1000 LBS. PREGNANT CARBONATE LIQUOR
25 LBS. U₃O₈
10 LBS. Mo
2.5 LBS. Zr

4 LBS. NaOH → ADJUST pH TO 10
PRECIPITATE Zr(CO)₂
BY DIGESTING AT 195°F
FILTER AND WASH → Zr PRODUCT
2.45 LBS. Zr

9 LBS. NaOH → PRECIPITATE YELLOW CAKE
FILTER AND WASH → U₃O₈ PRODUCT
25 LBS. U₃O₈
15 LB. Zr

57 LBS. H₂SO₄ → ACIDIFY TO pH 1.5
ABSORB Mo ON CHARCOAL → BARREN EFFLUENT
AND
18 LBS. NaOH → ELUTE
10 LBS. HCL → ADJUST pH TO pH 7
14 LBS. CaCl₂ → PRECIPITATE CaMoO₄
FILTER AND WASH → Mo PRODUCT
10 LBS. Mo
Nov. 29, 1966

A. V. HENRICKSON

3,288,570

PROCESS FOR THE SELECTIVE RECOVERY OF URANIUM, ZIRCONIUM AND MOLYBDENUM

Filed Aug. 16, 1963

2 Sheets-Sheet 2

PREGNANT CARBONATE
25 LBS. $U_3O_8$
15 LBS. Mo
8.5 LBS. $H_2SO_4$

48 LBS. $H_2SO_4$
.3 LBS. $NaClO$
ADJUST TO pH 3.5
TO PRECIPITATE URANYL MOLYBDATE

DIGEST 6 HRS. AT 25°C

FILTER - NO WASH
25 LBS. $U_3O_8$
1 LBS. Mo

14 LBS. NaOH
DISSOLVE Mo

DIGEST 1 HR. AT 80°C

FILTER - NO WASH
25 LBS. $U_3O_8$
.02 LBS. Mo

14 LBS. Mo
FILTRATE

3 LBS. HCl
ADJUST pH TO 8.0

18 LBS. $CoCl_2$
PRECIPITATE CoMoO$_4$

FILTER AND WASH
CoMoO$_4$ PRODUCT

PREPARE YELLOW CAKE pH II
FILTER & WASH
YELLOW CAKE PRODUCT

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BY
Sheridan & Ross
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This invention relates to a method for the selective recovery of uranium, zirconium and molybdenum from composite ores containing these metals together; more particularly, it relates to the process for the selective recovery from relatively low grade carbonaceous minerals of the metals uranium, molybdenum and zirconium existing together in the minerals.

The invention is illustrated by its application to carbonate strip liquors resulting from the treatment of lignite ores by conventional processes. More specifically, the invention is illustrated by its application to the selective recovery of uranium, zirconium and molybdenum from carbonate strip liquors resulting from solvent extraction of carbonate leach liquor of lignite ore. The invention is not limited in its application to carbonate strip liquor so formed but is applicable to carbonate strip and leach liquors of the three metals in general. Likewise, it is not limited in its application to strip or leach liquors but can be applied to carbonate solutions in general containing the three metals, and particularly to liquors formed by leaching ores with alkali metal carbonates and bicarbonates.

The process of the invention is particularly useful for the selective recovery of uranium, zirconium and molybdenum from ores associated with various carbonaceous materials, for example, coal, lignite, oil shale and others. It is illustrated herein by its application to lignite ores.

Ore grade unrefined lignite exists in commercial quantities in the Princenton, Missouri, and the Dakotas. Experience has shown that uranium recovery from lignite ores has a marginal profit potential using available recovery processes, and that burning the ore before leaching offers the best possibility for processing. The ore contains sufficient carbonaceous materials to support combustion and the residue more susceptible to the ore to treatment with an aqueous leaching solution, such as, a strong mineral acid or an alkali metal carbonate. The ash contains molybdenum and zirconium in addition to uranium, and the separation of these elements from the uranium is necessary in order to meet yellow cake specifications. These specifications include a limit for molybdenum of 0.6% of the U₂O₅, and will include a limit for zirconium of 2% of the U₂O₅. Aside from the fact that molybdenum and zirconium must not contaminate the yellow cake, their separation and recovery in saleable form would increase the income from the process and contribute to its commercial feasibility.

