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Hard et al.

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[54] **PROCESS FOR LEACHING BASE ELEMENTS, SUCH AS URANIUM ORE, IN SITU**

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[52] U.S. Cl. 299/5, 75/103

[51] Int. Cl. E21b 43/28

[58] Field of Search 299/4, 5; 75/101, 103, 121

[56] **References Cited**

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[57] **ABSTRACT**

This invention relates to a process for leaching base elements, such as uranium values, from an underground water saturated ore deposit containing oxidizable materials such as sulfides, carbon and the like. An oxygen bearing gas is introduced into the ore deposit prior to or simultaneously with a leach solution to oxidize the base elements within the ore deposit to a soluble state where they can then be dissolved in the leach solution. Thereafter the pregnant solution is withdrawn and treated by conventional techniques to remove the base elements.

21 Claims, 3 Drawing Figures

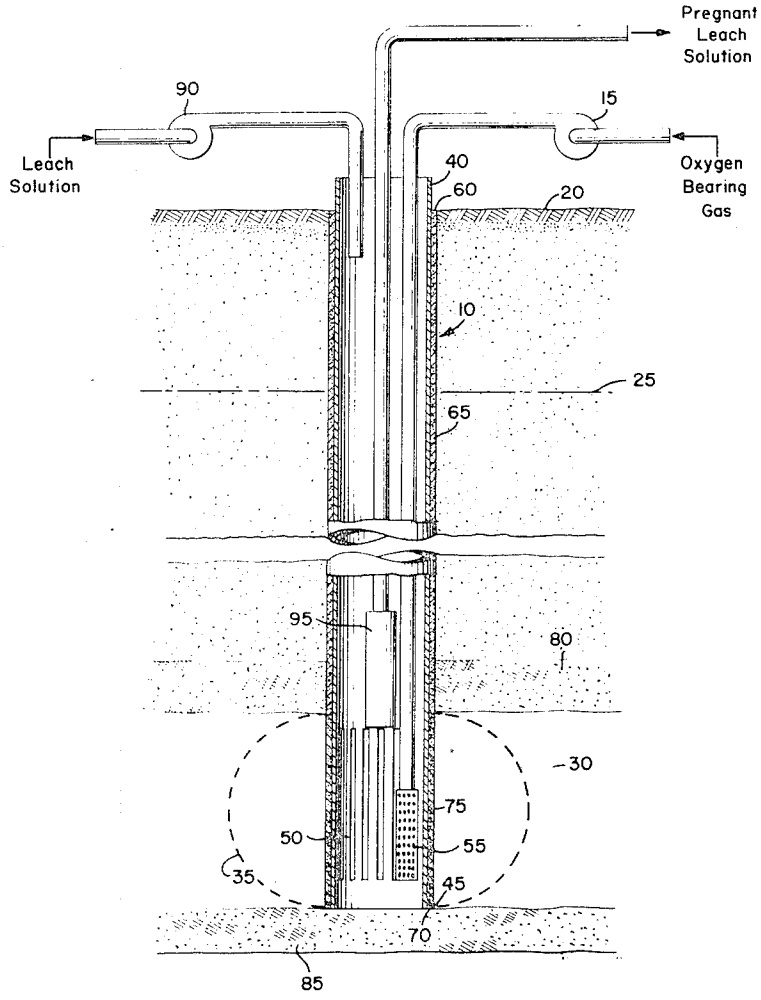
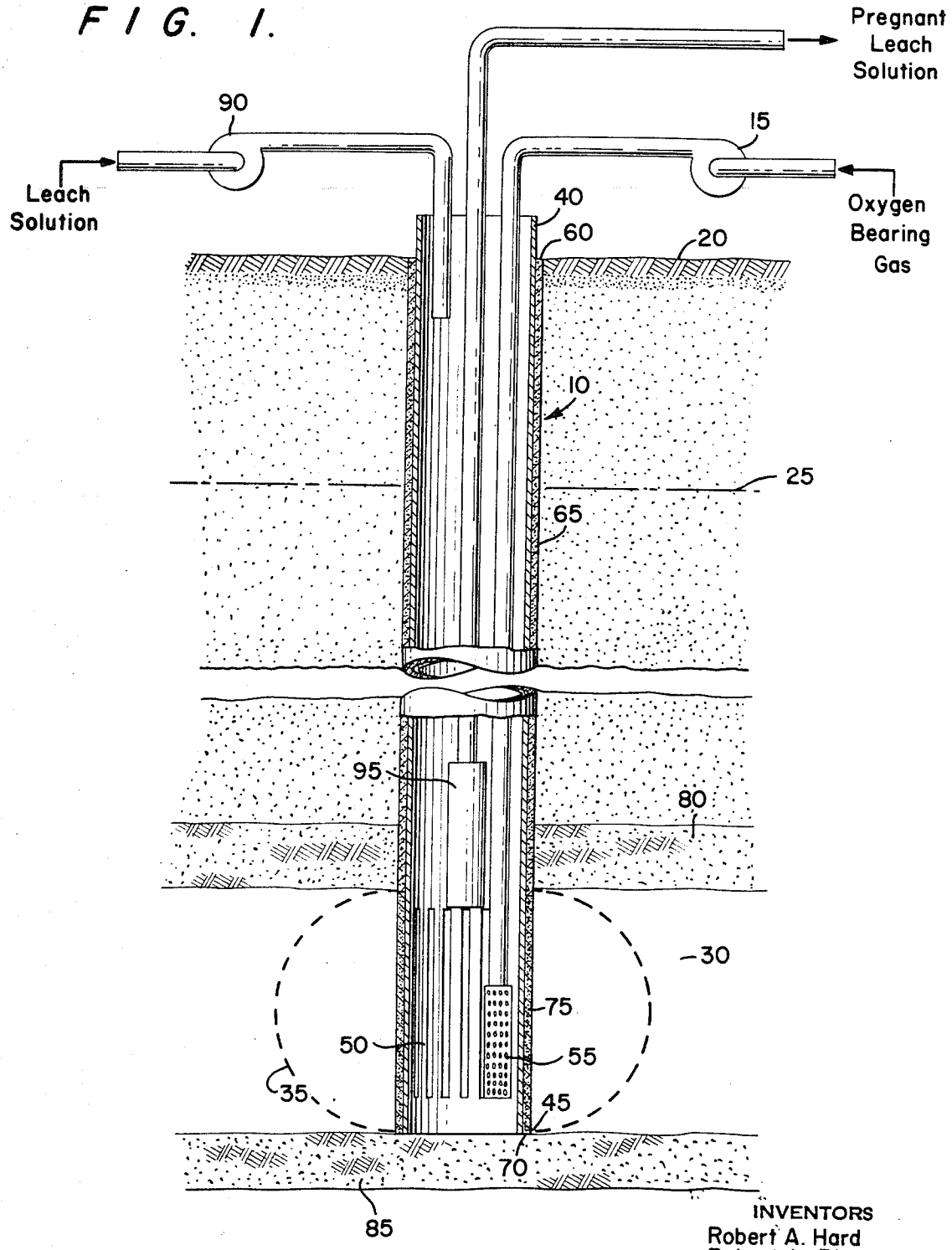


