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(54) **METHOD OF BIOTREATMENT FOR SOLID MATERIALS IN A NONSTIRRED SURFACE BIOREACTOR**

VERFAHREN ZUM BIOLOGISCHEN BEHANDELN VON FESTMATERIALIEN IN EINEM UNGERÜHRTEN OBERLÄCHENBIOREAKTOR

PROCEDE DE BIO-TRAITEMENT DE MATERIAUX SOLIDES DANS UN BIO-REACTEUR DE SURFACE SANS AGITATION

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Description

Background of the Invention

1. Field of the Invention

[0001] The present invention relates to the biotreatment of solid materials. In particular, the present invention relates to the ex situ biotreatment of solid materials in an aerobic process to degrade an undesired compound present in the solid material.

2. Description of the Prior Art

[0002] Biological treatment processes are finding application throughout industry. Such processes have been used in waste water treatment, hazardous waste remediation, desulfurization of coal, and biooxidation of refractory sulfide ores.

[0003] A variety of methods can be employed in the biological treatment of solid materials, including in situ treatment, landfarming, composting, heap treatment, and stirred or agitated tanks. In the ex situ biological treatment of solid materials, some sort of bioreactor is used to carry out the biotreatment. A bioreactor can be defined as a vessel or body in which biological reactions are carried out by microorganisms, or enzymes they produce, contained within the reactor itself. The main objective in the design of a bioreactor is to generate an optimal environment for the desired biological process to take place on a large and economic scale.

[0004] When a solid material is being biotreated, the desired biological reactions typically involve the degradation, either directly or indirectly, of some undesired compound present in the solid material. To accomplish this economically, the bioreactor needs to reduce the concentration of the undesired compound to an acceptable level in an acceptable quantity (in terms of flow rate) of solid material to be treated.

[0005] In general biotreatment processes are slow, and if they are aerobic, they require large amounts of oxygen for the aerobic microorganism(s) to metabolize, either directly or indirectly, the undesired compound. Oxygen transfer, therefore, is typically a major problem for the large class of aerobic biological treatment processes available. Current aerobic bioreactor designs attempt to ensure not only that the microorganisms being used have access to the material to be biooxidized or metabolized, but also that all areas of the bioreactor have an adequate oxygen and nutrient supply, as well as maintain the correct pH and temperature, for the biological process to proceed.

[0006] Stirred tank bioreactors are used in many types of aerobic biological processes, including biooxidation of refractory sulfide gold ores and bioremediation of contaminated soils. Stirred tank bioreactors provide very good contact between the bioleachant and the solid material to be treated. In addition, stirred tank processes typically have favorable oxygen conditions because the tank is sparged with air or oxygen. However, even in stirred tank bioreactors where oxygen is provided by air or oxygen sparging, the low solubility of oxygen in water (10 ppm) requires a large gas-water interface. This is generally achieved with impellers and significant expenditures of energy. The high energy costs associated with stirring and aerating the reactor make this type of bioreactor primarily applicable to bioprocess that come to a desired end point relatively quickly, typically less than a week. For slower biological processes, a low energy cost, large scale, generally static batch process, is the best solution. However, the goal of providing the bacteria, or other microorganism, with an optimal environment is still of primary importance.

[0007] There are three primary types of static batch bioreactors used to biotreat soils contaminated with toxic organic compounds. One of these methods is landfarming. This is an above grade treatment of contaminated soil in a large open space. The soil is spread over a high-density polyurethane lined area generally covered with sand to allow for drainage. Air can be introduced by perforated pipes and by tilling the soil once or twice a week. This method has been widely implemented at sites contaminated with polynuclear aromatic (PNA's) and pentachlorophenol (PCP). One limitation of this process is that a large area is needed because the soil is spread relatively thinly to ensure adequate air flow. This method also requires tilling and may be limiting in air if the layer of soil is too thick or does not mix well.

[0008] Another technology used in the bioremediation of contaminated soil is composting. The compost is made up of contaminated soil and various amendments necessary for composting to be sustained such as wood chips, straw, or manure. These amendments increase the amount of biodegradable organics, structurally improve the compost matrix by reducing bulk weight and increasing air voids, and increase the amount of inorganic nutrients in the mixture. The composting can be carried out in a vessel with forced air flow or in open piles that are aerated by air pipes or by tilling. One disadvantage to the addition of organic amendments is that their biodegradation generates heat and requires oxygen. Composting is usually run in batch mode and a portion of the compost is used to inoculate the next compost. This process has been used effectively on many types of organic contaminates including diesel fuel, 2,4,6 trinitrotoluene (TNT), polyaromatic hydrocarbons (PAH), benzene, and xylene.

[0009] Heap bioremediation is another static bioprocess used in the bioremediation of excavated contaminated soil. In this process the soil is placed in piles 2.4 to 3.7 meter high over a lined area. To improve air flow, air can be introduced

by perforated pipes. In such circumstances, the pipes are placed on approximately a 31 cm bed of the contaminated soil in regular intervals. The pipes are then typically covered with a layer of gravel to protect them from the heavy equipment. The excavated soil is then dumped in an 2.4 to 3.7 meter high pile on top of the gravel. Moisture is maintained with an irrigation system. The soil may need fertilizer or lime to adjust pH and may need sand to increase porosity. This process is low cost and thus is applicable to slow biological processes. However, this process may be too slow if the heap becomes air limited due to compaction of the soil during or after pile construction.

[0010] Therefore, air and liquid access remain important rate limiting considerations in existing static batch bioprocesses used for soil remediation, such as heap pile bioremediation, composting and landfarming. Air flow is improved in existing processes to the extent possible by introducing air through perforated air pipes or by tilling the soil. However, any flow constriction within the bioreactor will interfere with the efficiency of the process. Also, if parts of the contaminated soil are not exposed to bacteria or other nutrients as well as oxygen, the overall bioprocess will be slowed or not proceed to completion. Similarly, in the case of heap biooxidation of coal and refractory sulfide gold ore, biooxidation of the sulfides is efficiently carried out by the bacteria only when the metal sulfides are exposed to bacteria, water, nutrients, and air. If the sulfides are buried in the ore or in the solid pieces of coal, the biooxidation will not proceed. In addition, if air or liquid flow in the heap becomes limited, the biooxidation will also become limited. Consequently, a need exists for an improved bioreactor design which will permit the biotreatment of solid materials with improved air and fluid flow throughout the bioreactor and the solid material to be treated.

[0011] The use of acidophilic, autotrophic bacteria to biooxidize sulfide minerals in refractory sulfide ores is one biotreatment that has gained particular vigor in the last ten to twenty years.

[0012] Gold is one of the rarest metals on earth. Gold ores can be categorized into two types: free milling and refractory. Free milling ores are those that can be processed by simple gravity techniques or direct cyanidation. Refractory ores, on the other hand, are not amenable to conventional cyanidation treatment. Gold bearing deposits are deemed refractory if they cannot be economically processed using conventional cyanide leaching techniques because insufficient gold is solubilized. Such ores are often refractory because of their excessive content of metallic sulfides (e.g., pyrite and arsenopyrite) and/or organic carbonaceous matter.

[0013] A large number of refractory ores consist of ores with a precious metal such as gold occluded in iron sulfide particles or other metal sulfide particles. The iron sulfide particles consist principally of pyrite and arsenopyrite. Precious metal values are frequently occluded within the sulfide mineral. For example, gold often occurs as finely disseminated sub-microscopic particles within a refractory sulfide host of pyrite or arsenopyrite. If the gold, or other precious metal, remains occluded within the sulfide host, even after grinding, then the sulfides must be oxidized to liberate the encapsulated precious metal values and make them amenable to a leaching agent (or lixiviant); thus, the sulfide oxidation process reduces the refractory nature of the ore.

[0014] A number of processes for oxidizing the sulfide minerals to liberate the precious metal values are well known in the art. These methods can generally be broken down into two types: mill operations and heap operations. Mill operations are typically expensive processes having high operating and capital costs. As a result, even though the overall recovery rate is typically higher for mill type processes, mill operations are typically not applicable to low grade ores, that is ores having a gold concentration less than approximately 2.4g/tonne. Mill operations are even less applicable to ores having a gold concentration as low as .68g/tonne.

[0015] Two well known methods of oxidizing sulfides in mill type operations are pressure oxidation in an autoclave and roasting.

[0016] Oxidation of sulfides in refractory sulfide ores can also be accomplished using acidophilic, autotrophic microorganisms, such as Thiobacillus ferrooxidans, Sulfolobus, Acidianus species and facultative-thermophilic bacteria in a microbial pretreatment. These microorganisms utilize the oxidation of sulfide minerals as an energy source during metabolism. During the oxidation process, the foregoing microorganisms oxidize the iron sulfide particles to cause the solubilization of iron as ferric iron, and sulfide, as sulfate ion.

[0017] If the refractory ore being processed is a carbonaceous sulfide ore, then additional process steps may be required following microbial pretreatment to prevent preg-robbing of the aurocyanide complex or other precious metal-lixiviant complexes by the native carbonaceous matter upon treatment with a lixiviant.

[0018] As used herein, sulfide ore or refractory sulfide ore will be understood to also encompass refractory carbonaceous sulfide ores.

[0019] A known method of bioleaching carbonaceous sulfide ores is disclosed in U.S. Patent No. 4,729,788, issued March 8, 1988

According to the disclosed process, thermophilic bacteria, such as Sulfolobus and facultative-thermophilic bacteria, are used to oxidize the sulfide constituents of the ore. The bioleached ore is then treated with a blanking agent to inhibit the preg-robbing propensity of the carbonaceous component of the ore. The precious metals are then extracted from the ore using a conventional lixiviant of cyanide or thiourea.

[0020] Another known method of bioleaching carbonaceous sulfide ores is disclosed in U.S. Patent No. 5,127,942, issued July 7, 1992,

[0021] According to this method, the ore is subjected to an oxidative bioleach to oxidize the sulfide component of the ore and liberate the precious metal values. The ore is then inoculated with a bacterial consortium in the presence of nutrients therefor to promote the growth of the bacterial consortium, the bacterial consortium being characterized by the property of deactivating the preg-robbing propensity of the carbonaceous matter in the ore. In other words, the bacterial consortium functions as a biological blanking agent. Following treatment with the microbial consortium capable of deactivating the precious-metal-adsorbing carbon, the ore is then leached with an appropriate lixiviant to cause the dissolution of the precious metal in the ore.

[0022] Oxidation of refractory sulfide ores using microorganisms, or as often referred to biooxidation, can be accomplished in a mill process or a heap process. Compared to pressure oxidation and roasting, biooxidation processes are simpler to operate, require less capital, and have lower operating costs. Indeed, biooxidation is often chosen as the process for oxidizing sulfide minerals in refractory sulfide ores because it is economically favored over other means to oxidize the ore. However, because of the slower oxidation rates associated with microorganisms when compared to chemical and mechanical means to oxidize sulfide refractory ores, biooxidation is often the limiting step in the mining process.

[0023] One mill type biooxidation process involves comminution of the ore followed by treating a slurry of the ore in a stirred bioreactor where microorganisms can use the finely ground sulfides as an energy source. Such a mill process was used on a commercial scale at the Tonkin Springs mine. However, the mining industry has generally considered the Tonkin Springs biooxidation operation a failure. A second mill type biooxidation process involves separating the precious metal bearing sulfides from the ore using conventional sulfide concentrating technologies, such as floatation, and then oxidizing the sulfides in a stirred bioreactor to alleviate their refractory nature. Commercial operations of this type are in use in Africa, South America and Australia.

