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[54] **STIMULATION OF RECOVERY FROM UNDERGROUND DEPOSITS**

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[57] **ABSTRACT**

Uniform stimulating of a low permeability deposit by the use of a hydrogen peroxide solution containing a stabilizer therefor.

5 Claims, No Drawings

STIMULATION OF RECOVERY FROM UNDERGROUND DEPOSITS

This invention relates to the treatment of underground deposit-bearing formations. More particularly, it relates to an improved method for fracturing such underground formations to enhance or stimulate the recovery of the desired deposits therefrom.

The prior art considered in conjunction with the preparation of this specification are as follows:

U.S. Pat. No. 2,944,803; U.S. Pat. No. 285,342; U.S. Pat. No. 3,309,140; U.S. Pat. No. 3,387,888; U.S. Pat. No. 3,533,471; U.S. Pat. No. 3,561,532; U.S. Pat. No. 3,565,173, U.S. Pat. No. 3,574,599; U.S. Pat. No. 3,587,744; U.S. Pat. No. 3,593,788; U.S. Pat. No. 3,593,793; U.S. Pat. No. 3,640,579; U.S. Pat. No. 3,654,990; U.S. Pat. No. 3,708,206; and U.S. Pat. No. 3,713,698. All of these publications are to be considered as incorporated herein by reference.

It is well known in the art that the recovery of minerals and fluids from underground formations of relatively low permeability can be ehanced by fracturing the formation rock to create areas of high permeability. One commonly employed technique for fracturing such formations is hydro-fracturing. In this technique, a fracturing fluid is injected into the formation through a well-bore at a pressure above the formation breakdown pressure. The fracture initiates at the well-bore and hopefully propagates outward into the formation in a radial manner. While this technique is generally useful, complete radial coverage of the formation and controlled propagation of the fracture at increasing distances from the well-bore are generally not achieved.

The use of explosives implanted in crevices, cracks, or fissures is common in mining and quarrying operations. Such explosives have included both solid and liquid-type explosives. The detonation of an explosive device or materials in a well-bore to achieve explosive fracturing of the surrounding formation, however, suffers from the same disadvatange noted above with respect to hydrofracturing operations, namely the difficulty of propagating the fracture at increasing distances from the injection well-bore. Explosive fracturing by the detonation of an explosive device in a well-bore also requires a subsequent clean up operation before recovery of operations can be begun at that wellsite, increasing both the time and expense involved in such a treating action. Explosive fracturing also presents numerous safety problems; it has been experienced in the past that several people have been killed in conjunction with the utilization of explosives for carrying out the desired end result; i.e., fracturing underground formations.

The aforementioned disadvantages inherent in the prior art processes are now overcome by practicing the processes of the present invention.

Accordingly, it is an object of the present invention to provide an improved method for stimulating the recovery of materials from underground deposits.

It is another object of the invention to provide an improved process for fracturing underground formations.

It is another object of the invention to provide for enhancing the radial propagation of the fracture into the formation around a well-bore.

It is a further object of the invention to provide a process for extending the distance from the well-bore to which the fracture may be propagated.

It is a further object of the invention to provide a process for fracturing a formation in which the necessity for subsequently cleaning up the injection well-bore may be obviated.

These and other objects of the present invention will be readily apparent in conjunction with the description of the present invention hereinafter set forth, including the appended claims.

The objects of the present invention are accomplished by a process in which prior to any hydrometallurgical operation being conducted on the underground deposits, there is injected into the formation, via the wellbore, an aqueous hydrogen peroxide solution containing a stabilizing agent therefor. It has unexpectedly been found that the utilization of a stabilized aqueous hydrogen peroxide solution functions in such a manner, hereinafter described, to uniformly open up fractures and stimulate the underground formation.