FIG. 1.



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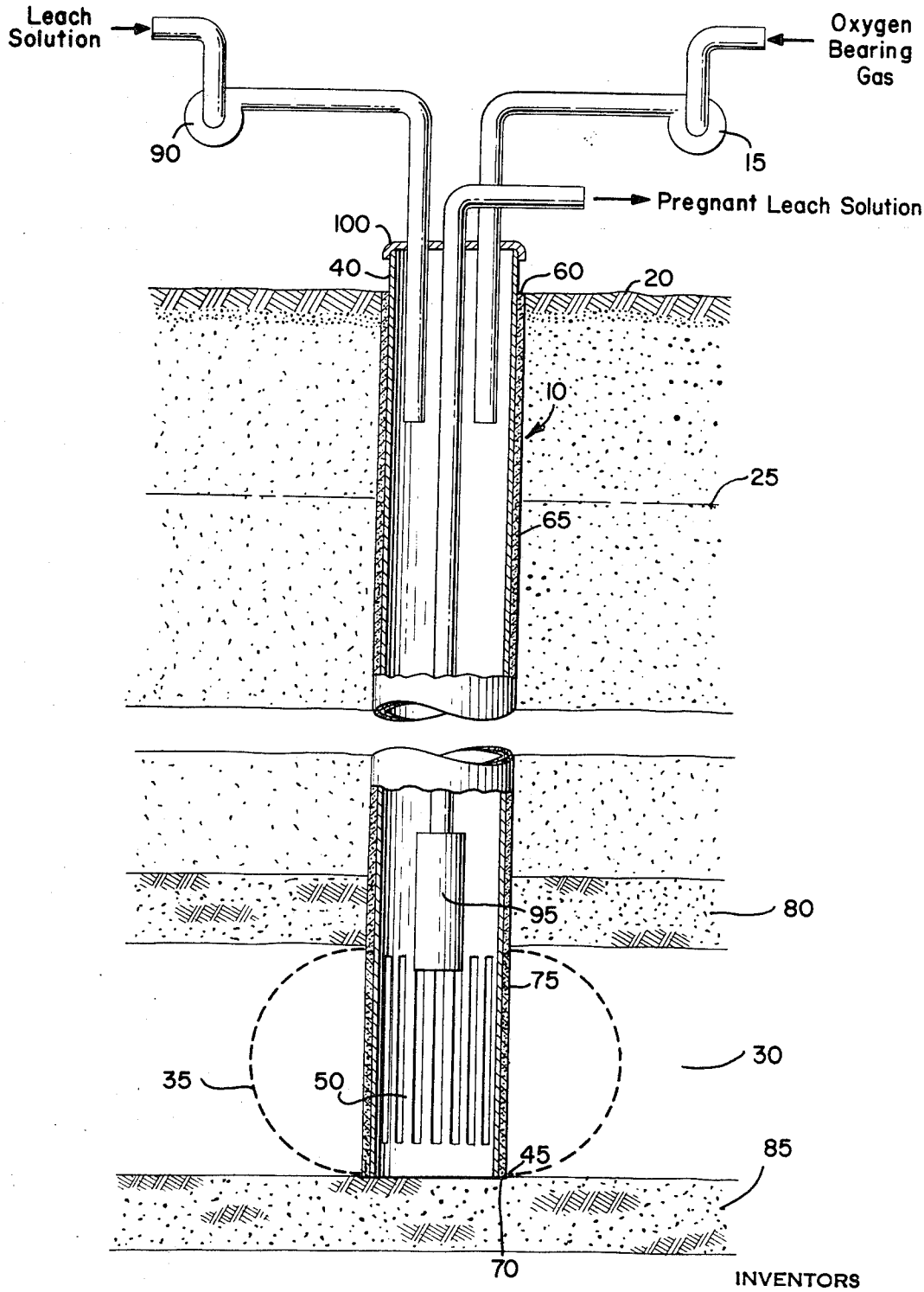