There are a number of disadvantages attendant to the selective separation of uranium, molybdenum and zirconium from carbonate leach or strip liquors in which they exist together. For example, it is known that zirconium can be precipitated free of uranium through pH control. Unfortunately the required pH range (2.5-3.5) results in uranium loss as uranium molybdate if molybdenum is present because this compound is insoluble in the same pH range. It would be possible to remove the molybdenum from the leach liquor by charcoal adsorption before solvent extraction of the uranium. This would require a large installation and high capital cost in order to treat approximately 250 gallons per minute, the approximate rate of treatment required for commercial feasibility. Further, as will be pointed out hereinafter, it is known that the presence of zirconium during charcoal adsorption of molybdenum seriously poisons the charcoal against molybdenum adsorption and thus renders such adsorption prohibitive in its presence. Uranium can be precipitated directly from the pregnant strip carbonate solution with sodium hydroxide or it can be precipitated after destroying the carbonate; however, such precipitation also precipitates zirconium as zirconium hydroxide and this compound ends up as an impurity in the yellow cake.

Accordingly, it is an object of this invention to provide a method for the selective recovery of uranium, zirconium and molybdenum from composite ores in which they exist together.

It is another object of this invention to provide a method for the selective recovery of uranium, zirconium and molybdenum existing together in ores having a high content of carbonaceous or organic material, such as, lignite ores.

It is still another object of this invention to provide a method for the selective recovery of the metals uranium, zirconium and molybdenum from carbonate solutions in general and from carbonate liquors and leach solutions formed by treatment of carbonaceous ores.

It is a further object of this invention to provide a process as stated which is commercially feasible and which produces the metals in a form meeting standard requirements of purity.

The above objects of the invention are accomplished by a process in which zirconium is first selectively recovered from a carbonate solution containing the three metals, followed by selective separation of uranium and molybdenum. The process includes two modifications. In accordance with modification (1) of the process of the invention, in step (1) zirconium is precipitated as the carbonate by adjusting the pH of the carbonate strip liquor to a point just below the incipient precipitation of uranium and the precipitate recovered by filtration. In step (2) uranium is removed from the filtrate of step (1) containing uranium and molybdenum by precipitation as yellow cake followed by filtration. In step (3) molybdenum is removed from the filtrate of step (2) by adsorption on charcoal and recovered by stripping from the charcoal and precipitation from the stripping solution as calcium molybdate.

In modification (2) of the invention, after step (1') in which zirconium is precipitated as basic zirconium carbonate as above, in step (2') the filtrate of step (1') is treated by pH adjustment and heating to precipitate the molybdenum as uranyl molybdate, followed by filtration. The filtrate from step (2') is treated to recover uranium not used in step (2') as yellow cake for the main stream recovery. In step (3') the molybdenum is dissolved from the precipitate of uranyl molybdate of step (2') and recovered from the solution as a calcium molybdate precipitate. The precipitated uranium of step (2') which remains after molybdenum is dissolved out is converted to yellow cake and re-cycled to maintain sufficient percentage of uranium in the pregnant carbonate for the succeeding precipitation of uranyl molybdate.

An improvement of the process comprises the oxidation of molybdenum to its highest valence state before its recovery. A further improvement of modification (2), the uranyl molybdate precipitation procedure, includes the treatment of the precipitate of step (3') containing sodium diuranate and some zirconium hydroxide, with sulfuric acid at the required pH value to separate the zirconium from the uranium. The separation can alternatively be accomplished by completely dissolving both the sodium diuranate and the zirconium hydroxide at pH 1 and separating the two compounds by re-precipitating the zirconium as the basic sulfate.
The detailed description of the operation of the process, including both modifications, is presented herein in conjunction with the flow sheets of Figs. 1 and 2. Fig. 1 being the flow sheet for modification (1) and Fig. 2 being the flow sheet for modification (2), that is that feature of the invention which is applied to the filtrate remaining after removal of zirconium as zirconium carbonate from the carbonate strip liquor. The flow sheets are based on reagent requirements for 1000 lbs. of pregnant carbonate liquor, the liquor on which the first flow sheet is based on containing 25 lbs. UO$_3$O$_2$ 10 lbs. Mo and 2.5 lbs. Zr and the liquor upon which the uranyl molybdate precipitation flow sheet is based containing 25 lbs. UO$_3$O$_2$ 15 lbs. Mo and originally 2.5 lbs. Zr. The flow sheets are based on actual examples using the respective modifications of the process. Results obtained utilizing the described process steps of the two modifications are included.