[0024] Biooxidation in a heap process typically entails forming a heap with crushed refractory sulfide ore particles and then inoculating the heap with a microorganism capable of biooxidizing the sulfide minerals in the ore. After biooxidation has come to a desired end point, the heap is drained and washed out by repeated flushing. The liberated precious metal values are then ready to be leached with a suitable lixiviant.

[0025] Typically precious metal containing ores are leached with cyanide because it is the most efficient leachant or lixiviant for the recovery of the precious metal values from the ore. However, if cyanide is used as the lixiviant, the heap must first be neutralized.

[0026] Because biooxidation occurs at a low, acidic pH while cyanide processing must occur at a high, basic pH, heap biooxidation followed by conventional cyanide processing is inherently a two step process. As a result, processing options utilizing heap biooxidation must separate the two steps of the process. This is conventionally done by separating the steps temporally. For example, in a heap biooxidation process of a refractory sulfide gold ore, the heap is first biooxidized and then rinsed, neutralized and treated with cyanide. To accomplish this economically and practically, most heap biooxidation operations use a permanent heap pad in one of several ore on -- ore off configurations.

[0027] Of the various biooxidation processes available, heap biooxidation has the lowest operating and capital costs. This makes heap biooxidation processes particularly applicable to low grade or waste type ores, that is ores having a gold (or an equivalent precious metal value) concentration of less than about 2.4g/tonne. Heap biooxidation, however, has very slow kinetics compared to mill biooxidation processes. Heap biooxidation typically require many months in order to sufficiently oxidize the sulfide minerals in the ore to permit the gold or other precious metal values to be recovered in sufficient quantities by subsequent cyanide leaching for the process to be considered economical. Heap biooxidation operations, therefore, become limited by the length of time required for sufficient biooxidation to occur to permit the economical recovery of gold. The longer the time required for biooxidation the larger the permanent pad facilities and the larger the necessary capital investment. At mine sites where the amount of land suitable for heap pad construction is limited, the size of the permanent pad can become a limiting factor in the amount of ore processed at the mine and thus the profitability of the mine. In such circumstances, rate limiting conditions of the biooxidation process become even more important.

[0028] The rate limiting conditions of the heap biooxidation process include inoculant access, nutrient access, air or oxygen access, toxins build up, and carbon dioxide access, which are required to make the process more efficient and thus an attractive treatment option. Moreover, for biooxidation, the induction times concerning biooxidants, the growth cycles, the biocide activities, viability of the bacteria and the like are important considerations because the variables such as accessibility, particle size, settling, compaction and the like are economically irreversible once a heap has been constructed. This is because heaps cannot be repaired once formed, except on a limited basis.

[0029] Ores that have a high clay and/or fines content are especially problematic when processing in a heap leaching or heap biooxidation process. The reason for this is that the clay and/or fines can migrate through the heap and plug channels of air and liquid flow, resulting in puddling; channelling; nutrient-, carbon dioxide-, or oxygen-starving; uneven biooxidant distribution, and the like. As a result, large areas of the heap may be blinded off and ineffectively leached. This is a common problem in cyanide leaching and has lead to processes of particle agglomeration with cement for high pH cyanide leaching and with polymers for low pH bioleaching. Polymer agglomerate aids may also be used in high pH

environments, which are customarily used for leaching the precious metals, following oxidative bioleaching of the iron sulfides in the ore.

[0030] Biooxidation of refractory sulfide ores is especially sensitive to blocked percolation channels by loose clay and fine material because the bacteria need large amounts of air or oxygen to grow and biooxidize the iron sulfide particles in the ore. Air flow is also important to dissipate heat generated by the exothermic biooxidation reaction, because excessive heat can kill the growing bacteria in a large, poorly ventilated heap.

[0031] The methods disclosed in U.S. Patent No. 5,246,486, issued September 21, 1993, and U.S. Patent No. 5,431,717, issued on July 11, 1995 to William Kohr, are directed to increasing the efficiency of the heap biooxidation process by ensuring good fluid flow (both gas and liquid) throughout the heap.

[0032] Ores that are low in sulfide or pyrite, or ores that are high in acid consuming materials such as calcium carbonate or other carbonates, may also be problematic when processing in a heap biooxidation. The reason for this is that the acid generated by these low pyrite ores is insufficient to maintain a low pH and high iron concentration needed for bacteria growth.

[0033] Solution inventory and solution management also pose important rate limiting considerations for heap biooxidation processes. The solution drained from the biooxidation heap will be acidic and contain bacteria and ferric ions. Therefore, this solution can be used advantageously in the agglomeration of new ore or by recycling it back to the top of the heap. However, toxic and inhibitory materials can build up in this off solution. For example, ferric ions, which are generally a useful aid in pyrite leaching, are inhibitory to bacteria growth when their concentration exceeds about 30 g/L. Other metals that retard the biooxidation process can also build-up in this solution. Such metals that are often found in refractory sulfide ores include arsenic, antimony, cadmium, lead, mercury, and molybdenum. Other toxic metals, biooxidation byproducts, dissolved salts and bacterially produced material can also be inhibitory to the biooxidation rate. When these inhibitory materials build up in the off solution to a sufficient level, recycling of the off solution becomes detrimental to the rate at which the biooxidation process proceeds. Indeed, continued recycling of an off solution having a sufficient build-up of inhibitory materials will stop the biooxidation process altogether.

[0034] The method disclosed in U.S. Patent Application Serial No. 08/329,002, filed October 25, 1994, by Kohr, et al., teaches a method of treating the bioleachate off solution to minimize the build-up of inhibitory materials. As a result, when the bioleachate off solution is recycled to the top of the heap, the biooxidation rate within the heap is not slowed, or it will be slowed to a lesser degree than if the off solution were recycled without treatment.

[0035] While the above methods have improved the rate at which heap biooxidation processes proceed, heap biooxidation still takes much longer than a mill biooxidation process such as a stirred bioreactor. Yet, as pointed out above, with low grade refractory sulfide ores, a stirred bioreactor is not a viable alternative due to its high initial capital cost and high operating costs.

[0036] A need exists, therefore, for a heap bioleaching technique that can be used to biooxidize precious metal bearing refractory sulfide ores and which provides improved air and fluid flow within the heap. In addition, a need exists for a heap bioleaching process in which ores that are low in sulfide minerals, or ores that are high in acid consuming materials such as calcium carbonate, may be processed.

[0037] A need also exists for a biooxidation process which can be used to liberate occluded precious metals in concentrates of refractory sulfide minerals. Mill processes that are currently used for oxidizing such concentrates include bioleaching in a stirred bioreactor, pressure oxidation in an autoclave, and roasting. These mill processes oxidize the sulfide minerals in the concentrate relatively quickly, thereby liberating the entrapped precious metals. However, unless the concentrate has a high concentration of gold, it does not economically justify the capital expense or high operating costs associated with these processes. And, while a mill bioleaching process is the least expensive mill process in terms of both the initial capital costs and its operating costs, it still does not justify processing concentrates having less than about 17 g of gold per tonne of concentrate, which typically requires an ore having a concentration greater than about 2.4 g of gold per tonne. Therefore, a need also exists for a process that can be used to biooxidize concentrates of precious metal bearing refractory sulfide minerals at a rate comparable to a stirred tank' bioreactor, but that has capital and operating costs more comparable to that of a heap bioleaching process.

[0038] In addition to concentrates of precious metal bearing sulfide minerals, there are many sulfide ores that contain metal sulfide minerals that can potentially be treated using a biooxidation process. For example, many copper ores contain copper sulfide minerals. Other examples include zinc ores, nickel ores, and uranium ores. Biooxidation could be used to cause the dissolution of metal values such as copper, zinc, nickel and uranium from concentrates of these ores. The dissolved metal values could then be recovered using known techniques such as solvent extraction, iron cementation, and precipitation. However, due to the sheer volume of the sulfide concentrate formed from sulfide ores, a stirred bioreactor would be prohibitively expensive, and standard heap operations would simply take too long to make it economically feasible to recover the desired metal values. A need also exists, therefore, for an economical process for biooxidizing concentrates of metal sulfide minerals produced from sulfide ores to thereby cause the dissolution of the metal values so that they may be subsequently recovered from the bioleachate solution.

[0039] Therefore, while a need exists for a method of biooxidation that can be used to process sulfide concentrates

from refractory sulfide ores at a rate which is much faster than that of existing heap biooxidation processes, yet which has initial capital costs and operating costs less than that of a stirred bioreactor, this need has gone unfulfilled. Further, while a need has also existed for a method of biooxidation that can be used to economically process sulfide concentrates of metal sulfide type ores, this need has also gone unfulfilled.

Summary of Invention

[0040] The present invention is directed to the biotreatment of solid materials in a nonstirred bioreactor. To this end, in a first aspect of the present invention, a method of biotreating a solid material to remove an undesired compound using a nonstirred surface bioreactor is provided. According to the method the surface of a plurality of coarse substrates is coated with a solid material to be biotreated to form a plurality of coated coarse substrates. A nonstirred surface reactor is then formed by stacking the plurality of coated coarse substrates into a heap or placing the plurality of coated coarse substrates into a tank so that the void volume of the reactor is greater than or equal to about 25 %. The reactor is inoculated with a microorganism capable of degrading the undesired compound in the solid material , thereby forming a nonstirred surface bioreactor and the solid material is then biotreated in the surface bioreactor until the undesired compound in the solid material is degraded to a desired concentration. To ensure adequate void volume in the bioreactor, the coarse substrates have a particle size greater than about 0.3 cm and the solid material to be biotreated has a particle size less than about 250 μm.

[0041] Preferred embodiments of the present invention are disclosed in dependent claims 2 to 56. The thickness of the solid material coating on the plurality of coarse substrates is preferably less than about 1 mm to ensure that the microorganism being used in the biotreatment have adequate access to all of the solid material being biotreated. Thicker coatings will increase the capacity of the bioreactor, but the rate at which the biotreatment process advances will be slowed due to the limited access of the microorganism being used to the underlying particles of solid material. To make full use of the capacity of the bioreactor while ensuring adequate microorganism access, the thickness of the solid material coating should be greater than about 0.5 mm and less than about 1 mm. For enhanced air and liquid access, the void volume of the bioreactor can be set to greater than or equal to about 35 %. This will greatly improve the rate at which the biotreatment process proceeds.

[0042] A variety of materials can be used for the coarse substrates, including rock, gravel, lava rock, rock containing carbonate minerals, brick, cinder block, slag, and plastic.

[0043] The method according to the first aspect of the invention is useful for many different biotreatment processes, including the bioremediation of contaminated soils, the desulfurization of coal, and the biooxidation of refractory sulfide ores. In bioremediation applications, the undesired compound is typically an organic compound. In coal desulfurization and refractory sulfide ore biooxidation applications, the undesired compound is sulfide minerals. A second aspect of the present invention is the above methods, wherein said solid material is a sulfide mineral concentrate comprised of fine metal sulfide particles containing metal values of interest, said undesired compound is said fine metal sulfide particles, and wherein said biotreatment of said sulfide mineral concentrate coated on the surface of said substrates biooxidizes said fine metal sulfide particles until a desired amount of said fine metal sulfide particles in said sulfide mineral concentrate is biooxidized and the metal values of interest are liberated.