FIG. 2.

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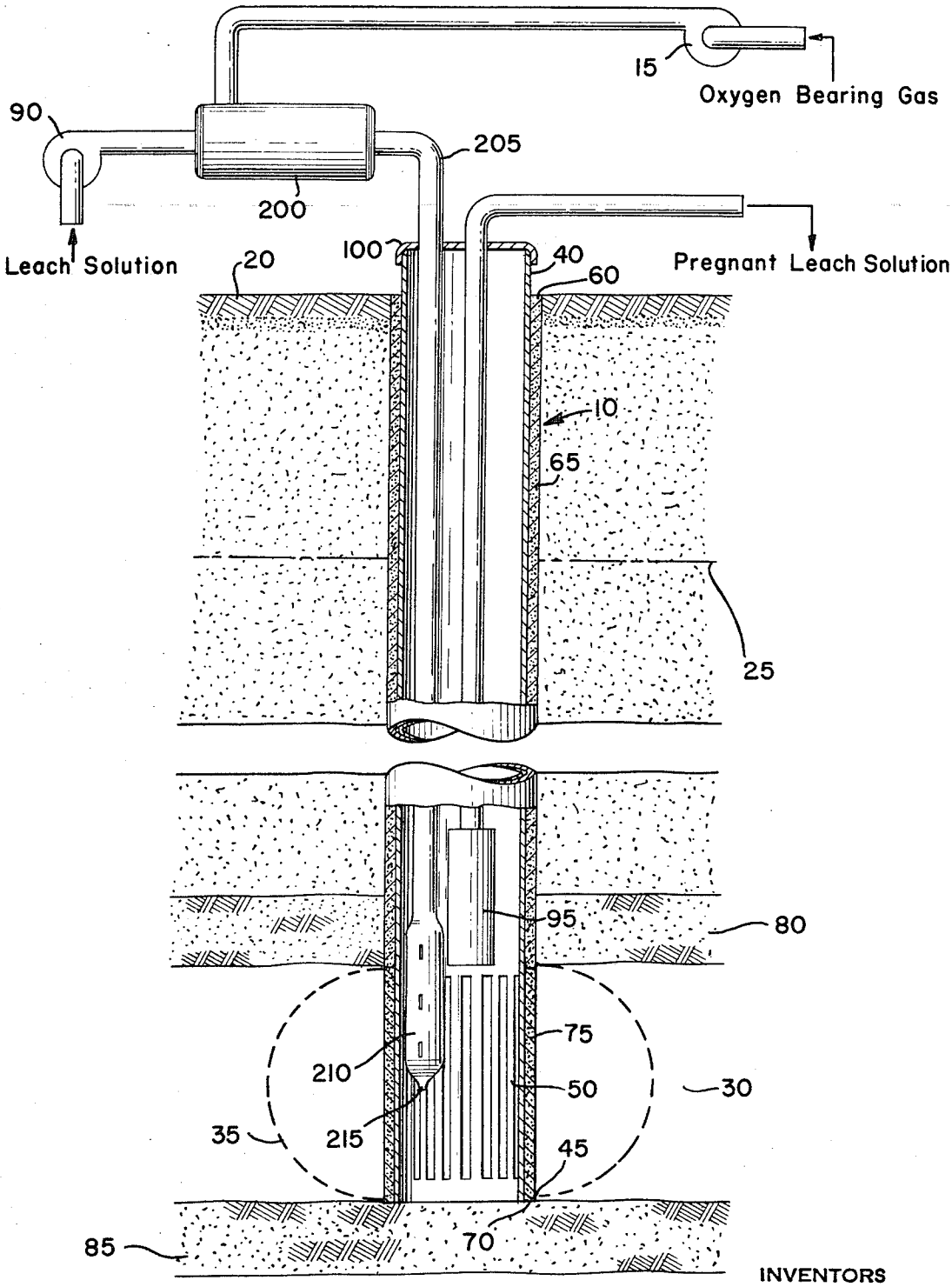


FIG. 3.