As used herein in the specification and claims, the expression "carbonate solution" includes carbonate liquors, carbonate leach solutions and carbonate solutions in general irrespective of how they are formed. The term "solution" includes leach liquor, strip liquor, slurry, etc.

The strip carbonate liquor used for the examples presented herein was obtained by acid leach of lignite ash followed by solvent extraction of uranium, zirconium and molybdenum with a tricapryl amine solution in kerosene and stripping the metals from the solvent with sodium carbonate. The invention, of course, is not limited in its application to a strip carbonate liquor formed in this manner but is equally applicable to carbonate strip or leach liquors in general. The lignite ash was produced from uraniumiferous lignite ores representative of those from Montana and the Dakotas.

The first step of both modifications of the process comprises the removal of zirconium from the strip carbonate liquor by precipitation as the basic carbonate and is described as follows: It has been found that the zirconium carbonate complex is unstable at higher temperatures. At about 85$^\circ$ C. it tends to lose CO$_2$ and precipitate from solution as a basic carbonate. The basic carbonate precipitated in this manner is quite stable and does not redissolve to any significant extent on cooling. This instability at higher temperatures provides a method for its removal from carbonate solutions and separation from both uranium and molybdenum.

Essentially, quantitative precipitation is obtained by adjusting the pH with sodium hydroxide to a point just below incipient precipitation of uranium and then digesting near boiling for about an hour. Accordingly, the pH of the pregnant carbonate strip liquor was adjusted to about 10, a point just below that of incipient precipitation of uranium in the particular solution, with a 50% solution of sodium hydroxide. The solution was heated to 195$^\circ$ F. and digested for 1 hour. Zirconium carbonate, precipitated in quantitative amount, was filtered and washed with water. The above procedure for recovering zirconium was used for the examples which follow.

The pH is measured at 25 to 30 degrees centigrade in order to get accurate readings. At higher temperatures the readings are subject to considerable error, even though the temperature compensator of the instrument is set correctly, because of the increased activity of the sodium ion.

![Table](https://example.com/table.png)

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.6</td>
<td>250</td>
<td>6.4</td>
<td>62.7</td>
<td>11.2</td>
<td>9.6</td>
<td>48.9</td>
<td>0.0</td>
<td>0.04</td>
<td>28.7</td>
<td>26.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>9.6</td>
<td>250</td>
<td>3.8</td>
<td>53.4</td>
<td>13.2</td>
<td>1.22</td>
<td>48.0</td>
<td>0.67</td>
<td>0.81</td>
<td>49.4</td>
<td>49.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>450</td>
<td>4.7</td>
<td>52.4</td>
<td>13.9</td>
<td>2.92</td>
<td>48.6</td>
<td>2.9</td>
<td>0.6</td>
<td>50.0</td>
<td>50.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A solution of sodium hydroxide is preferable for the pH adjustment to make caustic because it tends to minimize localized precipitation of sodium diuranate. Any local precipitation which does occur during addition of sodium hydroxide must be allowed to redissolve completely before the temperature is increased, otherwise separation from uranium will be poor.

The pH of the pregnant carbonate strip liquor before adjustment was close to 8. At this pH value about 30% of zirconium could be precipitated merely by heating. By increasing the pH to 10 about 90% of the zirconium was precipitated. Under normal operating conditions it was found that a pH between 9.5 and 10 was satisfactory for maximum precipitation of zirconium, this pH being slightly below the point of incipient precipitation for uranium. The strip liquor used is typical of that obtained from lignite ash produced from uraniumiferous lignite ores from Montana and the Dakotas.