[0044] Depending on the particular ore deposit being mined, the sulfide mineral concentrates used in this invention may comprise sulfide concentrates from precious metal bearing refractory sulfide ores or they may comprise sulfide concentrates from base metal sulfide type ores, such as chalcopyrite, millerite or sphalorite. The distinction being that in the former, the metal of interest is a precious metal occluded within the sulfide minerals, and in the latter, the metal to be recovered is a base metal such as copper, nickel, or zinc and is present as a metal sulfide in the sulfide concentrate.

[0045] A third aspect of the present invention is directed to be above method, wherein said solid material is a sulfide mineral concentrate comprised of fine metal sulfide particles containing occluded precious metal values, said undesired compound is said fine metal sulfide particles, and wherein said biotreatment of said sulfide mineral concentrate coated on the surface of said coarse substrate biooxidizes said fine metal sulfide particles until a desired amount of said fine metal sulfide particles in said sulfide mineral concentrate is biooxidized and precious metal values are liberated, the process further comprising the steps of: contacting the biooxidized fine metal sulfide particles with a precious metal lixiviant to thereby dissolve precious metal values from the biooxidized fine metal sulfide particles; and recovering precious metal values from the lixiviant.

[0046] A further aspect of the present invention is the above method wherein said solid material is a sulfide mineral concentrate comprised of fine metal sulfide particles containing metal values of interest, said undesired compound is said fine metal sulfide particles, and wherein said biotreatment of said sulfide mineral concentrate coated on the surface of said course substrates biooxidizes said fine metal sulfide particles thereby causing the production of a bioleachate off solution and the dissolution of the metal moiety of the metal sulfide particles, the method further comprising the step of: recovering the desired metal values from the bioleachate off solution. Ores of particular interest which can be processed using this process include sulfide ores of copper, zinc, nickel, molybdenum, cobalt, and uranium.

[0047] Gold is the preferred precious metal recovered using the method according to the present invention. However, other precious metals can also be recovered, including silver and platinum. Lava rock is particularly preferred substrate material due to its high surface area. As those skilled in the art will immediately recognize, a number of lixiviants can be used in conjunction with the present process, however, thiourea and cyanide are the preferred, cyanide being a particularly preferred lixiviant.

[0048] The above and other objects, features and advantages will become apparent to those skilled in the art from the following description of the preferred embodiments.

Brief Description of the Drawings

[0049]

Fig. 1 is a schematic illustration of a process flow chart according to one embodiment of the present invention;
Fig. 2 is a cross sectional view of a refractory sulfide ore substrate coated with a concentrate of metal sulfide particles in accordance with the present invention;
Fig. 3 is a schematic illustration of a process flow chart according to a another embodiment of the present invention;
Fig. 4 is a schematic illustration of a process flow chart according to yet another embodiment of the present invention;
Fig. 5 is a schematic illustration of a process flow chart according to yet another embodiment of the present invention;
Fig. 6 is a graph illustrating the percent of iron oxidation versus time for a whole ore compared to a process according to the present invention;
Fig. 7 is a graph comparing the average daily biooxidation rate of a whole ore against that of a process according to the present invention;
Fig. 8 is a graph illustrating the percentage of biooxidation for another process according to the present invention;
Fig. 9 is a graph illustrating the average daily rate of biooxidation for the process corresponding to Fig 8;
Fig. 10 is a graph illustrating the percentage of biooxidation as a function of time for a pyrite concentrate coated on a barren rock support and the same pyrite concentrate coated on a refractory sulfide ore support that contains a high concentration of mineral carbonate; and
Fig. 11 is a graph illustrating the biooxidation rate for a concentrate distributed on top of a lava rock heap process in accordance with an embodiment of the present invention versus a stirred tank type process.

Detailed Description of the Invention

[0050] A first embodiment of the invention is now described in which a solid material is biotreated in a nonstirred surface bioreactor in order to remove an undesired compound. According to the first embodiment, the surface of a plurality of coarse substrates having a particle size greater than about 0.3 cm is coated with the solid material to be biotreated to form a plurality of coated coarse substrates. The solid material to be biotreated has a particle size of less than about 250 μm so that it forms a fairly uniform coating on the coarse substrates. A nonstirred surface reactor is then formed by stacking the plurality of coated coarse substrates into a heap or placing the plurality of coated coarse substrates into a tank so that the void volume of the reactor is greater than or equal to about 25 %. The reactor is inoculated with a microorganism capable of degrading the undesired compound in the solid material, and the solid material is then biotreated in the surface bioreactor until the undesired compound in the solid material is degraded to a desired concentration.

[0051] The biotreatment method can be used in the bioremediation of contaminated soils, the desulfurization of coal, and the biooxidation of refractory sulfide ores to name a few. In bioremediation applications, the solid material is typically soil and the undesired compound is typically an organic compound within the soil. The present invention, therefore, has application at many of the existing superfund sites. A partial list of the organic contaminants which can be removed from soil using the present invention include: waste oil, grease, jet fuel, diesel fuel, crude oil, benzene, toluene, ethylbenzene, xylene, polyaromatic hydrocarbons (PAH), polynuclear aromatics (PNAs), pentachlorophenol (PCP), polychlorinated biphenyls (PCBs), creosote, pesticides, 2,4,6,-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), N-methyl-N-2,4,6-tetranitroaniline, and nitrocellulose (NC).

[0052] If, on the other hand, the present invention is used to desulfurize coal, the solid material will be comprised of coal particles and the undesired compound will be the sulfide mineral particles contained within the coal particles. In refractory sulfide ore biooxidation applications, the solid material will typically be ground ore or a sulfide concentrate produced from the ore and the undesired compound will be the metal sulfide particles within the ore or concentrate.

[0053] In some instances it may be beneficial to form a concentrate by flotation or by other means where by the fraction of the solid material to be biotreated is concentrated in a smaller weight fraction. This concentrate, if it contains the majority of the undesired metal sulfides or toxins, for example, can be processed more cost effectively than the entire material.

[0054] As those skilled in the art will appreciate from the foregoing and the ensuing description, the method according to the present invention has broad applicability in that it can be used to biotreat any solid material that contains an undesired compound which is susceptible to biodegradation or biooxidation by a microorganism or the enzymes produced by a microorganism.

[0055] The purpose of the coarse substrates is to provide a support with a relatively large surface area upon which the solid material to be biotreated can reside during the biotreatment process. Therefore, when a large number of coated coarse substrates are stacked in a heap or placed in a tank, a nonstirred surface reactor is formed that has a very large active surface area per cubic meter of reactor space. Although the exact surface area of the reactor per cubic meter of reactor space will depend on the particular size of the coarse substrates employed, it should be at least 100 square meters per cubic meter of reactor and will typically be 500 square meters or more per cubic meter of reactor space. Furthermore, by using coarse substrates that have a particle size greater than about 0.3 cm and restricting the particle size of the solid material to be biotreated to less than about 250 μm, the reactor will be ensured adequate void volume to permit air and nutrients to access all parts of the reactor during the biotreatment process. In this regard, the void volume of the reactor should be at least about 25 %. Such a void volume will also ensure adequate heat dissipation within the heap. For enhanced air and liquid access and heat dissipation, the void volume of the bioreactor can be set to greater than or equal to about 35 %. This will greatly improve the rate at which the biotreatment process proceeds.

[0056] While using larger coarse substrates will increase the void volume in the reactor and thus improve air and nutrient access, in addition to heat dissipation, throughout the entire reactor, the use of larger substrates reduces the loading capacity of the bioreactor. A good compromise between ensuring adequate void volume and ensuring adequate reactor capacity can be achieved by using coarse substrates having a nominal particle size that is greater than about 0.6 cm and less than about 2.54 cm.

[0057] A variety of materials can be used for the coarse substrates, including rock, gravel, lava rock, barren rock containing carbonate minerals, brick, cinder block, slag, and plastic. Lava rock is particularly preferred because of its rough, nonuniform surface, thus increasing its surface area for a given particle size substrate and improving the integrity of the coating of solid material which is applied to it. Coarse barren rock containing carbonate minerals is advantageous if the biotreatment process is acidic because the acid will react with the carbonate minerals to slowly cause the release of carbon dioxide, which autotrophic microorganisms can use as a source of carbon to carry out metabolic synthesis. The carbon dioxide production can thus be used to promote microorganism growth in the reactor.

[0058] When a refractory sulfide ore or sulfide concentrate is being biooxidized to reduce the sulfide mineral content therein, coarse ore particles can be used as the coarse substrates. Similarly, if the method is being used to desulfurize coal, coarse coal particles can be used as the coarse substrates. In both cases, the substrate may benefit from the biooxidation process carried out on its surface.

[0059] While the coarse substrates have been defined as having a particle size of greater than about 0.3 cm, it is recognized and contemplated that some of the coarse substrate material may actually be smaller than this. As those skilled in the art will recognize that if the coarse substrates are produced by crushing lager material to the desired size range, the crushed material will have a certain size distribution. And, even if the material is screened to exclude material less than about 0.3 cm, some material having a particle size less than the 0.3 cm target minimum will still be present in the coarse substrates due to inherent inefficiencies in the screening process and due to particle attrition during handling. Thus, by greater than about 0.3 cm it is intended that substantially all of the coarse substrates are above this size so that the void volume of the reactor remains above at least about 25 % during formation of the reactor and throughout its operation. Preferably the amount of coarse substrates below the 0.3 cm cutoff is less than 5% by weight.

[0060] In general, the solid material to be biotreated should be much smaller than the coarse substrate onto which it is coated. This material should be ground to a small enough size to allow the microorganism employed in the biotreatment to have access to all the material so that the undesired compound can be biooxidized or biodegraded in a time that is generally larger than a stirred tank process, but shorter than a heap process of the whole material. This time will generally be between 14 days and 90 days, depending on the undesired compound and the rate of its biodegradation or biooxidation.

[0061] The maximum solid material particle size has been set at about 250 μm so that the solid material will form a relatively uniform coating on the coarse substrates during the coating process, rather than forming agglomerates between themselves. Furthermore, particles larger than 250 μm may not adhere to the surface of the coarse substrates very well without the use of a binder.

[0062] It is desirable to form a relatively uniform coating of the fine particles on the coarse substrates during the coating process because this will maximize the integrity of the coating and the surface area of the solid material exposed to the active microorganism which is added to the bioreactor. If agglomerates of the solid material are formed during the coating process, the particles of solid material which are in the interior of the agglomerate will be blocked from the action of the microorganism and thus the amount of biological treatment they will receive will be reduced or nonexistent. Further, the agglomerates are not as structurally sound as the coated substrates and are likely to break apart during the stacking process used to form the reactor or during biotreatment, potentially leading to the formation of blockages within the reactor, which could blind off portions of the reactor from the biological treatment.

[0063] Typically as the particle size of the solid material to be biotreated decreases, the biotreatment process will proceed faster and more solid material can be loaded onto the coarse substrates. Smaller particle sizes will also tend to stick better to the surface of the coarse substrates. If the particle size of the solid material to be treated is less than about 25 μm, however, excessive dust problems could be encountered during handling and some clumping may be experienced during the coating process.