Specifically, it has been found that the stabilized aqueous hydrogen peroxide solution penetrates even the smallest fractures, for example, 1/32 of an inch or less, in all directions from the well-bore due to the solution's flow characteristics. Once the stabilized hydrogen peroxide solution comes into contact with metal values in the formation such as iron and copper values, the metal values react with the stabilizing agent in the hydrogen peroxide solution and there results a precipitation of the stabilizing agent from the solution. After the stabilizing agent has precipitated from the hydrogen peroxide solution, the hydrogen peroxide then undergoes rapid decomposition to form a gaseous medium which has a pressure greater than the formation breakdown pressure. Consequently, additional fractures are created in addition to the enlargement of the present fractures.

The hydrogen peroxide solution which contains a stabilizing agent therefor, is an aqueous solution containing from about 30 percent to about 98 percent by weight, based on the total weight of the solution, hydrogen peroxide. Lower concentrations of hydrogen peroxide can be utilized; however, it has been found that it is more desirable and effective to utilize a hydrogen peroxide solution containing at least 30 percent by weight hydrogen peroxide therein. The hydrogen peroxide solution also is desirably at a pH of less than 6.0 and preferably at a pH of about 4.0 or lower. When it is required to adjust the pH of the hydrogen peroxide solution, this may be accomplished by the addition thereto of an acid such as sulfuric acid, nitric acid, phosphoric acid, and acetic acid in any amount required to obtain the desired end pH value. The temperature of the overall hydrogen peroxide solution is initially at ambient temperature; however, temperatures of about 20° to about 90° C can be used where one so desires.

The critical feature in the present invention relates to the utilization of a stabilizing agent with the hydrogen peroxide solution. Such use is predicated upon the fact that the stabilizing agent is the safety feature in conjunction with the use of the hydrogen peroxide solution per se. The stabilizing agent thus provides a safe period of time during which hydrogen peroxide is pumped through the well-bore into the fractures surrounding the well-bore. Thus the possibility of a "blow-back" through the well-bore is substantially reduced. The stabilizing agent is any material which is slowly precipitated out of solution by metal values in the formation.

Preferably the material is an organophosphorus compound such as amino trimethylene phosphonic acid, ethylene diamine tetramethylene phosphonic acid, diethylene triamine pentamethylene phosphonic acid and the like and water soluble salts thereof. It is to be understood that other organophosphorus compounds can be used as long as they function in the required manner.

The preparation of a stabilized hydrogen peroxide solution may be undertaken by the procedure set forth in U.S. Pat. No. 3,383,174, which is incorporated herein by reference.

While the generic inventive concept described herein is applicable to increasing the permeability of any rock formation, the processes of the present invention are particularly effective in conjunction with the in-situ mining of underground formations which contain copper metal values in the form of chalcopyrite and pyrite ores. It has been found that the uniform stimulation of a low permeability deposit is an important factor for an economically viable in-situ mining operation. In the particular case relating to the underground (or solution) mining of chalcopyrite and pyrite ores, this uniform stimulation permits the leaching solvent to contact more of the copper minerals, thus increasing both the leach efficiency and copper loadings. Both of these parameters are critical for economically mining deep-lying low grade copper ores by in-situ mining techniques.

In general, the process comprises the steps wherein the aqueous hydrogen peroxide solution, containing the stabilizing agent therein, is pumped down a well and allowed to flow into the deposit. The hydrogen peroxide flows or diffuses into small fractures (or pores) where it comes into contact with copper and iron minerals, together with other minerals present in the formation. Upon coming into contact with these minerals, the stabilizing agent contained in said solution is precipitated out leaving the hydrogen peroxide in an unstabilized condition. The hydrogen peroxide then decomposes because of the catalytic action of the chalcopyrite and pyrite thereon, the rate of decomposition being a function of the minerals contacted, the solid exposed surface area in contact with the hydrogen peroxide, temperature, additives present in the hydrogen peroxide, strength of hydrogen peroxide solution and the like. As a result of this decomposition, a large gas pressure is built up and when this pressure exceeds the parting pressure of the formation, fracturing or stimulation occurs. It has been found that because of the rapid decomposition of the hydrogen peroxide, the fracturing or stimulation is conducted in a uniform, radial manner and at substantial distances from the well-bore due to the good penetration of the hydrogen peroxide into the smallest of fractures.

