Leaching as a Method of Mining Uranium

Rob L. Kane

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LEACHING AS A METHOD OF MINING URANIUM

For
MINING 68

BY
ROB L. KANE

BUTTE, MONTANA
MAY 28, 1954.
LEACHING AS A METHOD OF MINING URANIUM

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MINING 68

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Mr. Koehler Stout
Mining Department
Montana School of Mines
Butte, Montana

Dear Mr. Stout:

In compliance with your request for the Mining 68 course, I am presenting this report on "Leaching as a Method of Mining Uranium."

The following paper presents several aspects of leaching. A brief review is made of the past methods of leaching, mill treatment of uranium ores, and then a review is made of my ideas on leaching uranium ores.

This paper is the result of an original problem and therefore little information is available in literature. Due to lack of ore specimens, it has been impractical to run chemical laboratory tests. Therefore, some information in this paper may be subject to error but it is nearly as correct as the author can determine.

Respectfully submitted,

Rob L. Kane
ABSTRACT

This paper presents a new method of recovering uranium ores from the earth. By sinking drill holes into ore bearing beds, aqueous leach solutions can be circulated through the ores. Solutions of sulphuric acid, potassium carbonate and many other available reagents will put the ions of uranium and vanadium into the liquid leach. The pregnant solutions are then pumped to the surface so a recovery of the valuable portion of the ore can be made. Evaporation, precipitation on carbon, precipitation by chemical reagents are some of the methods that can be used for ore recovery from solution.

At present, it appears that most of the domestic uranium production of the future will come from the Colorado Plateau and Wyoming. The deposits of these areas are mainly secondary and the ore occurs in ground that is amenable to leaching. Therefore, the presented method of leaching is designed to be applicable to the Colorado Plateau type of deposit.

Leaching of ores should appreciably cut mining, milling, and transportation costs for uranium production.
INTRODUCTION

Object

Since the advent of the atomic bomb, the mining of uranium has become a major industry. Many new milling processes and unusual mining practices have evolved to facilitate the production of uranium. Yet, new and more economic methods will have to be developed if the numerous, remote, low-grade deposits are to be mined under present economic conditions. Even for the rich ore deposits, the operators are always looking for a more economical way of mining. This paper presents a method of leaching uranium from ores without actually mining the rock. The leaching of uranium ores in situ should considerably cut uranium production costs.

Brief Review of Method

At present, the majority of the existing uranium deposits are of a secondary origin. The uranium bearing minerals are usually carnitite and pitchblende. These minerals are found as a cement type filling between the grains of sandstones and conglomerates. Mineral bearing solutions formed the cement by depositing part of the mineral load between the grains of the sediments. Tests have shown that intergranular cements of carnitite and pitchblende are readily soluble in solutions with a pH below 5.8 or above 9. The author believes that by circulating prepared
solutions through a uranium deposit, a relatively cheap recovery can be made. The uranium would then be precipitated from the solution and the concentrates shipped to the mill. In this manner, transportation costs would be considerably cut, mining expenses lowered, and the amount of milling reduced.

Other variations of leaching could be practiced with the mining of uranium. The definition of leaching is "the term applied to the process of recovering a metal from an ore by a solvent or lixiviant and the removal of the resulting solution from the undissolved portion." 1. By this definition, leaching could occur in place, in heaps or in confined tanks. By using either of the last two methods, the ore has to be mined before leaching. Even mining before leaching might considerably cut transportation costs as concentrates instead of low grade ore would be shipped to the mill.

**BODY**

**Review of Leaching Methods**

The concept of leaching ores is not new. It has been tried with varying amounts of success at numerous locations. In general, attempts to leach ore in situ have met with failure. A greater degree of success has been achieved by the leaching of broken ores in mills. Van Arsdale 2 has the

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following to say on the subject; "Any discussion of 'leaching in place' has to begin with an admission and a warning. The admission is that there is probably no such thing as leaching in place, if by 'leaching' one means a well controlled process in which a fairly complete recovery is made of the metal available in the ore. The warning is that only under the most fortunate circumstances imaginable could leaching be economically successful on an unbroken, undeveloped orebody. Lack of appreciation of this fact has lead to several unsuccessful attempts to leach unbroken ore underground." Mr. Van Arsdale's warning should be listened to but not taken as law. It is almost certain that with a sufficient price incentive and a good knowledge of inorganic chemistry, many in situ ores could be recovered by hydrometallurgical methods.