In order to thoroughly test the zirconium carbonate precipitation step, a series of three precipitations were made at pH values of 8.6, 9.5 and 10.0 to determine what effect pH has on the completeness of precipitation and to determine the purity of the precipitate. The pregnant carbonate was spiked with zirconium and molybdenum to the desired concentration. The pH in each test was adjusted with sodium hydroxide and the solution heated to 95$^\circ$ C. and digested for 1 hour. The slurry was then cooled to about 50$^\circ$ C. and filtered. The precipitate was washed twice with water, dried and assayed for zirconium, uranium and molybdenum. The data obtained is tabulated in Table I.

It will be noted that good precipitation was obtained at a pH range of 9.5 to 10 from the solutions used in the test, this being at a point just below the incipient precipitation of uranium. Also, separation from uranium and molybdenum was excellent. These tests showed conclusively that optimum results are obtained when the pH used is just below the incipient precipitation of uranium. A temperature range between 80$^\circ$ C. and boiling is preferred for the zirconium carbonate precipitation step.

Removal of zirconium from carbonate solution by the above described procedure provides a solution which can then be processed directly for separation of uranium and molybdenum by either modification of the process, that is, with either the uranyl molybdate precipitation modification or the charcoal absorption modification. This is illustrated by the examples given below.

The coal ash adsorption modification of the process (No. 1) is performed as follows:

In step (2) the filtrate of step (1), containing uranium and molybdenum, was treated with 5 grams of sodium hydroxide per liter of solution plus .15 gram for each gram of UO$_3$O$_2$ per liter. Since the solution was already at the point of incipient uranium precipitation this procedure provides sufficient sodium hydroxide to precipitate Na$_2$UO$_2$ plus 5 grams per liter in excess. The yellow cake was filtered and washed in the standard manner as the main stream recovery product. The precipitation of yellow cake is, of course, conventional procedure and the amount of sodium hydroxide used is calculated as follows: In order to reduce the solubility of uranium to less than .05 gram per liter in a 10% sodium carbonate solution the free hydroxide concentration must be greater than 0.1 molar. 5 grams per liter is 0.125 molar. The additional 0.15 gram for each gram of UO$_3$O$_2$ per liter is
required to form the precipitated sodium diuranate. The amount of sodium hydroxide used will, of course, vary with recovery requirements and the carbonate concentra-
tion of the solution. Other alkaline metal hydroxides, such as, lithium and potassium hydroxides, may, of course, be used for the precipitation of the yellow cake.

Step (3) comprises the recovery of molybdenum from the filtrate of step (2) by adsorption on charcoal followed by elution and precipitation from the eluate. The filtrate of step (2) was acidified with sulfuric acid to a pH of 1.5. A pH range between about 1 and 2 is preferred. At this point if reduction of molybdenum to molybdenum blue had occurred, enough sodium chlorate was added to oxidize the molybdenum. Sodium hypochlorite or another suit-
able oxidizing agent may be used. The solution was then heated to approximately 120° F. and passed through a bed of charcoal at a preferred rate equal to 7.2 grams of molybdenum per hour per kilogram of charcoal. The filtered and washed with .1 percent calcium chloride solution.

Percentage recoveries of all three metals above 97 were consistently achieved with the above described process. Reduction of molybdenum to molybdenum blue may occur during acidification of the yellow cake filtrate. The reason for this is not definitely known but it is probably due to reaction with oxidizable residual material coming from the solvent extraction circuit. Approximately .3 pound sodium chloride per pound molybdenum is required for the oxidation.

The schematic flow sheet of FIG. 1 for the above procedure gives estimated relative reagent requirements for each step.

A final test was made following the entire procedure of modification (1) given above using strip carbonate liquor spiked with molybdenum and zirconium, the liquor being made by treatment of lignite ash from North Dakota ore. The results obtained are given in Table II.