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PROCESS FOR LEACHING BASE ELEMENTS, SUCH AS URANIUM ORE, IN SITU

FIELD OF THE INVENTION

This invention relates to a method for recovering at least one base element selected from a group consisting of uranium, copper, nickel, molybdenum, rhenium and selenium, from underground water saturated ore bodies, in situ, which contain oxidizable materials such as sulfides, carbon and the like. More specifically, the invention is directed to an improved method for economically solubilizing at least one base element, such as uranium, in underground ore bodies by utilizing an oxygen bearing gas in conjunction with a leach solution.

DESCRIPTION OF THE PRIOR ART

Presently many uranium and similar mineral mines, located throughout the Western United States, are not in a position to be commercially developed because of their low ore concentration and/or because they are located at remote regions which makes them economically unfeasible for conventional type exploitation. Even ore bodies possessing relatively high ore concentration and located in accessible regions may have its valuable deposit at a depth that conventional mining may not be mechanically or economically feasible.

In recent years a process for tapping these underground ore bodies, in situ, has evolved which has resulted in recovering some mineral values which were formally considered inaccessible by conventional mining techniques. The process consists mainly of drilling a well into an underground ore deposit and then introducing a leach solution to contact the ore therein. The leach solution dissolves the mineral within the ore deposit and thereafter the pregnant solution is recovered and processed by conventional extraction means to recover the particular mineral values therefrom.

However certain preliminary requirements or steps are necessary before the leaching process of minerals, in situ, can be employed. For example, when uranium is to be extracted, the following preliminary information is required:

a. Does the uranium ore occur in a relatively horizontal bed and is it located below the static water level?

b. What is the direction and velocity of the regional water flow?

c. What does a mineralogy test of a sample of the ore reveal as to its characteristics and composition?

The latter information is required so that an intelligent evaluation of the amenability of the ore to different leaching solutions can be made.

At the present time, leaching of minerals, such as uranium, in underground ore bodies, using an acidic leach solution, has been accomplished with some success. One of the primary obstacles encountered, however, is the fact that when leaching uranium, in situ, it is usually present in the tetravalent state and is therefore not amenable to dissolution in an acidic leach solution. Chemical oxidizing agents are presently incorporated in the leach solution to convert, by oxidation, the uranium from its tetravalent state to a soluble hexavalent state which can then be easily dissolved in the leach solution.

The use of chemical oxidizing agents in leach solutions is effective in many respects but has the disadvantage of being a relatively high price raw material. In ore deposits containing significant amounts of readily oxidizable materials other than the base elements, e.g., carbon and sulfur in the form of sulfides, the high cost necessary to extract the base elements by use of chemical oxidizing agents has economically made them inaccessible.

To economically leach these base elements from underground deposits containing other oxidizable materials, it is necessary to oxidize the base elements without consuming excessive amounts of the expensive chemical oxidizing agents or to use a low-cost oxidizing agent that will not provide a financial penalty from the co-oxidation of the oxidizable materials along with the base elements. Since it is almost impossible to selectively oxidize the base elements without consuming the oxidizing agent on other materials found with the base elements in ore deposits, most chemical oxidants are economically ruled out.

The present invention is therefore directed to an improved method in which an oxygen bearing gas is economically used as the oxidant in a leaching process for the recovery of at least one base element, such as uranium, located in an underground ore body below the static water level.

SUMMARY OF THE INVENTION

This invention relates to an improved method for recovering at least one base element selected from the group consisting of uranium, copper, nickel, molybdenum, rhenium and selenium, from an underground ore body containing oxidizable materials, such as carbon and sulfides, and which is located below the static water level. Specifically, an oxygen bearing gas is introduced, under pressure, prior to and/or simultaneously with a leach solution, into an ore bed to convert the relatively insoluble state of a deposited base element in the ore to the solubilizable state. The method of bringing this relatively inexpensive oxidizing agent in sufficient quantities to the ore is extremely important when the ore contains the base element in addition to other oxidizable materials, such as, carbon and sulfur in the form of various sulfides, since a percentage of the oxidant will be consumed in the oxidation of these materials. In addition, it is believed, although not factually proven, that the use of a pressurized oxygen bearing gas will penetrate into the ore body better than expensive chemical oxidizing agents and thereby possibly fracture crevices in the ore body thus exposing a greater surface of the base element for extraction.