Subsequent to the above described injection of the hydrogen peroxide solution, the copper leaching solution is injected in order to subsequently recover the copper values. The copper leaching procedures can be carried out in any manner known to those skilled in the art of in-situ mining such as those procedures described in U.S. Pat. No. 3,574,599, U.S. Pat. No. 3,640,579, and U.S. Pat. No. 3,708,206, all of which publications are incorporated herein by reference.

It is to be understood that the hydrogen peroxide solution can be used at any time where one so desires. Preferably the solution is used as a pretreatment of the formation or deposit. However, it is also within the scope of the invention that said solution can be employed where deposits have already been subjected to hydrometallurgical operations.

It is a preferred embodiment of the present invention to utilize the process for the solution mining of copper from subterranean formations in a particular pattern design of injection and production wells. It is preferred that the injection and production wells either be drilled in concentric patterns about each other with a single production well contained within the center of the pattern, for example a five-spot, or that the injection and production wells be drilled in offsetting line patterns so as to form a line drive mechanism within the copper formation. Generally, the distance between the injection and production wells will be from 20 to 1,000 feet, with particular depth, thickness, permeability, porosity, water saturation of the formation, and economic value of the copper mineral contained therein being the engineering constraints upon which the design of the solution mining patterns are based. Therefore, through patterned well completion in the copper formation, the process may be used sequentially across the copper deposit through a series of line drive wells or concentric pattern wells so that the entire copper deposit may be leached.

EXAMPLE I

An ore body 100 acres in area and averaging 1,000 feet in thickness lies at an average depth of 4,000 feet below the surface of the earth in Arizona. Samples of the ore show that it is composed primarily of granitic igneous rock and that it contains chalcopyrite as the principal copper mineral. The ore samples also show that it contains approximately 1.4 weight percent chalcopyrite and that the total copper content of the ore averages 0.5 percent. The volume of ore in the deposit is, therefore 10^4 acre-feet or 4.356×10^8 cubic feet. The specific gravity of the granitic ore is 2.6. Therefore, the total weight of the ore in the deposit is 3.54×10^7 tons, and the copper content of the ore body is 3.54×10^8 pounds.

Approximately 50 wells are drilled into the ore body in an array such as to provide a five-spot pattern, and the wells are completed such that fluids may be either injected or produced from individual wells. By measurements on core samples and by injection and production tests on individual wells, it is determined that the void volume within the randomly oriented fracture system is equivalent to 2 percent of the bulk ore volume, that the fracture spacing averages 6 inches, and that the permeability of the ore body to liquid averages less than about 2 millidarcys. This permeability is less than desired for economic recovery of copper.

Petrographic examination of core samples taken from the ore body shows that about 2 percent of the rock surface area exposed by the fractures is covered by the chalcopyrite mineral and that the rock matrix bounded by the fracture system is substantially cubical in configuration.

Thus, the surface-to-volume ratio of the ore blocks bounded by the fractures is approximately equal to that for cubically shaped blocks and the surface area to volume ratio for the ore blocks is equal to 6/L, where L is the length of the side of a cube. In this case L = 0.5 feet, and the surface area to volume ratio is equal to 12 square feet/cubic foot.

The total surface area of ore exposed by the fracture network is equal to $12 \times 4.36 \times 10^8$ or 5.227×10^9 square feet. The surface area of the chalcopyrite mineral exposed by the fracture system is equal to 2 percent of the total surface area, or 1.045×10^8 square feet.

Laboratory tests with the ore samples showed that ferric sulfate solutions will dissolve copper from the chalcopyrite of the ore body at a rate equal to 0.002 pound of copper per square foot of chalcopyrite surface area per day. The initial maximum rate of copper production attainable from the ore body by in-situ leaching with ferric sulfate would be $0.002 \times 1.045 \times 10^8 = 209{,}000$ pounds of copper per day. The laboratory tests also showed that by allowing a 0.4 molar solution of ferric sulfate to react completely with the chalcopyrite and other minerals in the ore, a pregnant leach solution containing 3.0 pounds of copper per barrel (42 gallons) could be obtained. Therefore, in order to supply 0.4 molar ferric sulfate solution to the ore body at the optimum rate; i.e., at the rate sufficient to produce the maximum amount of copper and at the same time allow total reaction of the ferric iron, the 0.4 molar ferric sulfate solution must be injected initially at a rate equal to 69,700 barrels/day. The required average residence time for the solution within the ore body is fixed by the injection rate and the void volume of the ore body;