Interfearing factors arise to hinder leaching at any orebody and the problems of each mine would have to be worked out individually. The North Butte Mining Company lost their leach solutions due to cracks in the rock, many orebodies have the wrong chemical make-up for advantageous leaching, and still other properties have rock that is not permeable to leach solutions. Rocks must be sufficiently porous to allow liquid solutions to get to the mineral, act on it, and then carry the dissolved mineral to the surface of the piece of rock. If the rock is not porous enough to allow this percolation, it must be broken into
pieces. The fact that the ore must be porous or broken for profitable leaching is a basic factor.

The profit sheets of industry, and scientific testing have shown that it is impractical to try leaching nonporous, or uncrushed ores. In Arizona, tests were run on porphyry copper ores. The results showed that 60 mesh ores took four to eight hours for a reasonable extraction of copper. Minus 1/4 inch ores took at least five days for the same recovery of copper. Both these tests were performed in agitation cells. In piled heaps of six inch material, it took four to six years for a reasonable extraction. Mr. Henry Tobelmann, an authority on leaching, showed that on selected porphyry tailing particles, an eight day leach with 3% sulphuric acid penetrated the rock an average of one-eighth of an inch and a sixteen day leach increased the depth less than one-sixteenth of an inch.

Heap leaching is becoming a very important mineral dressing process. At present much ore leaching is done by crushing and piling the ore. Anaconda Copper Mining Companies' Yerington, Nevada mine is a good example. Copper ore from the open pit mine is fed into crushers. The crushed ore is then piled and leached with sulphuric acid. The copper in the leach solution is passed over iron in a precipitating tank and thus the copper is recovered. The Yerington ore was not porous enough for percolation so it had to be crushed.

Industry has shown that leaching can be profitable. In the past most of the leaching has been done by letting
solutions percolate over the heaped ore or by agitating the ore and solutions in large tanks. A few of the mines and mills that use leaching as a primary ore extractive process are listed and commented on below.

<table>
<thead>
<tr>
<th>Mine or Mine Location</th>
<th>Leached Ore</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butte, Montana</td>
<td>Oxidized copper ores</td>
</tr>
<tr>
<td>Cyprus Mines, Cyprus</td>
<td>Oxidized copper ores</td>
</tr>
<tr>
<td>White Pine Project, Michigan</td>
<td>leaching of copper for flotation concentration</td>
</tr>
<tr>
<td>Sherritt-Gordon, Lynn Lake, Manitoba</td>
<td>Copper, nickel, and cobalt concentrates are leached by ammonia under pressure</td>
</tr>
<tr>
<td>Nicaro, Cuba</td>
<td>Ammonia leaching of nickel and cobalt oxides from laterites</td>
</tr>
<tr>
<td>Blackbird Project, Idaho</td>
<td>flotation concentrates are leached for cobalt</td>
</tr>
<tr>
<td>Rhokana, Northern Rhodesia</td>
<td></td>
</tr>
<tr>
<td>Vulcan Detinning Company, New Jersey</td>
<td>Tin is leached from cassiterite concentrates</td>
</tr>
<tr>
<td>Pine Creek, Colorado</td>
<td>leaching of tungsten ores</td>
</tr>
<tr>
<td>U.S. Bureau of Mines</td>
<td>They have found that the higher oxides of manganese, pyroslite, psilomelane, and wad are all readily soluble as sulphates in hot sulphurous acid.</td>
</tr>
</tbody>
</table>

Many other materials are recovered by leaching and probably more methods of recovering ore will be found in the future. Although various companies have used leaching, few have found it applicable as a means of mining the ore.