With basic compounds, such as limestone or other carbonates, present in the ore deposit, an acidic leach solution can not be economically employed since a large proportion of the acidic solution would be consumed by the carbonates. A basic leach solution, such as ammonium carbonate or sodium carbonate, in conjunction with an oxygen bearing gas such as oxygen, air and any and all mixtures thereof form the principal ingredients of the leaching process of this invention.

Although the process of this invention is directed to the leaching of a variety of base elements from underground ore bodies, the discussion hereinafter will be directed to the leaching of uranium, in situ, which will

serve as an example to explain how the process could be implemented to increase the recovery of the base elements from underground ore bodies.

To increase the recovery of uranium values from an underground ore body, it is necessary to convert the relatively insoluble tetravalent state of the uranium in the ore to the solubilizable hexavalent state.

The complete dissolution of uranium in a carbonate solution occurs in two steps, either of which may be considered rate-controlling for the recovery of uranium values. The first reaction involves the oxidation of uranium by absorbing oxygen and the second reaction is the dissolution of the oxidized uranium in a carbonate solution. The rate of dissolution of the latter reaction is dependent upon the surface area of the uranium exposed and the concentration of the carbonate ion in solution. With both reactions assumed to be rate-controlling, a finding that in a particular leach process the carbonate ion concentration is having little effect would indicate that the rate-controlling step is in the oxidation reaction. To increase the recovery of uranium values, the oxygen concentration would have to be increased which requires the pressure of the oxygen to be increased so that a sufficient supply of oxygen will be available to convert the uranium into its soluble tetravalent state. On the other hand, if oxygen pressure has little or no effect on the percentage of uranium being recovered, then the dissolution reaction is the rate-controlling step. To increase the percentage of uranium recovery, the carbonate ion concentration has to be increased to a sufficient level in the leach solution to dissolve all the uranium in the hexavalent state.

The proper analysis of an ore body, along with the effect produced by varying the oxygen pressure and carbonate concentration in the leach solution, can be used to provide the optimum combination of these ingredients for recovering maximum uranium from the ore body. However, a limiting factor in deciding the pressure is to limit it to a value at which rock failure and/or ground level uplift occurs. In addition the pressure limitation should depend on the permeability, depth of ore deposit, hydrostatic head pressure, extent of ore formation and rate of oxidation of the ore so that the volume penetrated by the oxygen bearing gas will be substantially confined to a zone that the leach solution can contact and be recovered from without being essentially diluted with ground water.

The object of this invention, as exemplified by the leaching of uranium, in situ, will be apparent from the following description and claims taken in conjunction with the drawings of FIGS. 1 through 3.

FIG. 1 is a cross-sectional elevated view of an arrangement suitable for the practice of this invention which shows a well communicating with an ore body for introducing of reagents;

FIG. 2 shows a modification of the arrangement of FIG. 1 wherein a pressurized casing cap is added so that the leach solution can be injected while holding the oxygen bearing gas under pressure.

FIG. 3 shows another arrangement of FIG. 1 whereby pressurizing means is added for supersaturating a leach solution with an oxygen bearing gas with respect to the hydrostatic ground water pressure.

The preliminary step to be conducted in the leaching operation of this invention is to test and analyze a sample of the ore body so as to ascertain the extent of its mineral contents. A lithological study of the ore body will reveal the porosity and permeability of the ore and the materials surrounding it. One method presently employed for this purpose is to drill out cores of the ore formation at different depth intervals and then have the cores chemically analyzed to determine permeability and ore level formation.

Once this information is obtained and evaluated, and found to contain uranium, a well bore is drilled into the ore body. An oxygen bearing gas is then introduced, under pressure, through the well into the uranium ore body located below the ground water level. Although the exact mechanism occuring in the ore body is not known, and since we don't want to be bound by theory, we are of the opinion that the oxygen bearing gas enters the ore body in the form of at least one large bubble which displaces the ground water about the well. This exposes the ore body in a zone surrounding the well to the oxygen bearing gas which oxidizes the ore, such as uranium, into a soluble state. A leach solution is thereafter introduced into this oxygen treated ore zone to dissolve the uranium therein and then the solution is recovered and treated by conventional means to extract the uranium values.

In a particular embodiment for practicing this invention, as shown in FIG. 1, a conventional well bore 10 is drilled from surface 20 into an underground body of uranium ore 30 which is located below the static water level 25 and sandwiched between impermeable clay seams 80 and 85. A casing tube 40 is positioned within and spaced from well 10 and terminated at a depth indicated by 45 which is within horizontal ore body 30. A slotted member 50, such as a screen or other similar arrangement, forms the lower extremity of casing 40 and extends in a downward direction through ore body 30. The length of the slotted member 50 depends upon the depth of ore body 30.