<table>
<thead>
<tr>
<th>TABLE II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>Hord Sample</td>
</tr>
<tr>
<td>Zr and UO₄, ppt.</td>
</tr>
<tr>
<td>Yellow Cake</td>
</tr>
<tr>
<td>Filtrate</td>
</tr>
<tr>
<td>Mo Adsorption (800 cc. yellow cake filtrate)</td>
</tr>
<tr>
<td>Fraction 1</td>
</tr>
<tr>
<td>Fraction 2</td>
</tr>
<tr>
<td>Fraction 3</td>
</tr>
<tr>
<td>Fraction 4</td>
</tr>
<tr>
<td>Fraction 5</td>
</tr>
<tr>
<td>Fraction 6</td>
</tr>
<tr>
<td>Fraction 7</td>
</tr>
<tr>
<td>Wash 8</td>
</tr>
<tr>
<td>Wash 9</td>
</tr>
<tr>
<td>Mo Elution</td>
</tr>
<tr>
<td>Fraction 10</td>
</tr>
<tr>
<td>Precipitate</td>
</tr>
<tr>
<td>Filtrate</td>
</tr>
</tbody>
</table>

flow was maintained through the bed until the molyb-
denum broke through. A preferred pH range for the solution is between about 1 and about 2.

Recoveries and analyses of products produced in an-
other representative test run of modification (1) of the process are given in Table III.

<p>| TABLE III—RECOVERY AND ANALYSIS OF UO₄, MO AND ZR PRODUCTS |
|----------------|-------------|--------------------|</p>
<table>
<thead>
<tr>
<th>Product</th>
<th>Percent Recovery</th>
<th>Analysis, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow Cake (UO₄)</td>
<td>93.43</td>
<td>80.38</td>
</tr>
<tr>
<td>Molybdenum ppt.</td>
<td>93.43</td>
<td>80.38</td>
</tr>
</tbody>
</table>

As the data in Tables II and III show, the process provides percentage recoveries of each of the three metals above 97. The metals were in a state of purity meeting AEC requirements. The effluent from the char-
coal adsorption step is suitable for recycling to the solvent extraction feed stream. The charcoal loading obtained by this procedure was 18%, operating with a column two feet deep at an adsorption rate of 7.2 gms. Mo/hr./kg. of charcoal at 120° F. The consumption of chemicals, including the chemicals used for stripping, based on a concentration of 25 grams of UO₄ and 10 grams Mo per liter, was well within feasible economic limits for a commercially operating flow chart.

The alternate procedure, or the uranyl molybdate pre-
cipitation modification of the process, modification (1),
is described in detail as follows, with reference to the flow chart of FIG. 2.

Step (1) of this modification is identical with step (1) of the modification of the process described above, that is, zirconium was precipitated as the carbonate and removed from the strip liquor as such in the same manner as in modification (1) described above. Results for the recovery of zirconium as carbonate (step 1) are given in Tables I, II and III above.

In step (2') the pregnant carbonate liquor filtrate from the zirconium carbonate precipitation was cooled to 25° C. or lower and neutralized with sulfuric acid to a pH of about 3.5 measured with a pH meter at 25° C. A pH within ±.5 of 3.5 is used. Uranmolybdate precipitation was precipitated. It should be lemon yellow in color. If it is olive green or dark color an oxidant such as sodium hypochlorite or sodium chlorate is added until a lemon yellow color is obtained indicating complete oxidation of molybdenum. The complete oxidation of molybdenum before precipitation of uranmolybdate is preferred. The slurry was agitated for about four hours at 25° C. in order to permit completion of crystal growth of the uranmolybdate and to obtain complete precipitation. It was then filtered.

Step (3') was precipitated from the filtrate with sodium hydroxide at a pH of about 11 in accordance with standard procedures to provide a pure recovery product which met AEC specifications in all respects.

Step (3') comprises the separation of molybdenum from the precipitate of step (2'). In step (3') the uranmolybdate precipitate was digested with sodium hydroxide for 1/2 hour at 80° C. to dissolve the molybdenum. A pH above about 10 is preferred. The molybdenum goes into solution as sodium molybdate and the uranium is converted to insoluble sodium diuranate. The sodium diuranate was filtered and washed with one replacement of water. The molybdenum was recovered from the filtrate by precipitation as calcium molybdate by adjusting the pH between about 7 and 8 with hydrochloric acid and adding calcium chloride. About 25% excess calcium chloride is required to complete the precipitation. The solution was agitated about one hour at ambient temperatures and filtered with the washing of the calcium molybdate precipitate.

