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[54] **ACID PRE-TREATMENT METHOD FOR IN SITU ORE LEACHING**

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[58] **Field of Search** ..... 299/4, 5; 75/101 R, 75/101 BE, 75/117; 166/247

[56] **References Cited**

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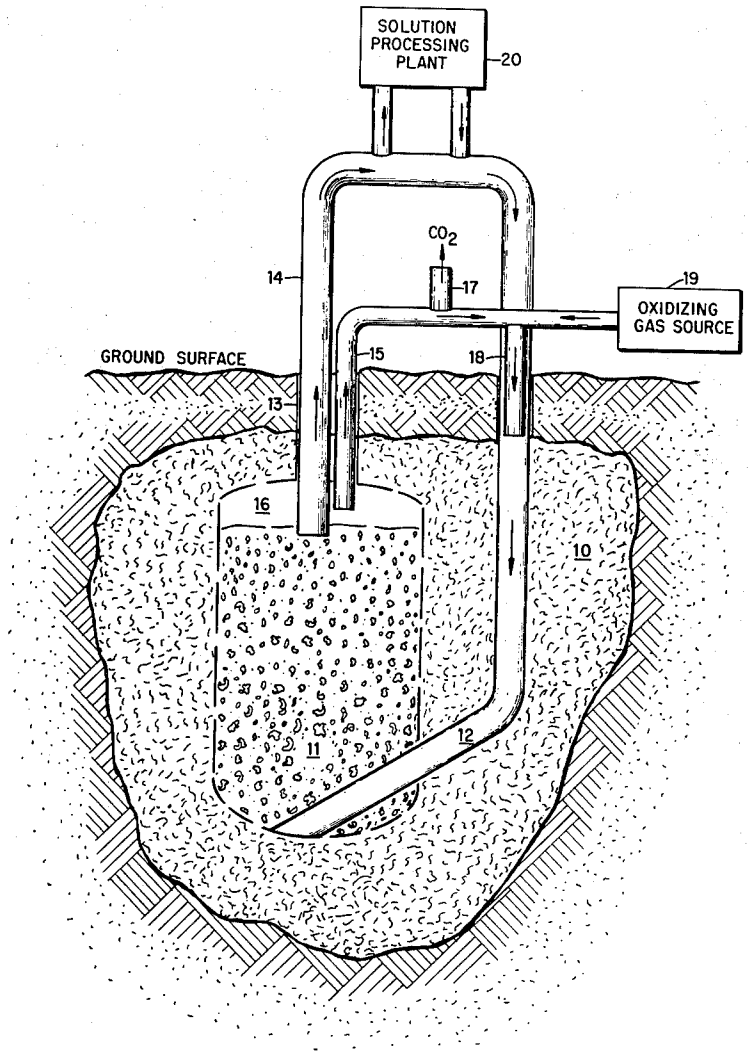
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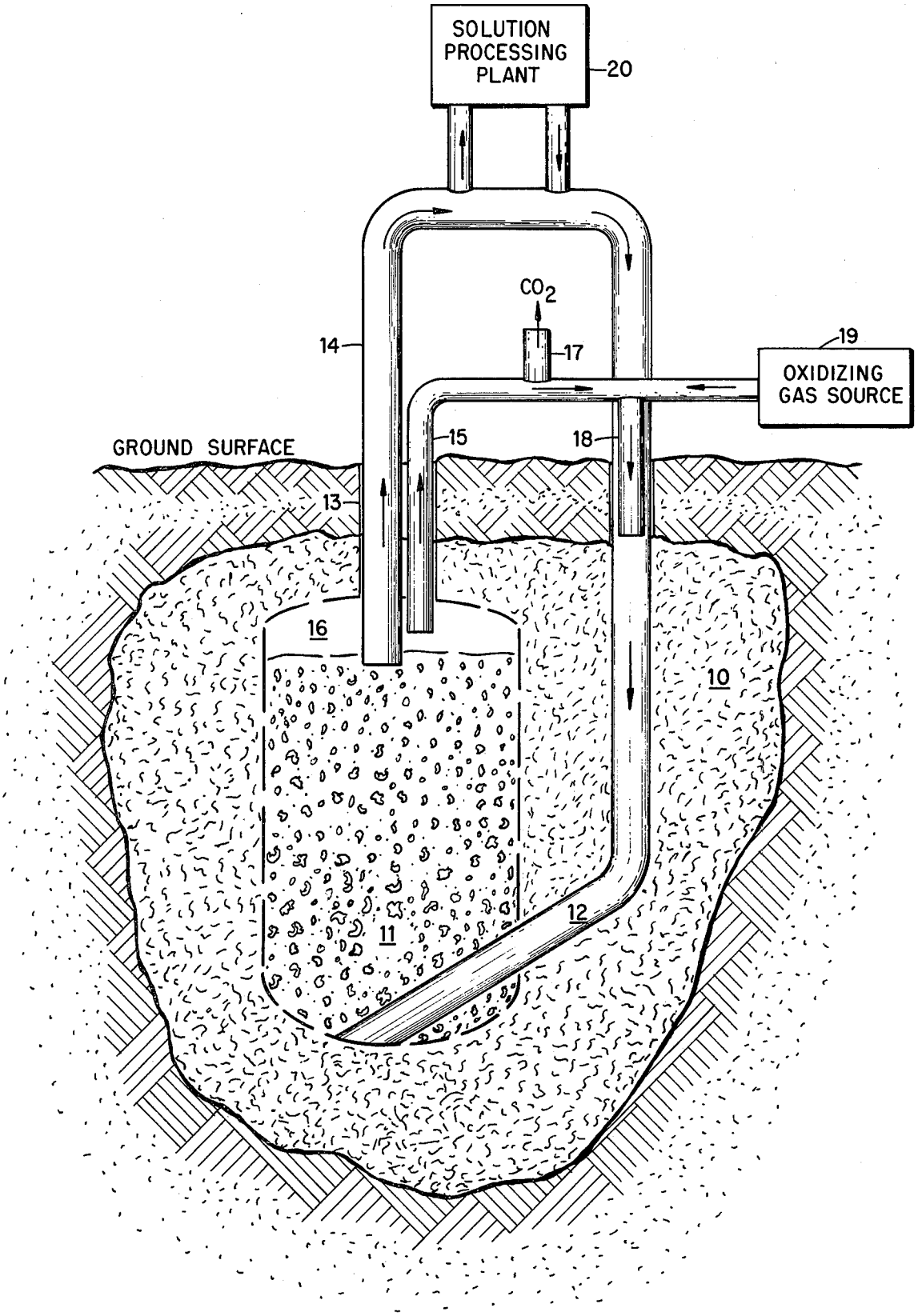
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[57] **ABSTRACT**