A water permeable material 75, such as sized gravel or the like is placed in annular cavity 70 between slotted member 50 and well bore 10, for the entire length of slotted member 50.

Annular cavity 60, between well 10 and casing 40, is sealed its entire length down to slotted member 50. Any suitable sealer 65 can be used such as cement or a solution of chemical gel which can be triggered to solidify once in position.

Compressor means 15 is coupled to diffuser 55 and together they are used to force feed the oxygen bearing gas, under pressure, through casing 40 into zone 35 surrounding screen member 50. During this injection feed it may be necessary to cap the casing, as shown in FIG. 2, so as to force the gas into zone 35. The exact contour of zone 35 is not known, but it is believed that the pressurized oxygen bearing gas displaces the water surrounding screen member 50 in a radially outward direction forming a somewhat circular to cylindrical zone 35. The size of zone 35 is variable and depends among other things on the porosity of the ore body, the presence of impermeable clay zones, the flow rate of the ground water and the pressure produced by the static head or through pumping.

In zone 35, the uranium values in the ore are contacted with the oxygen bearing gas which converts the uranium from the tetravalent state to the soluble hexavalent state in the same general manner as provided through the use of chemical oxidizing agents. After sufficient time has elapsed for this uranium conversion to occur, the pressure on the gas can be released and the ground water permitted to return into zone 35. The time for oxidizing the uranium in the ore body is a function of the physical and chemical properties of the ore body.

Thereafter a leach solution containing ammonium carbonate, sodium carbonate or sulfuric acid, depending upon the nature of the ore body, is introduced into well casing 40 by gravity or by using, for example, pump 90. The leach solution passes through well casing 40 and slotted member 50 into the water saturated, oxygen treated ore body 30. The solution displaces the ground water surrounding screen member 50 in approximately the location of previously established oxygen treatment zone 35. The leach solution reacts with and dissolves the previously oxidized hexavalent uranium values and is subsequently withdrawn by means of submersible pump 95. The pregnant leach solution is thereafter treated by conventional techniques to recover the uranium values.

In a further embodiment of the invention, as shown in FIG. 2 with some members identical to those shown in FIG. 1 and numbered accordingly, a pressure casing cap 100 is disposed on casing 40 to maintain pressure within the casing. Thus the pressurized oxygen bearing gas from compressor means 15 can be held under pressure while the leach solution is injected into zone 35 by means of pump 90.

In the operational mode an oxygen bearing gas, under pressure, is introduced into zone 35 to oxidize the uranium contained in ore zone 30. After a sufficient oxidation period has elapsed, the pressure on the oxygen bearing gas can be maintained while a leach solution is introduced from pump 90 through well casing 40 into zone 35. The advantage of maintaining the pressure on the oxygen bearing gas during the introduction of the leach solution is that the gas could possibly form somewhat of a barrier between the leach solution and the ground water thus decreasing the likelihood of dilution of the former with the latter. In addition, with an oxygen bearing gas present in sufficient quantity during the dissolution of the hexavalent uranium values, newly exposed or unoxidizable tetravalent uranium values can be oxidized and immediately dissolved in the leach solution.

It is also possible with this arrangement to introduce the oxygen bearing gas first and then after releasing the pressure to reintroduce an additional supply of the oxygen bearing gas at the same time as introducing the leach solution. This will provide a leach solution saturated with the oxygen bearing gas in zone 35 during the dissolution of the hexavalent uranium values.

Another embodiment of the invention, as shown in FIG. 3 and having some members identical to those shown in FIG. 2 and numbered accordingly, employs a pressurizing chamber 200 coupled to tube 205 having an enlarged injection pipe 210 at its lower portion. At the lower extremity of pipe 210 is an expansion orifice 215. A leach solution and an oxygen bearing gas is fed via pumps 90 and 15, respectively, into compressor 200 which in turn injects a leach-oxygenated foam into zone 35 via pipe 210 and orifice 215.