[0064] Preferably the particle size of the solid material to be treated has a nominal particle size which is greater than about 75 μm and less than about 106 μm. Particles in this size range will adhere well to the coarse substrates, and the incremental improvements which can be achieved in the rate of the biotreatment process with finer particle sizes are rarely justified by the added grinding costs of producing them.

[0065] The coated substrates can be produced by adding the coarse substrates and solid-material to a rotating drum in appropriate quantities. Preferably the coarse substrates are dry and the solid material is in a high pulp density slurry so that it will stick to the coarse substrates as the slurry coats the coarse substrates. Alternatively, both the coarse substrates and solid material can be dry when added to the rotating drum and water sprayed into the drum to promote adhesion of the solid material to the coarse substrates. In forming the coated substrates, it is desirable to maintain the moisture content of the solid material within the range of 5 to 30 weight % to promote proper adhesion between the solid material and coarse substrates.

[0066] As those skilled in the art will recognize many other techniques can also be used to coat the coarse substrates. For example, the solid material to be biotreated can be sprayed in a high pulp density slurry form onto the coarse substrates as the plurality of coarse substrates are being stacked to form the reactor.

[0067] If the solid material to be biotreated is applied as a slurry, adjustments can be made to the material to optimize the biotreatment process. For example, the pH can be adjusted to the optimum pH range for the microorganism that is to be used to break down the undesired compound. If nutrients, amendments, or inoculants are needed, they can also be added at this time. In some cases it may be advantageous to start the bioprocess in a tank prior to application of the particles of solid material to the coarse substrates.

[0068] The integrity of the coated coarse substrates should be sufficient enough to prevent a large number of blockages from forming in the flow channels of the reactor while the particles of solid material on the surface of the coated substrates are being biotreated. Such blockages will decrease oxygen flow and microorganism migration within the bioreactor and thereby reduce the rate of the biotreatment process. Of course, the larger the coarse substrates are in relation to the particle size of the solid material, the less likely such blockages will form because the solid material will be much smaller than the interstices between the coarse substrates. The integrity of the coated substrates should also be sufficient enough to prevent excessive amounts of the solid material from washing from the bioreactor during the biotreatment process.

[0069] Although the surface tension of water should hold the particles of solid material to the surface of the coarse substrates in most instances, if it is found that the particles of solid material are washing from the bioreactor in excessive concentrations or that blockages are forming in the bioreactor due to degradation of the coating, a binding agent can be used to improve the integrity of the coating. However, binding agents may interfere with the access of the biotreatment microorganism to some of the solid material to be biotreated, thus increasing the time necessary for the biotreatment process to reach the desired end point.

[0070] The thickness of the solid material coating on the plurality of coarse substrates is preferably less than about 1 mm to ensure that the microorganism being used in the biotreatment have adequate access to all of the solid material being biotreated. Thicker coatings will increase the capacity of the bioreactor, but the rate at which the biotreatment process advances will be slowed due to the limited access of the microorganism being used to the underlying particles of solid material. To make full use of the capacity of the bioreactor while ensuring adequate microorganism access, the thickness of the solid material coating should be greater than about 0.5 mm and less than about 1 mm. When a rock or brick substrate is being used, this will translate into a solid material loading of approximately 10 to 30 percent by weight.

[0071] The nonstirred surface reactor is formed by stacking a plurality of the coated substrates in a heap or in a tank. Conveyor stacking will minimize compaction of the coated substrates within the reactor. However, other means of stacking may be employed.

[0072] Preferably the reactor is inoculated with the microorganism (s) which is to be used in the biotreatment process while the plurality of coated substrates are being stacked to form the nonstirred surface reactor or immediately after formation of the reactor. Alternatively, if the microorganism(s) to be employed in the biotreatment process function best in a particular pH range, the pH of the reactor can be adjusted prior to inoculation as is well known in the art.

[0073] The microorganisms which are useful in the present biotreatment method are the same microorganisms that have traditionally been used to degrade a particular undesired compound in existing biodegradation and biooxidation processes. For example, acidophilic, autotrophic bacteria such as Thiobacillus ferrooxidans, Leptospirillum ferrooxidans, and Sulfolobus, can be used to biooxidize sulfide minerals in coal desulfurization or refractory sulfide ore biooxidation applications. Other bacteria that are useful in these applications are well within the ordinary skill of those in the art. Similarly, with respect to soil remediation applications, the microorganism(s) which should be employed are the same

as those currently employed in present bioremediation processes such as composting, landfarming, slurry biodegradation, and heap pile bioremediation. Those having ordinary skill in the art will be readily able to determine which microorganism (s) are applicable for the various undesired compounds which may be removed from the solid material using the method according to the present invention.

[0074] Once the reactor is inoculated with an appropriate microorganism, the conditions such as pH, temperature, nutrient supply, and moisture content within the reactor should be monitored and maintained throughout the biotreatment so as to promote the growth of the microorganism to the fullest extent possible. As the microorganism grows throughout the reactor, the reactor is transformed into a bioreactor having a very large surface area that will biodegrade or biooxidize the undesired compound in a time much shorter and to a greater extent than that of traditional static batch biotreatment processes such as heap bioleaching, composting, and landfarming.

[0075] The reactor can also be provided with perforated air pipes through which air can be blown or drawn as is well known in the art. Whether air is blown or drawn through the reactor will depend on the specific bioprocess occurring within the reactor, and such a selection is also well within the skill of those in the art.

[0076] The biotreatment process should be permitted to proceed until the undesired compound in the solid material is degraded to a desired concentration. In the case of soil remediation applications, this will typically be dictated by governmental regulations which define the acceptable level of a particular contaminant. In coal desulfurization applications, the amount of residual sulfur which is permitted to remain in the coal will also depend, to a large extent, on environmental regulations, because when sulfur bearing coal is burned it will produce sulfur dioxide as a byproduct. Thus, the amount of sulfur allowed to remain in the coal should be less than that which would violate environmental regulations when the coal is burned. This, of course, will depend to some extent on the equipment employed at the coal fired plant where the biotreated coal will be utilized. With respect to the biooxidation of refractory sulfide ores or concentrates, the amount of sulfide mineral that is permitted to remain in the ore will be dictated by the amount that must be biooxidized to achieve economical recoveries of the desired metal values from the ore or concentrate.

[0077] After the undesired compound has been reduced to a desired concentration, the bioreactor can be broken down and the biotreated solid material separated from the coarse substrates. After separation of the biotreated solid material, the coarse substrates can be reused. After one or more uses in the biotreatment process, a film of the microorganism used in the biotreatment process will develop on the substrates. This biofilm will have the advantage of adaptation to any toxic or inhibitory materials that are present in the solid material being processed. It is therefore best to remove the biotreated solid material in such a way as to not kill or entirely remove the biofilm that has built up on the coarse substrates. The biofilm is also an efficient way to inoculate the next coating of solid material applied to the coarse substrates. Finally, the adaptation of the microorganism after having been through the process many times will also speed up the rate at which the microorganism biodegrades or biooxidizes the undesired compound in the solid material being processed.

[0078] The present invention will now be described in further detail in connection with a number of possible embodiments that can be employed in the processing of refractory sulfide ores.

[0079] The second embodiment of the present invention is described in connection with Figs. 1 and 2. Fig. 1 illustrates a process flow chart for liberating and recovering precious metal values from precious metal bearing refractory sulfide ores. For purposes of describing the process illustrated in Fig. 1, the sulfide mineral concentrate 22 used in the present embodiment is produced from a gold bearing refractory sulfide ore. It follows, therefore, that the precious metal recovered in the present embodiment is gold. However, as one skilled in the art would understand, other precious metals, such as platinum and silver, can also be liberated and recovered from refractory sulfide ores using the process illustrated in Fig. 1. A combination of precious metals can also be recovered using the process according to the present embodiment if the refractory sulfide ore body used to produce the sulfide mineral concentrate 22 contains more than one precious metal.

[0080] According to the process flow chart shown in Fig. 1, a plurality of substrates 20 and a sulfide mineral concentrate 22 are added to a rotating drum 24. Preferably the sulfide mineral concentrate 22 is in a slurry form and the plurality of substrates 20 are dry when added to rotating drum 24 to improve the adhesion between the substrates 20 and the concentrate 22. Optionally, a polymeric binding agent can be added to rotating drum 24, although it is not necessary. As rotating drum 24 rotates, the substrates 20 added to drum 24 are coated with the wet sulfide mineral concentrate 22 to form coated substrates 39. Coated substrates 39 are then stacked to form static heap 26.

[0081] By using a slurry of concentrate in the coating process, the need and cost of drying the concentrate after its production is eliminated. Concentrate 22 and the plurality of substrates 20 can, however, be added to rotating drum 24 in the dry state, in which case after the mixture is added to drum 26 it is sprayed with water or an aqueous acid solution, preferably containing ferric ions, to cause the concentrate to stick to the substrates. The benefit of using an aqueous acid solution containing ferric ions to bind the concentrate to the surface of the substrates is that it will begin to chemically oxidize the sulfide mineral concentrate. Also it is acidic so that it will lower the pH of the coated substrates 39 in preparation for biooxidation. The disadvantage of using such an acid solution is that it will increase the cost of the equipment used to form the coated substrates 39 because it must be designed to be acid resistant.

[0082] Sulfide mineral concentrate 22 is comprised of a plurality of fine metal sulfide particles 40 which have finely

disseminated gold and possibly other precious metal values occluded within. Sulfide mineral concentrate 22 will also typically contain fine particles of sand or other gangue material 42 from the refractory sulfide ore from which concentrate 22 is obtained. As a result, each of the coated substrates 39 will be coated with the metal sulfide particles 40 and fines 42 as illustrated in Fig. 2.

[0083] The integrity of coated substrates 39 should be sufficient enough to prevent a large number of blockages from forming in the flow channels within heap 26 while the metal sulfide particles 40 on the surface of coated substrates 39 are being biooxidized. Such blockages decrease oxygen flow and bacteria migration within the heap and thereby reduce the rate of biooxidation.

[0084] Because metal sulfide particles 40 are hydrophobic, they will tend to stick to the dry substrates 20 without the use of a binding agent such as a polymeric agglomeration aid. This assumes, however, that the metal sulfide particles 40 are of an appropriate size. Therefore, if concentrate 22 contains an adequate concentration of metal sulfide particles 40, concentrate 22 will remain sufficiently adhered to coated substrates 39, even without the use of a binding agent, to permit coated substrates 39 to be handled while being stacked on heap 26 or placed in tank 45, which is described later in connection with the embodiment illustrated in Fig. 5. Furthermore, coated substrates 39 should retain their integrity throughout the biooxidation process. When forming coated substrates 39 without the use of a binding agent, therefore, it is important to use a sulfide mineral concentrate which has an adequate concentration of metal sulfide particles and an appropriate particle size.

[0085] While a polymeric binding agent can be used and would possibly improve the integrity of the coated substrates 39, the use of such agents will increase the operating cost of the process.

[0086] At least two factors militate against using a sulfide mineral concentrate 22 having a very high concentration of metal sulfide particles 40. First, the cost of producing concentrate 22 is typically proportional to its concentration of metal sulfide particles. Thus, as the concentration of metal sulfide particles 40 in concentrate 22 increases, the cost of producing concentrate 22 will likewise increase. The added cost of producing very high grades of concentrate 22 may not be offset by the incremental improvement in metal sulfides loading or integrity of the coated substrates 39. Second, as the grade of concentrate increases, the amount of metal sulfide particles 40 that remain with the tail fraction of the refractory sulfide ore will increase. Because these metal sulfide particles contain occluded precious metal values, any metal sulfide particles 40 that remain in the ore tail will decrease the total recovery rate for the process.