An acid leaching method for the recovery of a desired element from a subterranean rubblized body of primary ore containing the element and also having associated therewith a carbonate mineral wherein the rubblized ore body is flooded with an aqueous acidic solution in order to release carbon dioxide from the associated carbonate mineral. After a substantial portion of the available carbon dioxide is released and removed from the ore body, as by venting to the atmosphere, an oxidizing gas is introduced into the flooded, rubblized ore to oxidize the ore and form an acid leach solution effective in the presence of the dissolved oxidizing gas to dissolve the ore and cause the desired element to go into solution. The leach solution is then circulated to the surface where the metal values are recovered therefrom.

8 Claims, 1 Drawing Figure




SOLUTION PROCESSING PLANT
20
CO_2
14
17
19
OXIDIZING GAS SOURCE
GROUND SURFACE
15
18
13
16
10
11
12

ACID PRE-TREATMENT METHOD FOR IN SITU ORE LEACHING

The invention disclosed herein was made in the course of or under contract W-7405-ENG-48 with the United States Atomic Energy Commission.

BACKGROUND OF THE INVENTION

This invention relates to the acid leaching of primary ores, specifically, primary sulfide ores having carbonate minerals associated therewith, for the recovery of metal values therefrom.

Large ore deposits, particularly copper ore deposits, typically have a relatively shallow oxidized secondary ore zone above the water table and a much deeper unoxidized primary ore zone below the water table. Many of such primary deposits have been upgraded by processes of oxidation and supergene enrichment to concentrations that make them economically feasible to mine. The enrichment process is a near-surface process. Most ore deposits have been developed by mining the enriched and oxidized zone thereof. Only where the primary ore is rich enough has it been economical to mine at depth or, with large and efficient earth-moving equipment, to mine large deposits in open-pit mines. Leaching techniques have been applied economically to the oxidized parts of ore deposits or to those that can be oxidized by alternate solution and weathering or bacterial oxidation. Because of the low permeability of such ore deposits, this has not been done in place, with the exception of some leaching operations conducted on caved material in mine workings. Hence, large deposits of primary ores, e.g., primary sulfide ores, remain undeveloped because they lie too deep to mine economically, their size is too small to allow the economics of large-scale mining operations, the grade is too low, or various combinations of these factors. Reserves of copper and other elements would be considerably increased if an economical process of obtaining such elements from deep primary ore deposits were available.

With a view towards economic recovery of elements from deep ore deposits, it has been proposed to break up deep ore deposits, e.g., by contained nuclear explosion or by conventional mining methods such as block caving, to form a rubblized ore body, and then percolate a leach solution through the rubblized ore to oxidize the broken ore and cause the desired element to go into solution. Certain ores, such as chalcopyrite ($CuFeS_2$) and most other primary sulfide minerals, require the addition of an oxidizing gas, such as oxygen, to the leach solution or the ore in order to effectively leach the desired element therefrom. The oxygen, dissolved in water, oxidizes some of the sulfides, particularly pyrite (FeS_2) and produces an acid leaching solution which in the presence of the dissolved oxidizing gas dissolves the ore. Such acid leaching processes are disclosed, for example, by Arthur E. Lewis, U.S. Pat No. **3,640,579,** "In Situ Pressure Leaching Method," issued Feb. **8, 1972,** and in the copending application of Arthur E. Lewis, Ser. No. **347,757,** filed Apr. **4, 1973** now U.S. Pat. No. **3,823,981** issued July **16, 1974.**

In certain areas, however, the primary ore deposits have associated therewith carbonate minerals in quantities sufficient to interfere with the acid leaching process. The acidic leaching solution reacts with the carbonates present to liberate carbon dioxide which suppresses the leaching reactions by interfering with the transport of oxygen to the desired reaction sites. Furthermore, any undissolved oxidizing gas discharged from the rubblized ore region is contaminated with carbon dioxide which will further interfere with the transport of oxidizing gas.

SUMMARY OF THE INVENTION

It is, therefore, among the objects of this invention to provide an improved acid leaching process for the recovery of valuable elements from their primary ores, more particularly, from primary sulfide deposits having carbonate minerals associated therewith.

In accordance with the process of the present invention, well known technology, such as underground nuclear technology or conventional mining technology, is employed to form a rubblized ore region or chimney in a subterranean ore deposit, preferably well below the water table, to serve as an in situ leaching vessel. Thereafter, as a salient feature of the invention, the rubblized region is flooded with acidized water which decomposes at least a portion of any carbonate minerals present, thereby liberating carbon dioxide which is then discharged from the ore body, e.g., by venting to the atmosphere. After a substantial portion of the available carbon dioxide has been released and discharged from the rubble region, an oxidizing gas, preferably oxygen, is introduced into the region in order to form the oxygenated leach solution and dissolve the ore, as described above. The leach solution is subsequently pumped to the surface and the desired element recovered therefrom by conventional processes, such as replacement, electrolysis, hydrogen reduction, ion exchange, solvent extraction, etc.

Generally, according to the present invention it is preferred to provide and utilize a nuclear chimney created by the detonation of a contained nuclear explosive in a primary ore deposit well below the water table, as in the leaching operation disclosed in the above-cited Lewis U.S. Pat No. **3,640,579.** The broken ore in the filled chimney is thus subjected to hydrostatic pressures which are dependent upon the prevailing water head. The hydrostatic pressure acting on the chimney is utilized to enhance the dissolution of oxygen, thereby increasing the leaching rate.