In the operational mode, a pressurized oxygen bearing gas and a leach solution are introduced into pressurizing chamber 200 wherein the leach solution is saturated with the pressurized oxygen bearing gas. The solution is pumped through tube 205, pipe 210 and then expands through orifice 215 whereupon a supersaturated oxygen foam is created due to a drop in pressure. This oxygenated foam is fed into zone 35 of ore body 30 in the form of a multiple of small bubbles which contacts and oxidizes the uranium therein to the hexavalent state which is then dissolved by the leach solution. Thus, by having a leach-oxygenated foam solution introduced into zone 35, the oxygen bearing gas can then be dispersed in a multitude of small bubbles throughout ore body 30 in a manner somewhat analagous to the effervescence associated with common seltzer water. Although not factually known, it is believed that the small bubbles penetrate further into the crevices in the ore formation oxidizing the uranium into a more solubilized state whereby it can be dissolved in the leach solution. By supersaturating the leach solution with the oxygen bearing gas, ample oxygen will be available in small bubbles for the oxidation reaction of the uranium. It is also possible to precede the initial introduction of the supersaturated solution with an oxidation step wherein the oxygen bearing gas is introduced alone so as to prepare the uranium for solubilization. Whether or not to add this initial oxidation step will depend on the quality and concentration of the uranium and other minerals in the ore body along with the physical characteristics of the ore formation. Initial testing of an ore deposit will usually provide sufficient information for determining which approach to take, i.e., whether to employ the initial oxidation step or not. As stated above, in some ore deposits large quantities of oxidizable materials are present in addition to uranium, and therefore it might be advantageous to include this oxidation step since a portion of the oxygen would be consumed by such materials.

Although FIG. 3 shows one approach to producing an oxygenated foam, that is, dissolving oxygen in a leach solution at above atmospheric pressure and then releasing the pressure on the solution at the vicinity of the ore zone, any means for creating an oxygenated foam can be used as long as the foam can produce a multiple of oxygen bearing gas bubbles in the vicinity of the ore zone. For example, any oxygen bearing medium which is capable of being injected into the ore zone and thereafter, through chemical or physical mechanism, produce an oxygenated foam can be used.

It is to be understood that this invention can be practiced by using only one well for both introducing the reagents and then recovering the pregnant solution therefrom. Also two or more wells penetrating the ore body may be used so that the reagents can be introduced into the ore body through at least one well and the pregnant solution recovered from at least one different well.

EXAMPLE I

In the Palangana Dome section of Duval County, Texas, a uranium ore body was located in a calcareous sandstone formation. Core samples from a hole dug to a depth of 270 feet in the region were taken and chemically analyzed. A lithology of the core samples revealed a uranium ore zone about 7 feet thick sandwiched between layers of green clay. A permeability analysis of the ore zone disclosed a horizontal permeability between 600 to 1,900 millidarcys while the permeability in the clay layers varied between 4 to 8 millidarcys. The static ground water level was 100 feet below the ground surface.

A 4-foot cased and sealed well having a slotted member at its lower end, as illustrated in FIG. 2, except that a composite of bentonite and mud was used to seal the well to the upper clay layer, was embedded into the ore formation. A positive displacement pump was used to force air through the well into the uranium ore body. The rate of air introduction was 40 scfm at psig of 100. This was continued for 16 hours. Based on the porosity of the ore body and observations at monitor wells located circumferentially around the air carrying well, a zone containing about 23,000 cubic feet and essentially free of ground water extended radially into the ore body for about 29 feet from the air carrying well. The flow was discontinued and ground water returned to the zone from which it had been displaced. An aqueous leach solution containing 26 grams per liter of ammonium carbonate, $(NH_4)_2CO_3$, was introduced with the ore body at a rate of 8.7 gallons per minute. A total of 24,078 gallons of leach solution was introduced. After a period of 3 days, the leach solution was withdrawn through the well and analysis showed it to contain an average of 0.13 g/liter of U_3O_8 with a maximum grade of 0.30 g/liter. This compared to an analysis of an average of 0.08 g/liter of U_3O_8 with a maximum grade of 0.12 g/liter which was obtained following essentially the same procedure except that the air treatment was not used.

EXAMPLE II

In the Palangana Dome section of Duval County, Texas, an identical ore formation as in Example I was located and a cased and sealed well was embedded into the ore formation in an identical manner.

A positive displacement pump was used to force oxygen through the well into the uranium ore body. The rate of oxygen introduction was 69 scfm at psig of 104. This was continued for 9 hours and 42 minutes. Based on the porosity of the ore body and observations at monitor wells located circumferentially around the oxygen carrying well, a zone containing about 23,000 cubic feet and essentially free of ground water extended radially into the ore body for about 29 feet from the oxygen carrying well. The flow was discontinued and pressure was maintained in the well for 18 hours. At the end of this period pressure on the well was released on ground water returned to the zone from which it had been displaced. An aqueous leach solution containing 23 grams per liter of ammonium carbonate, $(NH_4)_2COB3$, was introduced into the ore body at a rate of 11.8 gallons per minute. A total of 21,272 gallons of leach solution was introduced after which the leach solution was immediately withdrawn through the well and analysis showed it to contain an average of 0.47 grams per liter of U_3O_8 with a maximum grade of 1.20 grams per liter. This compared to an analysis of an average of 0.08 grams per liter of U_3O_8 with a maximum of 0.12 grams per liter which was obtained following essentially the same procedure except that the oxygen treatment was not used.