The Ohio Copper Company at Bingham, Utah is one of the few mines that have been able to utilize leaching as a means of mining. The Ohio Copper Company had trouble with recovery, as the oxidized chalcocite interfered with
flotation. In their block caving zone, they had six or seven million tons of low grade ore. The whole ore bearing structure was a distorted truncated cone containing about 38,000,000 tons of ore at .38 per cent copper. The gangue was principally quartzite and monzonite porphyry. The summer rains and winter snows sent water down through the block caving zone. The water, circulating air, and chalcocite combined to form copper water. A recovery of .30 percent copper was received from the .38 per cent in the ore. A greater recovery might have been possible if the operators had not added additional water which clogged up the openings in the ore with clays and iron salts. As it was, the company recovered 50,000,000 pounds of copper. This is an outstanding example of underground leaching, but even in this case the rock had to be broken first.

Another example of underground leaching can be observed at the copper mines in Butte, Montana. Mine water that has circulated down through old stopes, picks up copper in solution. The copper water from the mines is sent to precipitating plants in order to extract the copper. In this case the large amount of pyrite that is in the wall rock has reacted with water to form sulphuric acid and ferric sulphate. This solution then leaches the copper that the old miners have left in and near their stopes. The resulting solution contains copper sulphate. This pregnant solution goes to the precipitating plant and is run over scrap iron. According to the Electromotive
Series, iron is a more active element than copper; therefore, the scrap iron goes into solution and the copper is precipitated out and the recovery is complete.

In the future, an operator interested in leaching uranium may find it profitable to check and study the older leaching reports in detail.

Methods of Processing Uranium Ores

A variety of methods have been used to process carnitite and pitchblende ores. Each method depends on the nature of the ore and the character of the other elements present. According to Katz and Rabinwitch\(^1\), the general procedure for all ores is similar to the following:

"(1.) leaching the ore with sulfuric, nitric, or hydrochloric acid to solubilize the uranium (occasionally, alkaline extraction or fusion has been used to open up the ore);
(2.) converting the uranium to a soluble complex carbonate, a treatment that removes iron, aluminum and manganese;
(3.) precipitation of PbS and CuS from the uranyl solution;
(4.) recovery of the uranium as Na\(_2\)U\(_2\)O\(_7\) or (NH\(_4\))\(_2\)U\(_2\)O\(_7\)."

In the case of carnitite, special steps must be taken to separate vanadium and phosphate from the uranium. The details for two flow sheets are given in the appendix. Parts of these two flow sheets and variations of them can be used to figure the proper leaching methods to be used on certain of the uranium orebodies.

Uranium, vanadium and radium have been commercially extracted from carnitite ores by the use of sulphuric acid at either normal or elevated temperatures. When the operation is carried on at normal temperatures, the ore is pulverized and then moistened with five to ten per cent by weight of sulphuric acid (60 degrees Baume) and allowed to age for twenty to ninety days. After this preparation more dilute sulphuric acid is added and the uranium and vanadium are leached out of the ore as an aqueous solution of the sulphates. An increase in temperature speeds up the reaction. The U.S. Bureau of Mines has also advocated the use of the more expensive hydrochloric and nitric acids.

It has been generally shown that solutions with a pH above 9 and below 5.8 are capable of leaching uranium. This means that alkali solutions can also be used to recover uranium. Tests using potassium carbonate as the reagent have gotten a high rate of recovery provided the ore was finely pulverized and the solutions heated. With continued tests, it appears that there are unlimited types of reagents that are capable of leaching uranium.

The preparing of the ore for leaching is a major problem. In the mills the ore is usually concentrated first by mechanical means. Much of the gangue is discarded and the \( \text{U}_3\text{O}_8 \) content can be raised to fifty per cent in the case of some carnitites. In leaching ores in situ, mechanical processes become impractical, but some chemical treat-
ment may be possible. Chlorination has been used on some low-grade ores. Chlorine gas will form UCl₅ and other volatile chlorides. The chlorination process may be used as a means of preparing ore for leaching or even as a means of complete recovery. At the University of Utah, work has been done on the use of bacteria for the preparations of ores for leaching. This may have its place in the future.