BRIEF DESCRIPTION OF THE DRAWING

The invention is illustrated in the accompanying drawing wherein the single FIGURE is a cross section of a geological formation with a rubblized ore region formed in a primary ore deposit and adapted to the conduct of a leaching method in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Referring now to the drawing in detail, there is shown a primary ore deposit **10** which includes compounds of a valuable element which is desired to be obtained. For example, in the case of copper the ore may comprise copper sulfides such as chalcopyrite, bornite, chalcocite, etc. Thereafter, a chimney **11** of broken ore is formed in the deposit. Although the column of rubblized ore is best prepared using a nuclear explosive placed well below the water table as noted above, preparation is also possible with more conventional mining processes, e.g., block caving.

The leaching operation of the present invention is preferably accomplished by drilling at least one shaft **12** which is provided with a casing to communicate with the bottom of the chimney **11** and at least one borehole **13** to communicate with the top portion thereof. The lower end of the casing of shaft **12** may be perforated over a length extending across the bottom of the cavity so as to disperse injected materials more effectively. Borehole **13** is provided with pipes **14** and **15** extending therethrough in spaced relation to each other and to the sides of the borehole, pipe **14** communicating with the top portion of the chimney for extraction of leach solution and pipe **15** communicating with the top portion of the chimney for discharge of gaseous material therefrom. Often times a void space **16** of considerable volume is formed in the upper portion of the chimney in which event pipe **15** communicates with the void space. Sufficient acidized water is then introduced via cased shaft or well bore **12** to fill the rubble column or chimney until the natural water level is restored. Since the rubblized ore column is preferably well below the water table, column **11** can be flooded at least partially by the natural inflow of water under the hydrostatic head of its vertical displacement below the water table. However, natural flooding is relatively time consuming, and, consequently, it is preferred to provide most of the required water by artificial inflow. To provide conditions suitable for the subsequent leaching operation, the pH of the flooding solution is preferably lower than that desired for leaching since a portion of the added acid will be consumed by reaction with carbonate minerals. For example, in the case of recovery of copper from primary copper sulfide ores the pH of the flooding solution is preferably below substantially **3,** specifically in the range of from substantially **0.1** to substantially **2.**

The acidized water added to column **11** reacts with carbonate minerals present to liberate carbon dioxide which rises upward through the chimney and through pipe **15.** The thus released carbon dioxide is then vented to the atmosphere by means of line **17.** Reaction with carbonates is permitted to proceed until a substantial portion of the available carbon dioxide is released and discharged from the rubblized ore. This acid flooding and pretreatment stage may require about **20** days or more, depending upon the proportion of carbonate mineral present in the primary ore and the volume of rubble column.

After a substantial portion of the carbon dioxide has been discharged from the rubblized ore, vent **17** is closed, and an oxidizing gas is then introduced to the bottom of the chimney via the shaft **12** as by means of a pipe **18** extending at least partially therethrough in spaced relation to the shaft wall and connected at its upper end to a suitable compressed gas source **19.** Preferably, pipe **18** terminates in a perforated nozzle section somewhat above the top of the chimney. Thus, the oxidizing gas exits as a stream of fine bubbles substantially uniformly dispersed in the downwardly flowing liquid leach solution; the bubbles of gas are carried downward with the liquid stream and are thus compressed by the increasing hydrostatic pressure. This method of injection also greatly reduces the problem of anhydrite (anhydrous calcium sulfate) deposition; if anhydrite should be deposited in the injection pipe, the pipe is readily accessible for maintenance.