Average Residence time = void volume/injection rate
$= (0.02)\ (4.36 \times 10^8)$ cubic feet/(69,700 bbl./day)
(5.615 cu. ft./bbl.) = 22.3 days

The injection and withdrawal rates of the wells are thus regulated to permit the ferric sulfate solution to remain in the ore body for approximately 22 days.

When the initial deposit permeability is substantially below the 1–5 millidarcy economical range, the hydrogen peroxide solution containing the stabilizer, therefore, is used to increase the permeability to the economical range.

Utilizing the above set of conditions, the wells are operated for a sufficient period of time to reach equilibrium and the copper produced averages about 187,000 pounds per day.

These wells are then shut down and treated with a 75 percent by weight aqueous hydrogen peroxide solution (pH 4.0) containing amino trimethylene phosphonic acid as the stabilizing agent therefor. Specifically each well is treated for approximately 4 hours at a pumping rate of 20 gallons of solution per minute. After this 4 hour period, the wells remain inoperative for 2 hours and then the leaching treatment is initiated under the same conditions specified heretofore. After equilibrium has been established, it is determined that copper is now being produced at an average rate of 235,000 pounds per day. Thus the use of the hydrogen peroxide solution has resulted in additional production directly as a result of the new fractures formed and enlargement of old fractures.

While Example I has been described as applicable to the copper sulfide ores, it should be understood that the process is also applicable to ores bearing native copper and also to ores of copper oxides and silicates where the copper is present in the cuprous valence state. When the copper is present in its elemental or lower valence state, it is susceptible to oxidation by ferric iron to form solutions of cupric sulfate.

It should also be understood that while it is preferred to conduct the process in an ore body between an input and withdrawal well, a single well process is also included within the scope of the invention. In a single well process, the leach solution will be injected through a well, permitted to remain in contact with the ore body for a period of time, and then withdrawn through the same well. The pregnant leach solution is then passed to a copper recovery stage, a regeneration stage and ultimately reinjected.

While the processes have been described as particularly effective in the in-situ mining of copper-bearing deposits, it is also within the scope of the present invention to treat other types of mineral-bearing deposits which contain, for example, silver, gold, molybdenum, uranium and the like. Furthermore, deposits containing oil may also be effectively treated.

The present invention has been described herein with reference to particular embodiments thereof. It will be appreciated by those skilled in the art, however, that various changes and modifications can be made therein without departing from the scope of the invention as presented.

What is claimed is:

1. In a hydrometallurgical operation for the in-situ underground mining of a low grade copper-containing formation by the use of a copper leaching solution for extracting copper values from said formation, the improvement which comprises the step of prior to contacting said copper-containing formation with said leaching solution, the formation is contacted with an aqueous hydrogen peroxide solution containing a stabilizing agent therefor and whereby said agent reacts with the copper-containing formation to form a precipitate and the resultant substantially unstabilized hydrogen peroxide decomposes to form a gaseous medium which causes additional fracturing of the formation whereby greater leaching efficiency and copper loading is achieved with the subsequent copper leaching step.

2. The method as set forth in claim **1** wherein the concentration of the hydrogen peroxide in solution is from about 30 percent to about 98 percent, by weight, based on the total weight of said solution and the pH of said solution is less than about 6.0.

3. The method as set forth in claim **2** wherein the stabilizing agent is an organophosphorus compound which precipitates out of said solution when said compound comes into contact with the copper-containing formation.

4. The method as set forth in claim **3** wherein the copper-containing formation contains chalcopyrite and pyrite.

5. The method as set forth in claim **4** wherein the stabilizing agent is amino trimethylene phosphonic acid or a water soluble salt thereof.

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