Chemistry of Leaching Uranium In Situ

The chemical make-up of every ore deposit is different; therefore an analysis of each deposit would have to be made before leaching. A cost comparison of the reagents that make a leach solution should then be made. Next, combine the two previous steps and adopt the cheapest liquor that will adequately leach the ore deposit under examination. A sulphuric acid solution would probably work the most economically in a sandstone that contained quartz grains with a carnitite cement. If this same deposit contained pyrite and other sulphide minerals that had been oxidized, a very dilute acid leach might be all that would be required. If an ore is high in lime (i.e., Charlie Steen's "Utex" deposit in Utah) an acid leach is impractical. High lime ores would require an alkaline leach such as sodium or potassium carbonate. In summary, the reagents should be picked for each individual deposit.

Once the valuable portion of the ore is in solution, it would be recovered and sent to the surface. The next
problem would be to precipitate the valuable portion for shipment. Sending the concentrates in the liquid form to the mill would probably be too costly and uneconomical. Several methods of precipitation are possible. To the author the most feasible procedure would be to circulate in a countercurrent path a solvent that is immiscible with water and would separate by precipitation, the mineral values in the aqueous solution. Several relatively expensive reagents that are immiscible in water will recover the uranium radicals (i.e. ethyl ether will recover uranyl nitrates.) The high price paid for uranium might justify the expensive reagents. This method would probably only be used in areas that are short of water. If the mine has an abundance of water, the solution could be pumped into basins or tanks and allowed to evaporate in the sun. Heated pipes could also be used for evaporation. In this manner the uranium salts would be recovered as a concentrate. In nature, carbonaceous material has been mainly responsible for uranium precipitation from circulating ground water. If a handy source of cheap carbonaceous material is available, it might be possible to precipitate the uranium and vanadium from solution by circulation through the carbon mass.

Under certain conditions it might be feasible to partially reduce the amount of liquid in the leach liquor and ship the concentrates in a solution form. Evaporation by the sun or heaters is the only method the author knows of reducing the amount of liquid. The handling of the
concentrates in the liquid form might make some of the cliff and rimrock deposits more profitable as the solutions could be piped over cliffs, through gullies and by obstacles that only costly roads could be built to cover. When the solutions have been piped over the rough terrain, they could be transferred to tank trucks or further evaporated or precipitated so that the concentrates could be shipped the remainder of the way to the mill by truck.

A favorable factor in uranium mining is that the U.S. Government has guaranteed set prices for the $U_3O_8$ content of ores until April of 1962. For domestic ores, the government guarantees a base price of $3.50 per pound for ores assaying $0.20\% U_3O_8$. Additional allowances are paid for higher grades of $U_3O_8$. A big item in leaching is that no penalties would arise to affect payments as the miner is paid on the $U_3O_8$ content.

Preparation of Ground for Leaching

In order to acquire information on leaching in situ, the author examined the course nature followed in depositing the ores. By following the same or part of the same practices nature uses, man might be able to make a recovery of the ore. The author therefore will give a brief review of his ideas on how the ore came to be where it is on the Colorado Plateau and in Wyoming.