The oxidizing gas is introduced into the bottom of chimney **11** at a pressure equal to or slightly above the hydrostatic pressure. As the bubbles rise through the chimney, part of the gas dissolves. The undissolved gas, as it rises through the chimney, provides a lifting force that induces enough circulation in the chimney to carry dissolved gas to all parts of the chimney. Since a major portion of the carbon dioxide is removed in the acid pre-treatment stage, only minor amounts of carbon dioxide are liberated during the leaching operation. Thus, circulation of the oxidizing gas and the subsequent oxidation reactions can proceed without interference from substantial amounts of carbon dioxide. By virtue of the high pressure in the chimney, the solubility of the oxidizing gas is increased such that it readily dissolves and oxidizes the ore minerals to form an acid leach solution in the reaction. The acid solution aids the oxidation of the ore minerals by the oxidizing gas and the desired ore element goes into solution at a relatively rapid rate. Any excess undissolved oxidizing gas rises to the surface and is discharged via pipe **15** for reuse in the leaching operation. As a consequence of the acid pre-treatment step of the present invention, the discharged oxidizing gas will not be contaminated with substantial amounts of carbon dioxide and can therefore be fed directly into resupply pipe **18.**

Leach solution is extracted from the chimney, preferably by pumping same to the ground surface as by means of a pump (not shown) communicating with the chimney via pipe **14.** The pump delivers the pregnant leach solution to a solution processing plant **20** to recover the desired element therefrom and/or recirculates the solution to the chimney through the clearance space existing between the pipe **18** and the wall of the shaft **12.** In this manner the leach solution can be recirculated until the concentration of the desired element dissolved therein is high enough for profitable recovery, e.g., in the range of from about **1** to about **20** or more grams per liter. Preferably, during production, the pregnant solution from the chimney is circulated to the surface continuously and reintroduced into the chimney along with added oxidizing gas, as hereinabove described, with a portion of the pregnant solution from the chimney being diverted to a solvent extraction plant where it is stripped of the desired element and returned to the chimney.

From the above description, it can be seen that many advantages accrue to the leaching operation by virtue of the acid pre-treatment step of the present invention. The pre-release of carbon dioxide renders the subsequent leaching operation more rapid and more efficient since substantial amounts of carbon dioxide are not present during leaching to interfere with the transport of oxidizing gas to the reaction sites and to suppress the leaching reactions. As a consequence, lesser volumes of fluids are required to be circulated resulting in reduced costs for circulation pumps and piping. In addition, since very little carbon dioxide will be discharged during leaching, the excess oxidizing gas discharged from the rubblized ore region can be recycled, thereby reducing gas requirements and cost.

The acid utilized in the acid pre-treatment step can be any of the acids which are known to decompose carbonates and release carbon dioxide. The common, inorganic acids, such as nitric, hydrochloric, sulfuric and the like, are most useful for this purpose. Since the fragmented ore region will probably be very extensive,

large volumes of solution will be required for flooding. Hence, it is most feasible to use a readily available, inexpensive acid such as sulfuric acid.

The leaching method outlined hereinbefore is particularly applicable to the economic recovery of copper from deep deposits of primary copper sulfides, such as chalcopyrite ($CuFeS_2$), wherein oxygen is employed as the oxidizing gas, as illustrated in the following example.

