiary apparent age is of course much greater than that in a pre-Cambrian for the same amount of leaching.

Recent leaching (being a chemical process) has little effect upon the $\text{Pb}^{207}/\text{Pb}^{206}$ ratios. When, however, such leaching has been active over a considerable interval of geologic time, the residual concentration of short-lived radium could lead to increased corrected ratios of Pb^{206} relative to Pb^{207} resulting in impossibly young $\text{Pb}^{207}/\text{Pb}^{206}$ apparent ages. Unfortunately lead-lead ages are so sensitive to experimental error and to the composition of the common lead used in the correction that they are of little value in age determinations on minerals younger than 200 million years (Holmes,

1946). As a result, in dealing with geologically young minerals impossibly young ages are usually attributed to experimental error in the isotopic analyses. Our data are scanty and based upon impure material but adequate to show that unaltered pitchblendes having the normal large excess of UO_2 over UO_3 are much less readily attacked by sulfuric acid solutions, and from this point of view they can be expected to yield more reasonable apparent ages.

We hand-picked the laboratory collection of ore from Great Bear Lake and obtained 20 grams free from alteration products. It contained a high percentage of metallic impurities, chiefly cobalt-nickel arsenides, and as a result had a low total uranium content (42.46 percent). The arsenic probably had a reducing effect during the analysis upon any UO_3 present because nearly all the uranium was found to be in the quadrivalent state. In view of their unreliability the figures for UO_2 are not given. The results of the leaching of a 2-g sample in sulfuric acid solutions are as follows:

Uranium contents of H_2SO_4 solutions in g/ml

<u>Time</u>	<u>Conc. H_2SO_4</u>	<u>1.84N H_2SO_4</u>	<u>0.17N H_2SO_4</u>
24 hours	0.0006	0.0027 (?)	0.0014
48 hours	0.0006	0.0008	0.0004
72 hours	0.0007	0.0013	0.0006
144 hours	0.0006	0.0012	0.0004

Again there is no systematic increase in uranium content of the solutions with respect to time.

Calculations show that the percentage of the original uranium leached from the UO_3 -rich Katanga sample is 10 to 15 times that leached from the Great Bear Lake pitchblende in the same solutions. It is apparent that

figures for the "solubility" of pitchblendes have little meaning unless the UO_2/UO_3 ratio is specified at least approximately.

Amount of uranium leached from 2-g samples
of Great Bear Lake pitchblende

1.84N H_2SO_4					0.17N H_2SO_4				
ml		U content (g/ml)		Total	ml		U content (g/ml)		Total
2	x	0.0027	=	0.0054	2	x	0.0014	=	0.0028
2	x	0.0008	=	0.0016	2	x	0.0004	=	0.0008
2	x	0.0013	=	0.0026	2	x	0.0006	=	0.0012
25	x	0.0012	=	0.0300	25	x	0.0004	=	0.0100
Total U leached				= 0.0396 g/2-g sample	Total U leached				= 0.0148 g/2-g sample
				or 0.0198 g/g sample					or 0.0074 g/g sample
Percent of original U leached				<u>4.66</u>	Percent of original U leached				<u>1.74</u>

APPLICATIONS TO URANIUM SURVEYS IN MINERALIZED AREAS

These results show clearly that unaltered pitchblende is itself relatively insoluble in even the most concentrated solutions of H_2SO_4 at room temperatures. Once, however, it has become partly oxidized by contact with oxygen either in the air or dissolved in the mine waters, the pitchblende is readily susceptible to solution by the H_2SO_4 invariably present in and around sulfide mines. Mine waters containing at least as much H_2SO_4 as the 0.17N solutions used in some of these experiments are inferred to be common in the pyritic mines of the Central City district.

Although the pitchblende remaining on the walls of the mine workings is on the whole less readily permeated by the solutions than were the pulps used in these experiments, ample time has been available for the leaching (20-50 years). The leaching on the scale indicated by the analyses of the dump material and demonstrated in the laboratory helps to explain several present-day peculiarities in the distribution of uranium in the Central City district, including:

1. The scarcity of pitchblende and of secondary uranium minerals on the dumps of the chief pitchblende producers.
2. The nearly complete absence of pitchblende and of secondary uranium minerals from the surface outcrops of mineralized veins known to carry pitchblende at depth.
3. The apparent absence of pitchblende from the oxidized zone. Very little pitchblende has been found within 100 feet of the present surface although the records show that the two largest uranium producers -- the Kirk and Wood mines -- have levels at 50 and 97 feet, respectively, which were worked for gold.
4. The scarcity of pitchblende and uranium minerals in the abandoned dewatered mines that are known to have produced pitchblende in the past. The evaluation of the uranium potential of such mines by radiometric surveys and by shallow channel sampling has been consistently discouraging. Important new discoveries throughout the Front Range have generally been the result of relatively recent stoping.

In a highly acid, oxidizing environment it is apparent that a small amount of pitchblende remaining on the surface of the leached mine walls may be indicative of considerably larger amounts at greater depth in the walls. Only by deep channel sampling or by drilling could the uranium

reserves of such a mine be properly assessed. Local high concentrations of radium relative to uranium commonly found in such workings have generally been neglected under the assumption that the radium has been transported in the mine waters and redeposited. The possibility for large-scale movement of radium in these sulfuric-acid-rich waters seems remote. The alternative interpretation that such radium concentrations are residual and as such may indicate the presence of unleached uranium ore at greater depth within the walls should be tested by deeper sampling methods.

Radium analyses, now a matter of routine in many laboratories, are necessary to establish the fact that the radioactive constituent of a given "hot spot" is radium and not one of a number of other radioactive elements belonging to the uranium and thorium series, all of which are much more readily transported in dilute H_2SO_4 solutions.

Many "hot spots", clearly of recent origin and generally assumed to be due to "transported" radium--in particular the high radioactivity shown by some rusted mine rails and nails -- may be due to an original coprecipitation of iron oxides and ionium, the thorium daughter of U^{232} which in turn decays to radium. Also the effects of the erratic and short-lived high radioactivity resulting from the occlusion of radon on moist dust, mud and similar material are familiar to anyone who has made extensive radiometric surveys in uraniferous sulfide mines.

Where the analytical data show (1) that the high radioactivity of two or more samples from the same "hot spot" is due to radium and (2) that the radium is present in constant (but excessive) proportions to the uranium, the concentrations are almost certainly residual. In such cases the Ra/U ratio can be used to estimate, within the limits of the sampling, the amount of uranium lost from the exposed walls through leaching processes

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during the recent past, say within the last 50 years. Where predictions as to hidden uranium reserves of badly leached mines must be based very largely on the results of shallow sampling, the quantitative implications of the Ra/U ratio may assume particular importance.

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