The Shinarump, Chinle, Morrison and Moenkopi formations are the main bearers of uranium. These beds are all Triassic age. The Entrada formation of the Jurassic is also uranium
bearing. During the Triassic and Jurassic periods, much volcanic ash was interstratified and laid on top of the sediments. Arid climates accompanied these depositions. The loose unconsolidated ash carried a low concentration of uranium which was easily leached by the solutions from the arid climate. The leach liquor circulated into surrounding sediments and came in contact with decaying organic matter. The carbon and hydrogen sulphide gas from the decaying vegetable matter reacted with the uranyl sulphate in solution and precipitated the uranium in the form of pitchblende. The vegetable matter is indicated as the precipitant as it is universally associated with uranium. During the Cretaceous, the central western states were underwater. This meant that the ground was saturated and no appreciable circulation took place. The volcanic ashes that were not leached and washed away had now become compacted into impervious layers of mudstone and siltstone. From what is left of the mudstone, it is estimated that the original volcanic ash contained about ten parts per million of uranium. Later during the Laramide Revolution the ground waters circulated along the impervious layers of mudstone and along the filled stream channels of the old Triassic beds and left the uranium in its present position. This means that the uranium is now often found between impervious beds of mudstone or in old stream channels with impervious bottoms. As an example we can again use Charlie Steen's multimillion dollar "Utex", Utah mine.
Mr. Dix 1 of the U.S.G.S., in describing the Utex Mine says: "The variable lithology of a channel provides favorable traps for uranium solutions, and uranium is often concentrated in a permeable unit between two impermeable units." Mr. Dix goes on to say that streams had cut into the Cutler formation and these channels were filled and covered with cross-bedded sandstones and conglomerates of the Chinle formation. The rock underlying the stream scour is impermeable siltstone and mudstone and would tend to reduce abruptly downward migration of mineralizing solutions. The pitchblends of the Utex Mine had been deposited from solutions circulating in the old stream scours.

It is believed that the uranium was deposited as pitchblends, uraninite or coffinite, Any ore that is extended under sufficient cover to be out of the zone of oxidation, would turn into a dark, almost black ore in which uranium would be present in the form of the previously mentioned minerals. When these ores are uncovered enough so they become in the zone of oxidation, they turn into carnotite and uranophane.

In leaching ores in situ, the author would apply as many of natures practices as possible. The ore was apparently deposited from circulating solutions so should be leachable by circulating solutions. Stream channels and impermeable beds should control the path of leach solutions.

as they did the depositional liquors.

Controlling the inflow and recovery of the leach solutions will be a problem of the mine operators. Each deposit would have to be examined carefully and a leaching method selected. One suggestion is to put down numerous drill holes on a grid pattern and thus determine the depth, size, dip, impermeable zones, chemical make-up, fault pattern and any other necessary information. When the problems of the orebody have been worked out, these same drill holes could be used to circulate solutions. If undesirable faults or porous beds were found that might drain off the leach solution, drill holes could be used to install grout curtains. The spacing of the holes on the grid pattern would depend on the porosity, permeability, depth, faults and various other factors. Tests would have to be run on each deposit to determine the proper hole pattern. Almost all beds have some dip to them; therefore the leach solutions would be put in at the highest spot on the ore bearing beds and pumped out at the next row of holes down hill. To leach the whole deposit, solutions would be circulated between rows one and two until the area was completely leached. Then the solutions would be run between rows two and three until that area was leached. This procedure would continue on down the orebody. Plate number 1. illustrates how this would work on a hypothetical deposit.

Leaching through holes would be somewhat similar to the Frasch Process used in mining sulphur. An examination
of the Frasch Process as well as the methods the oil industry uses in water flooding, might be of help in determining valuable information such as pressures required, types of pumps used, and rates of circulation.

The cements of some of the sandstones and conglomerates may be too dense to allow proper circulation. To overcome this problem, the beds could be soaked by preparatory solutions that might leach away some of the undesirable elements such as iron, carbon and calcium. The preparatory leaching would tend to open up the rock and chemically prepare the uranium for future leaching. Another method of opening the rock would be to explode charges in any area that is impermeable. Again, lessons can be learned by examining the methods the oil industry uses.

Other leaching practices could be used under the proper circumstances. Shinking a shaft and driving a drift or just putting an adit under a thick low-grade deposit might allow the operator to recover the ore by vertical circulation. Various combinations of grouting, mining and leaching might work on some orebodies. Each deposit would have special problems that would have to be worked out.