The yellow cake remaining after removal of molybdenum from the uranmolybdate precipitate is dissolved in sulfuric acid and recycled for the succeeding precipitation of molybdenum. This recycle cycle is necessary in order to maintain an excess of uranium in the uranmolybdate precipitation. The amount of uranium in the recycle will be proportional to the molybdenum precipitated. The uranmolybdate compound precipitated under the given condition approximates the formula $\text{UO}_2 \cdot 2\text{MoO}_3$.

Results obtained by practice of the above described uranmolybdate precipitation modification of the process are presented in Table IV.

<table>
<thead>
<tr>
<th>Test Product</th>
<th>Wt. or Vol.</th>
<th>Assay, Percent or g/l.</th>
<th>Content, gms.</th>
<th>by Distribution, Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Head Sample</td>
<td>250 ml</td>
<td>45.80</td>
<td>4.45</td>
<td>2.45</td>
</tr>
<tr>
<td>Uranmolybdate Filtrate</td>
<td>310 cc</td>
<td>18.37</td>
<td>.39</td>
<td>.39</td>
</tr>
<tr>
<td>Yellowcake</td>
<td>4.34 gms</td>
<td>1.2</td>
<td>.002</td>
<td>.2</td>
</tr>
<tr>
<td>Calcium Molybdate</td>
<td>370 cc</td>
<td>3.13</td>
<td>.003</td>
<td>.2</td>
</tr>
<tr>
<td>Calcium Molybdate</td>
<td>8.53 gms</td>
<td>3.34</td>
<td>.22.8</td>
<td>88.1</td>
</tr>
</tbody>
</table>

As the results of Table IV show, total recoveries of uranium and molybdenum were obtained in percentages of 99.8 and 89.1, respectively. The purity of the metals met AEC requirements.

In order to investigate the advantage of oxidizing molybdenum before the charcoal adsorption step, three adsorption runs were made under different conditions. All three runs were made with acidified yellow cake filtrate. Run No. 1 was not oxidized prior to step (3'). Run No. 2 was oxidized with 3.0% sodium chlorate per gram of molybdenum and Run No. 3 was operated on 7.5 bed volumes on unoxidized feed then the feed of this latter run was oxidized as in Run No. 2 to determine if the charcoal would recover and determine conclusively if oxidation is beneficial. Run No. 2 operated at 7.0 and 9.7 bed volumes gave effluents assaying 1.90 and 1.57 gm. Mo/liter, respectively, while Run No. 2 operated at 16 bed volumes never gave effluents assaying more than .005 gm. Mo/liter. Run No. 3 demonstrated that the charcoal does recover, as the effluent of the run operated at 7.5 bed volumes assayed .29 gm. Mo/liter before oxidation and a run-operated 8.6 bed-volumes after oxidation gave an effluent assaying only .15 gm. Mo/liter. The results of these runs demonstrated the desirability of oxidizing the molybdenum prior to the charcoal adsorption step. It is preferable to perform the oxidation prior to the uranmolybdate precipitation step.

An improvement in the uranmolybdate precipitation modification of the process comprises the separation of residual zirconium from the recycle uranium in the sodium diuranate precipitate resulting from the separation of molybdenum from the recycle uranium. In the sodium hydroxide treatment to dissolve molybdenum both uranium and any zirconium which is present remains undissolved in the precipitate. The uranium is in the form of sodium diuranate and the zirconium is present as zirconium hydroxide. The precipitate was treated with sulfuric acid at a pH of about 3 or 3.5 and digested at about 80° C. at which point the zirconium hydroxide remains insoluble and sodium diuranate was dissolved. Alternatively, separation was accomplished by completely dissolving the precipitate at pH 1 and reprecipitating zirconium as the basic sulfate with sulfuric acid.