[0087] Taking the above factors into consideration, sulfide mineral concentrate 22 should contain at least 20 weight % metal sulfides to ensure adequate handling characteristics and integrity during biooxidation. Preferably, however, the concentrate will contain at least about 40 weight % metal sulfides, and more preferably at least about 70 weight %. Typically, concentrate 22 will contain between about 40 to 80 weight % metal sulfides.

[0088] In general, as the particle size of the sulfide mineral concentrate 20 decreases, the faster the biooxidation process will proceed. Smaller particle sizes also tend to result in improved concentrate grades. This is because it is typically easier to separate the metal sulfide particles 40 from the bulk of gangue material as the particle size of the ore is decreased. Sulfide mineral concentrate 22, therefore, preferably has a particle size of less than about 250 μm. Particles larger than 250 μm may not adhere to substrates 20 very well without the use of a binding agent. In addition, unless the refractory sulfide ore from which concentrate 22 is produced is ground to at least 100% passing 250 μm, it is difficult obtain a good separation of the metal sulfide particles 40 from the bulk of gangue material during concentration. This is especially true if flotation is used to form concentrate 22, because particles larger than 250 μm do not float very well. On the other hand, if the particle size of concentrate 22 is less than about 38 μm to 25 μm, the concentrate particles will tend to clump together during the coating process rather than form a relatively uniform coating on coated substrate 39. These clumps of concentrate can block air flow and bacteria migration during biooxidation, thereby reducing the rate of biooxidation in the heap.

[0089] Preferably the particle size of concentrate 22 is about 100 % passing 106 μm to 75 μm. Particles in this size range adhere well to substrates 20, and the incremental improvements which can be achieved in the rate of biooxidation and the concentrate grade with finer particle sizes are rarely justified by the added grinding costs of producing them.

[0090] Sulfide mineral concentrate 22 can be produced from any precious metal bearing refractory sulfide ore body being mined using techniques well known in the art and thus need not be explained in detail here. The production of concentrate 22, however, will typically include the crushing and grinding of the refractory sulfide ore to an appropriate particle size followed by one or more gravity separations or one or more sulfide flotations.

[0091] Some potential refractory sulfide ore bodies may already be of sufficient grade such that further concentration is not required. Such ore bodies may include tailings or waste heaps at existing mines. When these types of ores are processed, the sulfide mineral concentrate need only be transported to the location of the biooxidation facility and possibly some additional comminution to achieve the desired particle size.

[0092] With respect to gold concentration, the process according to the present embodiment can be performed economically even if concentrate 22 contains as little as 5 g Au/tonne of concentrate (or an equivalent economic value of other precious metal values). This number of course will vary to a large extent based on the cost of producing concentrate 22 and the prevailing price of gold. As those skilled in the art will recognize, however, traditional autoclaves or stirred

tank bioreactors cannot come close to economically processing a sulfide mineral concentrate having such a low concentration of gold.

[0093] Many different materials can be used for substrates 20. Preferred substrates include coarse refractory sulfide ore particles, lava rock, gravel, and barren rock which includes a mineral carbonate component. Substrates 20 can also be man made objects such as plastic balls, recycled styrofoam, ground tires and the like. The purpose of the substrates 20 is to provide a support with a relatively large surface area upon which the concentrate 22 can reside during the biooxidation process. The surface area of each substrate 20 in effect acts as a small surface bioreactor during biooxidation. Therefore, when a large number of coated substrates 39 are stacked in heap 26 for biooxidation, a nonstirred surface bioreactor is created that has a very large total surface area.

[0094] The total surface area of the bioreactor or heap 26 can be increased by decreasing the particle size of substrates 20, using substrates that have a rough, nonuniform surface morphology and/or increasing the number of coated substrates 39 stacked on heap 26. The advantage of increasing the total surface area of the substrates 20 within heap 26 is that the amount of concentrate 22 that can be loaded on substrates 20 increases proportionately, which in turn increases the amount of concentrate 22 that can be biooxidized in a particular heap 26.

[0095] The preferred particle size range for substrates 20 is nominally from about +0.62 cm to about -2.5 cm with particles less than about 0.3 cm removed by screening or other suitable method. However, substrates 20 having a particle size down to approximately +600 μm can be used. While increased loading is achieved with smaller substrate particle sizes, increased air flow, fluid flow and heat dissipation is achieved with larger particle sizes. The nominal +0.62 to -2.5 cm size range provides a good compromise between concentrate loading and ensuring adequate air flow, fluid flow, and heat dissipation.

[0096] Substrates 20 are preferably loaded with as much concentrate 22 during the coating process as possible to maximize the process throughput. The amount of concentrate 22 that can be loaded on substrates 20 will depend on particle size and surface morphology of the substrates 20. Coarse substrates 20 and sulfide mineral concentrate 22 should, therefore, be added to rotating drum 24 in sufficient quantities to maximize the amount of sulfide mineral concentrate 22 loaded on each substrate 39. while minimizing the formation of agglomerates of the sulfide mineral concentrate particles. Clumps or agglomerates of the sulfide mineral concentrate 22 particles may be formed if the particle size of the concentrate is too fine, as discussed above, or if an excess amount of the concentrate is added to drum 24. To ensure adequate loading of substrates 20 while simultaneously avoiding formation of agglomerates of the concentrate particles, preferably approximately 10 to 30 weight % concentrate is added to rotating drum 24, which will result in a loading of approximately 10 to 30 weight % of concentrate 22 on coated substrates 39.

[0097] In forming coated substrates 39, it is desirable to maintain the moisture content of concentrate 22 within the range of 5 to 30 weight %. If the moisture content of the concentrate is below 5 weight %, the concentrate will not adhere properly to the substrates, and if the moisture content exceeds 40 weight %, the concentrate slurry will be too thin to from a thick enough coating on the substrate. This would limit the amount of concentrate that would adhere to the substrates 20.

[0098] Although other means of heap construction may be used, conveyor stacking is preferred. Conveyor stacking minimizes compaction of the coated substrates within the heap. Other means of stacking such as end dumping with a dozer or top dumping can lead to regions of reduced fluid flow within the heap due to increased compaction and degradation of the coated substrates.

[0099] If desired, heap 26 can be provided with perforated pipes 27 connected to an air supply source (not shown) in order to increase the air flow within the heap. Increasing the air flow within heap 26 will increase the rate of biooxidation and improve the rate at which heat is dissipated from the heap. Furthermore, because of the large air and fluid flow channels between the coated substrates 39, the air supply source connected to perforated pipes 27 can be a low cost blower rather than a more expensive compressor.

[0100] Heap 26 is preferably inoculated with a bacteria capable of biooxidizing metal sulfide particles 40 while coated substrates 39 are being stacked on to heap 26 or immediately after formation of heap 26 or after the pH of heap 26 has been lowered to below 2.5. The following bacteria may be used in the practice of the present invention:

> Thiobacillus ferrooxidans; Thiobacillus thiooxidans; Thiobacillus organoparus; Thiobacillus acidophilus; Leptospirillum ferrooxidans; Sulfobacillus thermosulfidooxidans; Sulfolobus acidocaldarius; Sulfolobus BC; Sulfolobus solfataricus and Acidianus brierlevi and the like.

[0101] These bacteria are all available from the American Type Culture Collection or like culture collections. Whether one or more of the above bacteria and the particular bacteria selected for use in the present process will depend on factors such as the type of ore being processed and the expected temperatures in heap 26 during biooxidation. These selection criteria, however, are well within the skill of those in the art and need not be described in detail here. The most common and preferred bacteria for biooxidation is Thiobacillus ferrooxidans.

[0102] During the biooxidation of the metal sulfide particles 40 coated on the surface of the coated substrates 39,

additional inoculant and microbial nutrient solutions can be supplied through a sprinkler system 28. Additions of these bioleachant maintenance solutions will typically be made in response to certain performance indicators used to monitor the progress of the biooxidation process.

[0103] The rate of biooxidation is preferably monitored throughout the biooxidation process based on selected performance indicators such as the solubilization rate of arsenic, iron, or sulfur, or the oxidation rate of sulfides which can be calculated therefrom. Other biooxidation performance indicators that may be used include measuring pH, titratable acidity, and solution Eh.

[0104] Preferably the bioleachate off solution that percolates through the heap is collected at drain 29 and recycled to the top of heap 26. This minimizes the amount of fresh water required by the biooxidation process. And, because the bioleachate off solution will be acidic and contain a high concentration of ferric ions, its reapplication to the top of heap 26 is advantageous to the biooxidation process. However, the effluent solution generated early in the biooxidation process will also contain significant concentrations of base and heavy metals, including components that lead to microbial inhibition. As the inhibitory materials build-up in the bioleachate off solution, the biooxidation process is retarded. Indeed, continued recycling of an off solution without treatment can lead to a build-up of inhibitory materials sufficient to stop the biooxidation process altogether.

[0105] To minimize the build-up of inhibitory materials and thus their effect on the biooxidation process, the off solution can be treated in acid circuit 30 prior to recycling to remove the inhibitory materials when their concentration becomes excessive. One method of conditioning the bioleachate off solution before recycling comprises raising its pH above 5, removing any precipitate that forms and then lowering its pH to a pH appropriate for biooxidation using an untreated portion of the off solution or other acid solution. Such a conditioning process is disclosed in U.S. Patent Application Serial No. 08/547,894, filed October 25, 1995 by Kohr et al

[0106] The bioleachate off solution will tend to be very acidic in the present invention. This is because a concentrate having a relatively high concentration of metal sulfide minerals is being biooxidized rather than an entire ore. As a result, the biooxidation process according to the present invention will tend to produce large amounts of excess acid. That is the process will produce more acid than can be practically recycled to the top of heap 26. This excess acid must be disposed of or used for other purposes. One possible use for the excess acid is in a copper oxide ore leaching process because sulfuric acid is an effective lixiviant for copper oxide ores. However, the sulfuric acid solution produced as a byproduct of the present process will also typically contain a high concentration of ferric ions. This also makes it an effective lixiviant for some copper sulfide ores such as chalcocite. The ferric ion in the acid solution chemically oxidizes the copper sulfide minerals to cause their dissolution. Thus, the excess acid from the present process can be beneficially used in a copper leaching operation to avoid the neutralization costs associated with disposal while simultaneously reducing the acid costs for the copper leaching operation.

[0107] After the biooxidation reaction has reached an economically defined end point, that is after the metal sulfide particles 40 on the surface of the coarse substrates 20 are biooxidized to a desired degree, the heap is broken down and the biooxidized concentrate 22 is separated from the coarse substrates 20. Prior to breaking the heap down, however, the heap will typically be drained and then washed by repeated flushings with water. The number of wash cycles employed is typically determined by a suitable marker element such as iron and the pH of the wash effluent.

[0108] Separation can be accomplished by placing the coated substrates 39 on a screen and then spraying the coated substrates with water. Alternatively, the coated substrates can be tumbled in water using a trommel.