Many areas in Wyoming and on the edges of the Colorado Plateau contain uranium deposits that are left untouched because transportation costs are too high. The government will pay operators a rate of six cents per ton-mile for the first one hundred miles the ore is shipped to the mill. The costs for any shipment over one hundred miles must be carried
by the miner. At present there are no uranium mills in Wyoming; therefore only the high grade deposits can be mined at a profit. To overcome the transportation costs, some mines might find it economical to mine the ore and then leach the uranium from it. Surface tanks could be cheaply constructed to leach mined and maybe crushed ore. If the concentration of uranium oxide in an ore was raised from .20% to 50%, the costs of shipping the ore should be cut by approximately the same ratio. If necessary the ore could be diluted again at the mill in order that the tonnage rates might be paid. Surface leaching may be the answer to some out of the way deposits that have high transportation costs.

CONCLUSIONS

In the past several years many new milling methods have come into existence in the uranium fields. In this paper the author has presented a process of leaching that might be helpful in mining uranium. In order to aid in the study of leaching uranium the author makes a brief review of previous leaching practices and of the chemical reactions used in milling the uranium ores.

To leach the ore, drill holes would be put down into the sandstones and conglomerates that contain the uranium and vanadium. Cheap leach solutions that have a pH below 5.8 or above 9 would be used to leach the ore. Sulphuric acid appears to be the most practical leach liquor as it is relatively cheap and will easily take many of the ores into
solution as uranyl and vanadyl sulphates. Many other reagents can be used. These leach solutions would be sent down one set of drill holes and back up another set of holes. In this manner the uranium and other valuable portions of the ore could be recovered without the costs of the conventional underground mining.

After the leach liquor is pumped to the surface, the valuable portion would be precipitated chemically or by evaporation. The resulting concentrates would be shipped to the mill and the costs of handling large amounts of low-grade ore would be avoided.

As far as the author knows, this method of recovering uranium has never been used commercially. If proper study is given to an orebody, the author feels that leaching can be used successfully on many of the secondary uranium deposits.
URANIUM IN STREAM CHANNEL

LEACH SOLUTION GO DOWN ROW 1 & UP ROW 2.

PLATE #1
ORE CONCENTRATE

BALL MILL ← Sufficient Water to Yield a Slurry That Can Be Pumped

\[ \{\text{H}_2\text{SO}_4 \text{ (d=1.8)}\]  
\[ \text{BaCl}_2 \]  
\[ \text{MnO}_2 \]  

Acid Leach, 3 Hours at 90°  
← Na₂CO₃ to pH-10; Digested at 60°C

Ba, Ba, Al, Fe, etc.

To Radium Refinery

Alternatively

Uranyl Carbonate Solution ← Na₂S

Concentrate by Boiling to 25° Be

PbS

Purified Uranyl ← NaOH Carbonate Solution

\[ \text{H}_2\text{SO}_4 \text{ (NH}_4\text{)}_2\text{SO}_4 \]  
\[ \text{Na}_2\text{U}_3\text{O}_7 \]  
\[ \text{Na}_2\text{U}_2\text{O}_7 \]  
\[ \text{NH}_4\text{)}_2\text{U}_2\text{O}_7 \]  

Flow sheet for production of U₃O₈ from African pitchblende

From: The Chemistry of Uranium
By: Katz and Rabinwitch

Plate 2
Roast Ore at 700° C

Grind in a Pebble Mill
with Hot Soda Solution
Filter and Wash

Residue
Digest with HNO₃
Filter, Wash

Alkaline Solution
Containing Some U, V

Residue
Discard

Nitrate Solution
of Metal Values
Add NaOH too. 25N
Acidity, BaCl₂, Na₂SO₄

Ra₂BaSO₄
To Radium Refinery

U, V Nitrates
NaOH to Neutrality
Heat and Add FeSO₄

Na₂SO₄
Fusion
Leach with Water

U + V
To Nitrate
Recovery

H₂SO₄
Residue

Uranyl Sulfate
Solution

Purified through Tricarbonate

(NH₄)₂U₂O₇

UO₃

Vanadyl Sulfate
Heat

HVO₃

Flow sheet for Bureau of Mines nitric acid process for carnotite ore

Plate 3
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