Although the above examples are directed to the leaching of uranium, in situ, it is to be understood that the process of this invention, wherein an oxygen bearing gas is used as an oxidant for underground leaching, can be utilized to leach other base elements such as nickel, copper, molybdenum, rhenium and selenium. For example, small quantities of the latter four elements were leached out along with the uranium in the above examples. The exact per cent of each of these elements recovered was not ascertained since only miniscule amounts of each element was present in the original ore body. However, if substantial amounts of these elements were present in the ore body then the recovery of these elements would have been noticeably increased using the process of this invention.

The process of this invention is therefore intended for use where an inexpensive oxidant is required prior to or along with a leach solution for the purpose of oxidizing any of a number of base elements within an ore body to a state that will be amenable to solubilization. For example, when sulfides of nickel are present in an ore body, the oxygen bearing gas will react with the NiS to form $NiSo_4$ which can then react with a leach solution, such as NH_3, to form $Ni(NH_3)_6^{++} + SO_4 - -$. This pregnant nickel-bearing solution can then be extracted from the ore body and thereafter treated by conventional techniques to remove the nickel values.

What is claimed is:

1. A process of leaching at least one base element selected from the group consisting of uranium, copper, nickel, molybdenum, rhenium and selenium, from an underground body of ore, in situ, which is saturated with ground water comprising:
   a. drilling at least one well into the underground body of ore;
   b. casing and sealing said well;
   c. introducing an oxygen bearing gas through at least one well into a zone in said ore body surrounding the well so that the oxygen bearing gas can contact and oxidize the base element in said zone of the ore body;
   d. discontinuing said introduction of the oxygen bearing gas;
   e. subsequently introducing a leach solution into said oxygen treated zone to dissolve the solubilized base element therein;
   f. recovering the pregnant leach solution containing the dissolved base element from at least one well; and
   g. treating said pregnant leach solution to extract the base element values therefrom.

2. The process of claim 1 wherein said oxygen bearing gas is introduced into the zone in said ore body in the form of a oxygenated foam.

3. The process of claim 2 wherein said base element is uranium.

4. The process of claim 1 wherein said oxygen bearing gas in step (c) is introduced under pressure, said pressure determined by the permeability, depth of ore deposit, hydrostatic head pressure, extent of ore formation and rate of oxidation of the ore so that the volume of the zone penetrated by the oxygen bearing gas will be substantially confined to a zone that the leach solution can contact and be recovered from without being essentially diluted with ground water.

5. The process of claim 4 wherein said oxygen bearing gas is selected from a group consisting of air, oxygen and mixtures thereof.

6. The process of claim 5 wherein the leach solution is introduced into at least one well and recovered from at least one different well located within the oxidized treated zone.

7. The process of claim 5 wherein after step (d) the step of maintaining the pressure on the oxygen bearing gas during introduction of the leach solution is added.

8. The process of claim 7 wherein said base element is uranium.

9. The process of claim 5 wherein said leach solution is selected from a group consisting of ammonium carbonate, sodium carbonate and sulfuric acid.

10. The process of claim 9 wherein said leach solution is saturated with an oxygen bearing gas under pressure.

11. The process of claim 10 wherein said base element is uranium.

12. The process of claim 9 wherein said leach solution is supersaturated with an oxygen bearing gas with respect to the hydrostatic ground water pressure.

13. The process of claim 12 wherein said base element is uranium.

14. A process of leaching at least one base element selected from a group consisting of uranium, copper, nickel, molybdenum, rhenium and selinium, from an underground body of ore, in situ, which is saturated with ground water comprising:

a. drilling at least one well into the underground body of ore;

b. casing and sealing said well;

c. introducing under pressure a leach solution saturated with an oxygen bearing gas into at least one well so that the solution will displace the ground water in a zone of the ore body surrounding the well so that the oxygen bearing gas can contact and oxidize the base element therein and the leach solution can contact and dissolve the solubilized base element so formed;

d. recovering the pregnant leach solution containing the dissolved base element from at least one well; and

e. treating said pregnant leach solution to extract the base element values therefrom.

15. The process of claim 14 wherein the leach solution is introduced into at least one well and recovered from at least one different well located within the zone.

16. The process of claim 14 wherein the oxygen bearing gas is selected from a group consisting of air, oxygen and mixtures thereof.

17. The process of claim 16 wherein the leach solution is selected from a group consisting of ammonium carbonate, sodium carbonate and sulfuric acid.

18. The process of claim 17 wherein said base element is uranium.

19. The process of claim 14 wherein the leach solution is supersaturated with an oxygen bearing gas with respect to the hydrostatic ground water pressure.

20. The process of claim 19 wherein said oxygen bearing gas is selected from a group consisting of air, oxygen and mixtures thereof, and wherein said leach solution is selected from a group consisting of ammonium carbonate, sodium carbonate and sulfuric acid.

21. The process of claim 20 wherein said base material is uranium.

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