EXAMPLE

Consider the case of a deep deposit having an ore grade of **0.5** percent copper, bulking factor of **0.15**, and rock density of **2.7** g/cc in an area where the water table is at **50** meters. The lower limit of copper content which may be treated can be considerably lower while higher contents can even more readily be treated. From well established nuclear explosive technology, it can be shown that a nuclear explosive with a yield of **100** kt emplaced and detonated in the ore deposit at a burial depth of **750** meters is productive of a cavity or nuclear chimney with a radius of about **41** meters and volume of 2.9×10^5 cubic meters. Assuming a chimney wall slope of 3° from the vertical, it can be calculated that the chimney has a height of **250** meters above the shot point and contains 1.6×10^6 cubic meters of broken ore. With the chimney thus positioned and proportioned, the hydrostatic pressure acting thereon when filled varies from **7000** kilopascals (**1000** psi) at the bottom of the chimney to **4500** kilopascals (**650** psi) at the top. The resulting chimney is then filled with an aqueous sulfuric solution having a pH of about **1** until the original water level is restored. During this acid pretreatment stage the solution is not circulated and very little leaching, if any, occurs at this time. Carbon dioxide is liberated from the carbonate minerals associated with the ore and is vented to the atmosphere. The flooding solution is in contact with the rubblized ore for a period of about **30** days prior to introduction of oxygen and a substantial portion of the available carbon dioxide is discharged before the leaching operation is initiated. Oxygen at a pressure of about **7000** kilopascals (**1000** psi) is introduced into the chimney at a rate of **140** cubic meters per hour for a time sufficient to provide an average oxygen concentration throughout the chimney solution equal to **0.65** of the solubility limit at the temperature and pressure which prevail at the top of the chimney and produce an acid leach solution in the pH range of from **1.5** to **3.0**, preferably **1.5** to **2.0**, whereby copper ore is dissolved and copper goes into solution. The pregnant leach solution is then circulated to the surface and used to compress oxygen as it is reinjected. Part of the flow discharged to the surface is diverted to a conventional solvent extraction plant where it is stripped of copper and returned to the chimney. This part of the flow is passed through a heat exchanger to drop the temperature from about **90**°C to approximately **50**°C prior to solvent extraction. The copper concentration to the extraction plant is of the order of from about **5** to about **10** grams per liter.

It will be appreciated that the leaching method of the present invention may be likewise applied to the recovery of other elements from their primary ores in a substantially similar manner to that detailed for copper. For primary ores of elements similar to copper, oxygen is a suitable oxidizing gas. For ores of various other elements, such as gold, chlorine may be a suitable oxidizing gas for employment in the leaching process. Moreover, although the oxidation process is exothermic and the addition of heat to the chimney is generally not required once production has begun, it may be desirable in some cases to add heat initially so as to reach optimum production more quickly. To this end the oxidizing gas and/or the recirculated solution may be heated prior to its introduction to the chimney, or steam may be injected into the chimney.

Although the invention has been hereinbefore described and illustrated in the accompanying drawing with respect to specific steps of the method thereof, it will be appreciated that various modifications and changes may be made therein without departing from the true spirit and scope of the invention, and thus it is not intended to limit the invention except by the terms of the following claims.

What we claim is:

1. An acid leaching method for the recovery of a desired element from a subterranean rubblized ore body of a primary ore containing same and also having associated therewith a carbonate mineral comprising the steps of:

a. flooding the subterranean rubblized ore body with an aqueous acidic solution, thereby decomposing at least a portion of the associated carbonate mineral and releasing carbon dioxide,

b. discharging a substantial portion of the released carbon dioxide from the ore body,

c. introducing an oxidizing gas into the flooded, rubblized ore body thereby oxidizing said ore to form an acid leach solution effective in the presence of the oxidizing gas to dissolve said ore and cause said desired element to go into solution, and

d. recovering said desired element from said solution.

2. A method according to claim **1** further defined by maintaining the acidic solution in contact with the rubblized ore body for a period of time sufficient to release a substantial portion of the available carbon dioxide and discharge same from the ore body prior to introduction of the oxidizing gas.

3. A method according to claim **1** further defined by the aqueous acidic solution being an aqueous sulfuric acid solution.

4. A method according to claim **1** further defined by the primary ore being a primary sulfide ore.

5. A method according to claim **4** further defined by said desired element being copper, said ore being primary copper sulfides, and said oxidizing gas being oxygen.

6. A method according to claim **5** further defined by flooding the rubblized ore body with an aqueous acidic solution having a pH in the range of from substantially **0.1** to substantially **2.**

7. A method according to claim **1** further defined by locating a primary ore deposit containing the desired element existing beneath the water table, and detonating a contained nuclear explosive in said ore deposit to form a chimney of rubblized ore at a substantial depth beneath said water table subjected to the hydrostatic pressure head of the vertical displacement of said chimney therefrom.

8. A method according to claim **7** further defined by said desired element being copper, said ore being primary copper sulfides, and said gas being oxygen.

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