It is seen from the above description that a process has been provided for the selective recovery of the metals uranium, zirconium and molybdenum existing together in their ores, including carbonaceous ores, and in carbonate solutions in general, including carbonate leach and strip liquors. The method provides metals in a state of commercial grade purity, and is economically feasible.

Although the invention has been illustrated and described with reference to the preferred embodiment thereof, it is to be understood that it is in no way limited to the details of such embodiments, but is capable of numerous modifications within the scope of the appended claims.

What is claimed is:

1. The process of selectively recovering uranium, zirconium and molybdenum values from carbonate solutions containing said values which comprises: adjusting the pH of the pregnant carbonate solution to a point not in excess of that slightly below the precipitation point of uranium for the solution to precipitate zirconium from the carbonate solution as the carbonate and separating the precipitate of zirconium carbonate from the remaining solution thereby forming a second solution; precipitating uranium from said second solution by adding to said second solution an excess of an alkali metal hydroxide to precipitate uranium as alkali metal diuranate, separating
the precipitate of the last precipitation from the remaining solution and thereby forming a third solution; adjusting the pH of said third solution to acidic and adsorbing molybdenum from said third solution on charcoal.

2. The process of claim 1 in which the molybdenum is eluted from the charcoal and recovered from the eluate.

3. The process for selectively recovering uranium, zirconium and molybdenum values from carbonate solutions formed from composite ores containing said values which comprises: adjusting the pH of the pregnant carbonate solution to a point not in excess of slightly below the precipitation point of uranium for the solutions to precipitate zirconium as a precipitate of zirconium carbonate, separating said zirconium carbonate precipitate from the remaining solution and thereby forming a second solution; precipitating uranium from said second solution by adding to said second solution an excess of an alkali metal hydroxide to precipitate uranium as alkali metal diuranate, separating the precipitate of the last precipitation from the remaining solution and thereby forming a third solution; adjusting the pH of said third solution to acidic, separating the molybdenum from said third solution by allowing the solution through charcoal to adsorb the molybdenum on the charcoal; eluting the molybdenum from the charcoal; and recovering molybdenum from the eluate by precipitating it as an insoluble compound.

4. The process of claim 3 in which the molybdenum is oxidized before adsorption on charcoal.

5. The process of claim 3 in which the carbonate solution is digested at a temperature between about 80° C. and the boiling point of the solution during the precipitation of zirconium carbonate.

6. The process of claim 3 in which the pH of said third solution is adjusted to between about 1 and 2 for adsorption of the molybdenum.

7. The process of claim 3 in which molybdenum is recovered from said eluate as calcium molybdate and the pH of said eluate is adjusted to a point between about 7 and 9 for precipitation of the calcium molybdate.

8. The process for selectively recovering uranium, zirconium and molybdenum values from carbonate solutions containing said values which comprises precipitating the zirconium from the carbonate solution as the carbonate by adjusting the pH of the pregnant carbonate solution to a point not in excess of slightly below the precipitation point of uranium for the solutions to precipitate zirconium as a precipitate of zirconium carbonate from the remaining solution and thereby forming a second solution; precipitating molybdenum and some of the uranium from said second solution as uranyl molybdate by adjusting the pH of said second solution to between about 3 and 4, separating the precipitate from the last precipitation from the remaining solution and thereby forming a third solution; precipitating uranium from said third solution by adding to said third solution an excess of an alkali metal hydroxide to precipitate uranium as alkali metal diuranate; separating the precipitate of the last precipitation from the remaining solution; separating molybdenum from said uranyl molybdate precipitate at a pH of about 10 or above, separating the precipitate of the last precipitation from the remaining solution; and thereby forming a fourth solution; and recovering molybdenum from said fourth solution.

9. The process of claim 8 in which the uranium remaining after separation of molybdenum from said uranyl molybdate precipitate is recycled for succeeding precipitation of uranyl molybdate.