[0109] Following separation, gold is extracted from the biooxidized concentrate 22. This can be accomplished using a number of techniques well known in the art. Typically, however, the biooxidized concentrate will be leached with a lixiviant such as cyanide in a carbon-in-pulp or a carbon-in-leach process. In these processes, the lixiviant dissolves the liberated gold or other precious metal values which are then adsorbed onto activated carbon as is well known in the art.

[0110] If cyanide is used as the lixiviant, the concentrate will need to be neutralized prior to leaching. To avoid the need for neutralization, thiourea can be used as the lixiviant to extract the gold from the biooxidized concentrate. The thiourea extraction process can be improved by adjusting the Eh of the leach solution using sodium metabisulfite as disclosed in U.S. Patent No. 4,561,947. If thiourea is used as the lixiviant, preferably a synthetic resin, rather than activated carbon, is used to adsorb the dissolved precious metal values from the lixiviant solution.

[0111] After the liberated gold or other precious metal values are extracted from the biooxidized concentrate, the biooxidized concentrate is taken to a waste or tailings pile 36 and gold is recovered from the carbon or synthetic resin using techniques well known in the art.

[0112] The coarse substrates 20 which have been separated from the biooxidized concentrates can be recycled to the rotating drum for a new coating of sulfide mineral concentrate 22. Substrates 20 can be reused so long as they retain their mechanical integrity. If coarse refractory sulfide ore particles are used for substrates 20, they are preferably processed at some point, preferably after one to three cycles, to recover liberated gold values.

[0113] As illustrated in Fig. 2, coarse refractory sulfide ore substrates 20 will contain metal sulfide particles 40 which contain occluded gold and other precious metal values. After one to three cycles through the process, many of the metal sulfide particles 40 within the coarse ore substrates 20 will be partially biooxidized. Rather than continuing to recycle

the coarse ore substrates in this situation and allow the liberated gold values to go unclaimed, the coarse ore substrates can be processed to recover their gold values. This is preferably accomplished by grinding the coarse ore substrates in grinding circuit 32 to a particle size suitable to permit the metal sulfide particles to be separated from the bulk of the gangue material. A concentrate 22 of the metal sulfide particles 40 from the ground coarse ore substrates is then produced in the sulfide concentrator 34. Preferably sulfide concentrator 34 is a flotation cell and the biooxidized coarse ore substrates are ground to a size appropriate for sulfide flotation and coating on substrates 20. The concentrate 22 produced from the ground ore substrates is then combined with the supply of sulfide mineral concentrate 22 from which it is coated on a second plurality of coarse substrates 20 and added to a new heap 26 for further biooxidation.

[0114] The flotation tail from sulfide concentrator 34 should be treated in the gold extraction process along with the biooxidized concentrate 22 from heap 26. The flotation tail will contain a number of fully and partially oxidized metal sulfide particles that did not float. These oxidized particles will contain significant gold values, and as much of these gold values will already be liberated, they can be readily leached from the flotation tail using cyanide or thiourea. After lixiviation, the flotation tail is disposed of along with the biooxidized concentrate which has gone through gold extraction in waste or tailings pile 36.

[0115] Refractory sulfide coarse ore substrates 20 that have gone through the biooxidation process can alternatively be processed simply by grinding followed by lixiviation. This process alternative, however, will result in a lower overall recovery, because many of the metal sulfide particles 40 within the coarse ore substrates will not be sufficiently oxidized to liberate their entrapped gold values.

[0116] With respect to material selection for substrates 20, there are several advantages of using coarse refractory sulfide ore particles.

[0117] First, the refractory sulfide ore body being mined will typically have to go through several crushing and grinding steps before an appropriate particle size is achieved for producing concentrate 22. As a result, coarse refractory sulfide ore substrates can be removed from an appropriate stage of the crushing process, which makes coarse refractory sulfide ore particles an inexpensive source of substrates 20.

[0118] Second, as illustrated in Fig. 2 and discussed above, if coarse refractory sulfide ore is used as the substrate material, it will contain metal sulfide particles 40. These metal sulfide particles will be partially biooxidized during the biooxidation process, and, if the coarse ore particles are recycled through the process several times, the metal sulfide particles 40 will eventually become sufficiently biooxidized to permit recovery of their precious metal values.

[0119] A third advantage, which is somewhat related to the second, is that a fraction of the iron sulfide or other metal sulfide particles 40 in the refractory sulfide ore are so fine that they will not float very well in the concentration process. By using coarse particles of the ore for substrates 20, these very fine metal sulfide particles will be chemically oxidized over time by the ferric ion in the bioleachant. Then, when the coarse ore particles are eventually ground and floated to produce a concentrate of metal sulfide particles, the oxidized fine metal sulfide particles will end up in the flotation tails. Because the flotation tails are leached with cyanide or other lixiviant, the liberated gold values from these very fine sulfide particles will be recovered. On the other hand, if the coarse ore particles were not used as substrates 20 prior to grinding and flotation, the very fine metal sulfide particles would still end up in the flotation tails when producing concentrate 22. However, because these very fine sulfide particles would not be partially biooxidized at this point, their occluded gold values cannot be recovered by lixiviation.

[0120] A fourth advantage of using refractory sulfide coarse ore as substrates 20 is that the metal sulfide particles in the biooxidized support material will be easier to float following biooxidation. This is because the surface of the metal sulfide particles is altered during the biooxidation process. Thus, after the coarse ore support material has been reused several times and it is ground and floated to produce a sulfide mineral concentrate, improved flotation results can be achieved.

[0121] If the coarse ore particles also contain a carbonate mineral component, a fifth advantage exists for using coarse refractory sulfide ore particles as the coarse substrates 20. Carbonate minerals tend to be very acid consuming. As a result, ores which contain these minerals have traditionally required a lot of acid conditioning prior to biooxidation. Acid conditioning of these ores is required to remove or reduce the carbonate mineral component prior to biooxidation so that the biooxidation reaction can proceed. And, while coarse refractory sulfide ore particles in general tend to biooxidize very slowly--often taking up to nine months or more--if lots of carbonate minerals are included in the ore, without pre-conditioning, the coarse ore particles may never biooxidize. In the process according to the present invention, however, coarse refractory sulfide ore particles that contain carbonate minerals can be advantageously used for substrates 20. During the biooxidation process, the acid produced from the biooxidation of the concentrate 22 on the surface of the coarse ore substrates will slowly neutralize the carbonate minerals in the substrates. A byproduct of the neutralization process is carbon dioxide, which the autotrophic bacteria used in the present invention can use as a source of carbon to carry out metabolic synthesis. The carbon dioxide production, therefore, will promote bacteria growth in heap 26, which in turn increases the rate of biooxidation of concentrate 22. Thus, by using coarse ore that contains carbonate minerals for support material 20, the coarse ore will be slowly neutralized for future biooxidation and bacteria growth in heap 26 will be promoted. A concomitant benefit, as noted above, will be the biooxidation of the very fine nonfloatable

sulfide particles that are in the coarse ore.

[0122] As those skilled in the art will recognize, the coarse refractory sulfide ore particles used for substrates 20 do not have to originate from the same ore body as that used to produce concentrate 22. In fact, in some situations, it may be beneficial to use a concentrate 22 from one ore body and coarse ore substrates 20 from another. For example, one ore body may be easily concentrated or already have the characteristics desirable of a concentrate and another ore body may have a high concentration of carbonate minerals. In such a situation, it would be advantageous to use the first ore body to produce concentrate 22 and the second ore body to produce substrates 20. In this way, the ore from the second ore body can be neutralized in preparation for biooxidation while simultaneously improving the biooxidation results of the concentrate from the first ore body. Similarly, if an ore body contains a high concentration of metal sulfides that are difficult to float, improved flotation results can be achieved by first using the ore as coarse ore substrates 20 in the process according to the present invention.

[0123] Other preferred materials for substrates 20 include lava rock, gravel, and coarse rock containing carbonate minerals. These types of substrates will typically be used when the refractory sulfide ore body being mined is a waste heap or tailings pile, and, as a result, the ore has already gone through crushing and grinding.

[0124] An advantage of using lava rock is that it has a very rough, nonuniform surface morphology which increases the overall surface area of the substrates 20 for a particular particle size. Thus, for a given particle size, lava rock can be loaded with more concentrate than other substrates having a smoother surface.

[0125] Gravel, while typically having a fairly smooth surface, is an inexpensive substrate material. Coarse rock containing carbonate minerals is advantageous, because it will slowly release carbon dioxide as the acid from the biooxidation process neutralizes the carbonate minerals as explained above. This type of substrate would preferably be reused in the process only as long as it continues to release carbon dioxide during the biooxidation process.

[0126] A third embodiment of the present invention is now described in connection with Fig. 3. The process according to the present embodiment is essentially a variation on the embodiment described in connection with Fig. 1. Accordingly, like items are referred to with the same reference numbers, and the description and considerations expressed with respect to these items in connection with Fig. 1 will be understood to apply equally to the present embodiment.

[0127] As with the second embodiment, the process according to the present embodiment can be used to liberate and recover precious metal values from a precious metal bearing refractory sulfide ore. For purposes of the present description, however, it is assumed that the sulfide mineral concentrate 22 is produced from a gold bearing refractory sulfide ore.

[0128] According to the present embodiment, a plurality of substrates 20 are coated with a sulfide mineral concentrate 22 in rotating drum 24 to produce a plurality of coated substrates 39. The plurality of coated substrates 39 are then stacked to form heap 26, which is used as a large nonstirred surface bioreactor.

[0129] The various considerations discussed above in connection with substrates 20, sulfide mineral concentrates 22, the formation of coated substrates 39, and the formation of heap 26 are all equally applicable here.

[0130] After heap 26 is formed the heap is inoculated with a biooxidizing bacteria to initiate the biooxidation process. As the biooxidation process proceeds, additional sulfide mineral concentrate 22 can be added to the top of heap 26. An advantage of adding additional sulfide mineral concentrate 22 to the top of heap 26 throughout the biooxidation process is that the amount of concentrate processed in the heap can be increased before tearing down and rebuilding. Furthermore, if coarse refractory sulfide ore is used for substrates 20, concentrate 22 will tend to biooxidize more quickly than the metal sulfide particles 40 found in the coarse ore. Thus, by adding additional concentrate 22 to the top of heap 26, the degree of biooxidation of the coarse ore substrates can be increased before heap tear down. In addition, by adding the sulfide mineral concentrate 22 to the top of heap 26, acid and ferric ions produced during its biooxidation will migrate to the lower part of the heap where bacterial growth may be inhibited due to toxins, which have not been washed from the ore early in the biooxidation process, or due to the lack of oxygen. As a result, biooxidation of the sulfide mineral concentrate and coarse ore substrates will proceed even if bacterial growth is not favored in this region.

[0131] There is another advantage to adding sulfide mineral concentrate 22 to the top of heap 26 after it has been undergoing biooxidation for some time, because such additions will increase the biooxidation rate in the heap. In the later stages of biooxidation of the coated substrates 39, most of the exposed and reactive sulfides will have already been oxidized, resulting in a slow down in the rate of biooxidation. This slow down in the rate of biooxidation can lead to a drop in iron levels and an increase in pH within heap 26. Addition of fresh reactive sulfide mineral concentrate 22 to the top of heap 26 can restart an active biooxidation process due to the high ferric levels produced from the biooxidation of the added concentrate, which in turn will increase indirect chemical leaching of the sulfide mineral concentrate 22 coated on substrates 20 and of metal sulfide particles imbedded in coarse ore substrates 20.