10. The process of claim 8 in which molybdenum is oxidized before adsorption of uranyl molybdate.

11. The process for selectively recovering uranium, zirconium and molybdenum values from carbonate solutions of composite ores containing said values which comprises precipitating zirconium from the carbonate solution by adjusting the pH of the carbonate solution to a point slightly below the precipitation point of uranium for the solution and digesting the solution at a temperature between about 80° C. and the boiling point of the liquor to precipitate the zirconium as carbonate, separating the zirconium carbonate precipitate from the remaining solution and thereby forming a second solution; adjusting the pH of said second solution to between about 3 and 4 to precipitate uranyl molybdate, separating the last precipitate from the remaining solution; and thereby forming a third solution; precipitating uranium from said third solution by adding to said third solution an excess of an alkali metal hydroxide to precipitate uranium as an alkali metal diuranate; separating the last precipitate from the remaining solution; treating said uranyl molybdate precipitate with an alkali metal hydroxide at a pH of about 10 or above to dissolve the molybdenum from the uranyl molybdate precipitate and converting the uranium to sodium diuranate thereby forming a fourth solution; re-precipitating the uranium from the uranyl molybdate precipitate for succeeding precipitation of uranyl molybdate; adjusting the pH of said fourth solution to between about 7 and 9 and recovering the molybdenum therefrom as calcium molybdate.

12. The process of claim 11 in which the molybdenum is oxidized before precipitating zirconium.

13. The process of claim 11 in which the sodium diuranate precipitate is treated with sulfuric acid at a pH between about 3 and 4 to selectively separate residual zirconium and uranium.

14. The process of claim 11 in which the sodium diuranate is treated with sulfuric acid at a pH of about 1 to completely dissolve the precipitate and residual zirconium is selectively separated from uranium in the filtrate by precipitation as the sulfate.

15. In the process for the selective recovery of zirconium, uranium and molybdenum values from carbonate solutions, the improvement which comprises first separating zirconium from the other two metals by adjusting the pH of the carbonate solution to a point slightly below the precipitation point of uranium for the solution, adjusting the temperature of the solution to between about 80° C. and the boiling point of the liquor to precipitate zirconium carbonate and separating the precipitate from the remaining solution.

16. In the process for selectively recovering zirconium, uranium and molybdenum values from carbonate solutions by which zirconium and uranium are selectively recovered leaving the molybdenum contained in a basic carbonate liquor, the improvement which comprises adjusting the pH of the leach liquor to between about 1 and 2 and adsorbing the molybdenum on charcoal.

17. In the process for selectively recovering uranum, zirconium and molybdenum from carbonate leach liquors, by which zirconium and uranium are selectively recovered leaving molybdenum contained in a basic carbonate liquor, the improvement which comprises oxidizing the molybdenum, adjusting the pH of the carbonate solution to a point slightly below the precipitation point of uranium for the solution, digesting the solution at a temperature between about 80° C. and the boiling point of the solution to precipitate zirconium carbonate and separating the precipitate thereby forming a second solution containing uranium and separating the uranium by adding to said second solution an excess of an alkali metal hydroxide to precipitate uranium as an alkali metal diuranate and separating the last precipitate from the remaining solution thereby forming a third
solution containing molybdenum; adjusting the pH of said third solution to between about 1 and 2 and adsorbing the molybdenum on charcoal; stripping the molybdenum from the charcoal with an alkali metal hydroxide at a pH between about 7 and 9 and recovering molybdenum from the eluate of the stripping step by precipitation as calcium molybdate.

19. The process for the selective recovery of zirconium, uranium and molybdenum values from carbonate solutions which comprises adjusting the pH of the carbonate solution to a point slightly below the precipitation point of uranium for the solution, digesting the solution at a temperature between 80°C. and the boiling point of the solution to precipitate zirconium carbonate and separating the precipitate thereby forming a second solution containing uranium and molybdenum, oxidizing the molybdenum in said second solution; adjusting the pH of said second solution to between about 3 and about 4 to precipitate uranyl molybdate and separating the precipitate thereby forming a third solution; precipitating uranium from said third solution by adding to said third solution an alkali metal hydroxide to precipitate uranium as an alkali metal diuranate; dissolving molybdenum from the uranyl molybdate precipitate with an alkali metal hydroxide at a pH of about 10 to form a fourth solution containing molybdenum; and recovering molybdenum from said fourth solution as calcium molybdate.

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