[0132] Fresh concentrate 22 can be added to the top of heap 26 until the flow channels within the heap begin to become plugged with the concentrate and biooxidized residue from the concentrate.

[0133] A second variation in the present embodiment from that in Fig. 1 is with respect to how the precious metal values are recovered from the heap following biooxidation. In the present embodiment, instead of tearing down the heap and then separating the biooxidized concentrate from the heap for gold extraction, gold is extracted from the biooxidized

concentrate--and if a coarse ore substrate is used, from the substrates--by directly lixiviating the heap with a precious metal lixiviant. Preferably the lixiviant is one that functions at a low pH, such as thiourea, so the heap does not need to be neutralized prior to lixiviation. Furthermore, by using thiourea or other acid compatible lixiviant, the liberated gold values can be extracted from the heap on an intermittent basis. For example, heap 26 can be biooxidized for a period, liberated gold values extracted with an appropriate lixiviant, and then the biooxidation process resumed. A fresh concentrate 22 is preferably added to the top of heap 26 in slurry form with the resumption of the biooxidation process.

[0134] Gold is extracted from heap 26 by first allowing the bioleachate solution to drain from the heap to acid circuit 30 following a desired degree of biooxidation. After the heap is drained, an acid compatible lixiviant such as thiourea is pumped from the lixiviant supply 38 to the sprinkler system 28 where it is dispersed onto heap 26. As the lixiviant percolates through the heap, it dissolves liberated gold values from the sulfide mineral concentrate 22 and coarse ore substrates. The loaded lixiviant then collects at drain 29 where it diverted from the acid circuit to a gold removal process 44, which preferably comprises adsorbing the dissolved gold onto activated carbon or a synthetic resin. The barren lixiviant is then recycled to the lixiviant supply 38 and gold is recovered from the loaded activated carbon or synthetic resin. Processes for stripping adsorbed gold values from activated carbon and synthetic resin are well known in the art and need not be described herein.

[0135] A process according to a fourth embodiment of the present invention is illustrated in Fig. 4.

[0136] Fig. 4 illustrates a process for liberating and recovering metal values from a sulfide ore. As the process according to the present embodiment has certain similarities to the embodiment described in connection with Fig. 1, like items have been referred to with the same reference numbers. Furthermore, the description and considerations expressed with respect to these items in connection with Fig. 1 will be understood to apply equally to the present embodiment.

[0137] According to the present embodiment, a sulfide mineral concentrate 22 is first produced from a sulfide ore. Concentrate 22 is comprised of a plurality of fine metal sulfide particles 40 and fine particles of sand or other gangue material 42.

[0138] Many different sulfide ores can be used to produce sulfide mineral concentrate 22. Foremost amongst the sulfide ores that can be treated in the present process are sulfide ores that contain sulfide minerals of base metals such as copper, zinc, nickel, iron, molybdenum, cobalt, or uranium. The metal values of interest in these ores are present in the metal moiety of the sulfide mineral particles in the ore. The metal values which are liberated and recovered, therefore, will depend on the specific sulfide minerals present in concentrate 22 produced from the ore. For example, if the sulfide ore used to produce concentrate 22 contains chalcocite, bornite, and/or chalcopyrite, then the metal values recovered will be that of copper. On the other hand, if concentrate 22 is a concentrate of sphalorite, the metal values recovered will be that of zinc.

[0139] After concentrate 22 is produced, sulfide mineral concentrate 22 is then coated on a plurality of substrates 20 to form coated substrates 39. This is accomplished as described in connection with Fig. 1 by adding a plurality of dry substrates 20 and a slurry of concentrate 22 to rotating drum 24, or, alternatively, by adding a plurality of dry substrates 20 and concentrate 22 to rotating drum 24 and then spraying the mixture with an aqueous solution. The plurality of coated substrates 39 produced in rotating drum 24 are stacked to form heap 26, which forms a large nonstirred surface bioreactor.

[0140] The various considerations discussed above in connection with substrates 20, sulfide mineral concentrates 22, the formation of coated substrates 39, and the formation of heap 26 are all equally applicable here.

[0141] After heap 26 is formed, the heap is inoculated with a biooxidizing bacteria to initiate the biooxidation process. As the metal sulfide particles 40 in concentrate 22 biooxidize, the metal moiety of the sulfide particles dissolves in the bioleachate solution as it percolates through the heap. After the bioleachate solution percolates through the heap, it is collected at drain 29. The bioleachate solution is then processed to recover one or more desired base metal values by removing them from the bioleachate solution using techniques well known in the art.

[0142] Following recovery of the desired metal values from the bioleachate solution, the solution can be processed in acid circuit 30 to remove any excess toxins as described in connection with Fig. 1 and then reapplied to the top of heap 26.

[0143] Once the biooxidation reaction has reached an economically defined end point, that is after the metal sulfide particles 40 on the surface of the coarse substrates 20 are biooxidized to a desired degree, the heap is broken down and the biooxidized concentrate separated from the coarse substrates 20. The biooxidized concentrate is then disposed of in waste or tailings pile 36. It is to be understood, however, that while the present embodiment has been described in terms of liberating and recovering base metal values from the metal moiety of the metal sulfide particles 40 in sulfide mineral concentrate 22, sulfide particles 40 can also include occluded precious metal values. After biooxidation of concentrate 22, therefore, any precious metal values that are liberated in concentrate 22 can be extracted and recovered as described in connection with Fig. 1 prior to the disposal of the biooxidized concentrate.

[0144] The coarse substrates 20 which have been separated from the biooxidized concentrate can be recycled to the rotating drum for a new coating of sulfide mineral concentrate 22. Alternatively, if coarse sulfide ore particles are used for substrates 20, they are preferably processed after one or more cycles through the process to form a sulfide mineral concentrate of any metal sulfide particles 40 which remain unoxidized in the coarse ore substrates. Sulfide mineral

concentrate 22 is produced from the biooxidized coarse ore substrates as described in connection with the second embodiment.

[0145] A process according to a fifth embodiment of the present invention is illustrated in Fig. 5. The process illustrated in Fig. 5 is for liberating and recovering precious metal values from precious metal bearing refractory sulfide ores using a nonstirred bioreactor. The process comprises producing a concentrate 22 of metal sulfide particles 40 from the refractory sulfide ore being processed. Concentrate 22 is then coated on a plurality of coarse substrates 20 to form coated substrates 39 using rotating drum 24 as described in connection with the second embodiment. After formation, coated substrates 39 are placed in a tank 45 for biooxidation. By biooxidizing substrates 39 in tank 45, a large nonstirred surface bioreactor is created which has a very large surface area. Thus, tank 45 takes the place of heap 26 in the process according to the second embodiment. Accordingly, the various considerations discussed above in the second embodiment with respect to substrates 20, sulfide mineral concentrates 22, the formation of coated substrates 39, and the formation of heap 26 are all equally applicable to the biooxidation of coated substrates 39 in tank 45 in the present embodiment.

[0146] During the biooxidation of concentrate 22 on coated substrates 39, bioleachant maintenance solutions are added to the tank from the top using any of a number of well known techniques. The bioleachate solution that percolates through the tank is drained from the tank and processed in acid circuit 30 as described in connection with Fig. 1 prior to reuse in the process.

[0147] Air can be blown into the tank during the biooxidation process to improve the oxygen levels in the bioreactor and to improve heat dissipation. Air is preferably blown into tank 45 through a series of perforated pipes 46 which are connected to a blower (not shown).

[0148] If desired, additional concentrate 22 can be added to the top of the coated substrates 39 in tank 45 throughout the biooxidation process. As described above in connection with the third embodiment, by adding additional concentrate to the bioreactor during the biooxidation process, the rate of biooxidation within the bioreactor can be maintained at a high level throughout the biooxidation process.

[0149] An advantage of using tank 45 over heap 26 for the bioreactor is that it makes separation of the biooxidized concentrate 22 from the substrates 20 easier. After the concentrate 22 is biooxidized to a desired end point, separation of the biooxidized concentrate from the substrates is accomplished by filling the tank with water, and then rapidly draining the tank. The biooxidized concentrate will be carried with the draining water. This process can be repeated several times to improve separation results. Tank 45 is also preferably equipped with a screen in the bottom of the tank which has a mesh size that is less than the size of the substrates, but larger than the concentrate particle size to aid the separation process.

[0150] After separation, the biooxidized concentrate is leached with a precious metal lixiviant to extract the liberated gold or other precious metal values. The dissolved gold values are then recovered from the lixiviant by contacting the solution with activated carbon or a synthetic resin. Preferably the lixiviation is carried out in the presence of the activated carbon or a synthetic resin so that the dissolved gold values are immediately removed from the solution as they are dissolved. The gold adsorbed on the activated carbon or synthetic resins can be recovered using techniques well known in the art.

[0151] Once the precious metal values have been extracted from the biooxidized concentrate, the concentrate can be disposed of in waste or tailings pile 36.

[0152] As in the second embodiment, the coarse substrates 20 that have been separated from the biooxidized concentrates can be recycled to the rotating drum for a new coating of sulfide mineral concentrate 22. Substrates 20 can be reused as long as they retain their mechanical integrity. If coarse refractory sulfide ore particles are used as substrates 20, they are preferably processed at some point, preferably after one to three cycles, to recover liberated gold values. This is accomplished in the same manner as described in connection with the second embodiment.

[0153] Another aspect of the present invention is now described. In this aspect of the invention, a process for recovering precious metal values from a concentrate of precious metal bearing refractory sulfide minerals is described. The process comprises (a.) distributing a concentrate comprised of fine refractory sulfide minerals on top of a heap of coarse support material; (b.) biooxidizing the concentrate of refractory sulfide minerals; (c.) leaching precious metal values from the biooxidized refractory sulfide minerals with a lixiviant; and (d.) recovering precious metal values from the lixiviant.

[0154] A concentrate of precious metal bearing refractory sulfide minerals will typically be prepared from a precious metal bearing refractory sulfide ore. The concentrate can be prepared from such ores using well known gravity separation or flotation techniques. Although gravity separation is cheaper, flotation is the preferred method of separation because of the selectivity of the process. The most frequently used collector for concentrating sulfide minerals in a flotation process is Xanthate. Xanthate flotation processes are well known to those skilled in the art and need not be described in detail herein.

[0155] Preferably the particle size of the concentrate is such that 80 to 90% of the concentrate is less than 100 to 45 μm. More preferably, 80 to 90% of the concentrate is less than 150 μm to 100 μm.

[0156] The optimum size may, however, vary with various ore types. In general, the operator should strive for a particle size which permits optimum separation in the concentration process and which provides for the optimal rate of biooxidation

versus the incremental costs of additional fine grinding.

[0157] The smaller the particle size of the sulfide minerals within the concentrate, the more quickly the concentrate will oxidize during bioleaching. However, the faster biooxidation rate does not always justify the added energy costs associated with fine grinding an ore or a flotation concentrate.

[0158] With the process according to the present aspect of the invention, the cost of leaving the concentrate on the heap to biooxidize is minimal. Therefore, a slightly longer biooxidation period may be justified to avoid having to incur additional grinding related expenses. In this regard, the present process has an advantage over mill type processes. In mill type processes, the sulfide mineral concentrate must be very finely ground to ensure high biooxidation rates so that the bioreactor can process as much concentrate as possible in as short of period of time as possible to maintain the economics of the process.

[0159] After the sulfide mineral concentrate is formed, it is distributed over the top of a heap of support material. Preferably, the concentrate is distributed on top of the heap in a slurry form so that the concentrate can be piped directly to the heap without having to be dried first. The pulp density of the concentrate should be adjusted so that the concentrate flows well, but does not simply wash through the heap of support material. Because the sulfide mineral particles are hydrophobic, they will tend to stick to the support material rather than migrating completely through the heap if the appropriate support material is selected. Nor should blockage of flow channels be a problem if an appropriate size support material is selected. The purpose of the support material is to capture and retain the sulfide minerals as they slowly migrate down through the heap so that the support material acts as a large surface area bioreactor. For this reason support materials having a high degree of porosity or a rough surface are preferred since these types of surfaces will tend to capture and retain the concentrate. The more concentrate that the support rock can support without blockage of the flow channels the better. Support materials that can be used in practicing the present aspect of the invention include lava rock, gravel, or barren rock containing small amounts of mineral carbonate as a source of CO_2 for the biooxidizing bacteria. Other suitable coarse substrates include brick, cinder block, and slag. Lava rock is a particularly preferred support material due to its roughness and high degree of porosity.

[0160] Support material which contains a small amount of mineral carbonate is beneficial not only for the CO_2 that it produces but is also beneficial because it will help buffer the acid solution produced as a result of the biooxidation process. This will make it easier to control the pH of the bioreactor during the biooxidation process.

[0161] With respect to selection of an appropriate size of support material, there are several competing interests that should be considered. Smaller diameter support materials have greater surface area and thus increase the effective area of the bioreactor created by the heap of support material. However, smaller diameter support material may be more expensive depending on the amount of grinding required to produce the desired size. Further, smaller diameter support material may be subject to more blockage of fluid flow channels by the concentrate which is added to the top of the heap. Larger support material will permit taller heaps to be formed without risk of flow channels becoming plugged.

[0162] Typically, the support material will be larger than about .62 cm in diameter and smaller than about 2.54 cm in diameter. Preferably the support material is greater than about .95 cm in diameter and less than about 1.9 cm in diameter. A support material having a diameter of about 1.27 cm should be the optimum size.

[0163] To biooxidize the concentrate, the heap is inoculated with bacteria or other microbe capable of biooxidizing the sulfide minerals in the concentrate. Such microbial treatments are well known in the art. Bacteria that can be used for this purpose include Thiobacillus ferrooxidans, Leptospirillum ferrooxidans, and Thiobacillus thiooxidans. Thiobacillus ferrooxidans is an especially preferred microorganism for biooxidation processes.

[0164] If the bioleachate solution is recycled, precautionary steps may be required to prevent toxic materials from building up in the recycled solution so that the rate of biooxidation is not retarded significantly. The process described in U.S. Patent Application Serial No. 08/329,002, filed October 25, 1994, can be used to ensure that inhibitory materials do not build up to the point that they become detrimental to the biooxidation process.

[0165] After the refractory sulfide concentrate is sufficiently biooxidized, the liberated precious metal values can be leached with a lixiviant of thiourea or cyanide. Cyanide is the preferred lixiviant even though the pH of the heap must first be raised prior to leaching. An advantage of thiourea is that it is not toxic to the biooxidizing microorganisms. As a result, intermittent leachings can be performed to dissolve the liberated precious metal values and then the biooxidation process can be resumed.

[0166] Dissolved precious metal values can be recovered from the lixiviant using well known techniques to those skilled in the art such as carbon in leach and carbon in column processes.

[0167] Another advantage of the present process is that it can be used as a continuous process by intermittently adding fresh or new concentrate to the top of the heap. The advantage of adding fresh concentrate to the top of the heap is that once the heap is established and biooxidation is occurring rapidly, the fresh concentrate can be added to maintain the high rate of biooxidation within the heap without having to tear down the heap to process the biooxidized material.

[0168] Due to the relatively low capital and operating costs of the process according to the present aspect of the invention, it can be used to economically process much lower grade concentrates, and as a result lower grade ores,

than a mill biooxidation process. Further, by distributing the concentrate of precious metal bearing refractory sulfide minerals on top of a heap of support material, good fluid flow (both air and liquid) is ensured within the heap.

[0169] Another aspect of the present invention is now described. In this aspect of the invention, a process is provided for recovering base metal values from sulfide ores. Such ores include, by way of example, chalcopyrite, sphalorite, nickel sulfide ores, and uranium sulfide ores. The process according to this aspect of the invention comprises (a.) forming a sulfide mineral concentrate comprised of fine metal sulfide particles; (b.) distributing the concentrate on top of a heap of coarse support material; (c.) biooxidizing the concentrate; and (d.) recovering metal values from the solution used to biooxidize the metal sulfide minerals. Due to the fact that this process, like the process described in connection with the previous aspect of the invention for processing concentrates of precious metal bearing sulfide minerals, uses a heap of coarse support material for the bioreactor, its capital and operating costs are less than that of a mill bioleaching operation. However, due to the good air flow in the heap, the biooxidation rate of the sulfide minerals is quite high and can approach that of what would be observed in a mill type operation.

[0170] Depending on the sulfide ore from which the concentrate is obtained, the base metal values that can be recovered from the process according to the present aspect of the invention include copper, zinc, nickel and uranium.

[0171] The process parameters and considerations for the process according to the present aspect of the invention are much the same as those set forth above for the previous aspect of the invention for processing precious metal bearing concentrates of refractory sulfide minerals.

[0172] The primary difference between the two processes, however, is that the base metal values of interest in the present process dissolve during the biooxidation process. As a result, the metal values are recoverable directly from the solution used to biooxidize the concentrate of metal sulfide minerals. The technique used to extract the metal values of interest from the bioleachate will depend on the specific metal of interest. As those skilled in the art will immediately recognize, such techniques may include solvent extraction, iron cementation, and precipitation through pH adjustments. Solvent extraction is a particularly preferred method of removing copper from the bioleachate solution.

[0173] As with the process according to the previous aspect of the invention, the present process can be operated in a continuous mode by adding concentrate on an intermittent basis. For example, concentrate can be added on a daily or weekly basis. As described above, such additions will ensure that the rate of biooxidation remains high for the concentrate that is distributed over the heap and which has migrated through the heap.

[0174] As one skilled in the art will recognize, the process according to the present aspect of the invention can be combined with the process according to the previous aspect of the invention for recovering precious metal values from a concentrate of refractory sulfide minerals. This is because base metal values from the refractory sulfide minerals will inherently dissolve into the bioleachate solution during the biooxidation process while simultaneously liberating occluded precious metal values contained in the sulfide minerals. These values can then be recovered if desired using the techniques described above.

[0175] The preferred embodiments of the invention having been described, various aspects of the invention are further amplified in the examples that follow. Such amplifications are intended to illustrate the invention disclosed herein, and not to limit the invention to the examples set forth.

Example 1

[0176] A sample of low grade (3.4 ppm) gold ore, which was known to be refractory to leaching with cyanide due to sulfides, was crushed. The ore was then separated into a -0.62 cm fraction (47.4 wt%) and a -0.31 cm fraction (remainder). The -0.31 cm fraction was then further ground to 95% passing a 75 μm sieve to aid in producing a refractory pyrite concentrate by flotation.

[0177] Water was added to the ground sample until it reached a 30% pulp density. The ore pulp was then adjusted to a pH of 10 and treated with Na_2SiO_3 at 6 Kg/tonne of ore for 12 hours to remove the clay material. The clay material was removed as the fraction that did not settle after 12 hours.

[0178] Because clays can cause problems with flotation, a step that permits the non clay material to settle out was added to remove the clay fraction before floating the sample.

[0179] The clay fraction was under 3% of the total ore weight, yet it contained almost 5% of the gold in the ore. The removal and subsequent flotation of the clay fraction produced a very small weight fraction (0.1% of the total ore weight), but it contained over 17 ppm gold. Cyanide leaching of the clay flotation tail extracted over 76% of the gold contained therein. The total amount of gold contained in the clay flotation tail was 1.08 ppm. Before floating, the main fraction of ground ore (+5 μm to -75 μm was conditioned with $CaSO_4$ at 2.0 Kg/tonne for ten minutes by mixing in a Wemco flotation cell. This was followed by 10 minutes of mixing with Xanthate at 100g/tonne which was then followed by 5 minutes of mixing with Dowfroth D-200 at 50 g/tonne. The sample was then floated for 20 minutes at a pulp density of 30%. Four Kg of the main fraction was processed in 8 separate batches of 500 g each. The sulfide concentrates obtained from these flotations were collected and combined and refloated in a column.

[0180] Three fractions were collected, the tail from the Wemco float, the tail from the column float, and the sulfide

concentrate, each of these fractions were dried and weighed. The tail from the Wemco float was 35.4 wt% of total ore weight and contained 1.88 ppm of gold. Cyanide leaching of this fraction yielded 67% of its gold. This was higher than the recovery for cyanide leaching of the whole ore, which was 63%. The column tail contained 3.56 ppm of gold. The gold recovery from this fraction by cyanide leaching was 76.6%.

[0181] The sulfide concentrate weighed 753 g which represented 8.8% of the total ore (+0.31 cm and -0.31 cm fractions). Analysis of a small fraction of the concentrate indicated it contained 6.5 ppm of gold. This fraction was coated on to the 47.4 weight percent of the +0.31 cm ore. The dry pyrite concentrate was spread over the surface of the coarse ore by rolling in a drum rotating at 30 rpm while spraying a mixture of 2,000 ppm ferric ion and 1% Nalco #7534, which is an agglomeration aid. The pH of the solution was 1.8.

[0182] The mixture of concentrate on coarse ore support was placed into a 7.62 cm column. Air and liquid were introduced from the top. The column was inoculated with 10 ml of Thiobacillus ferrooxidans bacteria at an O.D. of 2.6 or about 1.1 x 10^{10} bacteria per ml.

[0183] The bacteria were grown in an acidic nutrient solution containing 5 g/l ammonium sulfate and 0.83 g/l magnesium sulfate heptahydrate. The pH of the solution was maintained in the range of 1.7 to 1.9 by adjustment with sulfuric acid (H_2SO_4) . The solution also contained iron at 20 g/liter in the form of ferric and ferrous sulfate.

[0184] The bacteria were added to the top of the column after the pH was adjusted to a pH of 1.8. The liquid, introduced to the top of the column throughout the experiment, was pH 1.8; with 0.2 x 9 K salts and 2,000 ppm ferric. The extent of iron oxidation was determined by analysis of the solution eluting off the column minus the iron introduced by the 2,000 ppm ferric feed.

[0185] The composition of the standard 9 K salts medium for T. ferrooxidans is listed below. The concentrations are provided in grams/liter.

$(NH_4)SO_4$	5
KCl	0.17
K_2HPO_4	0.083
$MgSO_4 \cdot 7H_2O$	0.833
$Ca(NO_3) \cdot 4H_2O$	0.024

[0186] The notation 0.2 x 9 K salts indicates that the 9 K salt solution strength was at twenty percent that of the standard 9 K salt medium.

[0187] After 60 days the amount of iron leached off of the column indicated that about 50% of the pyrite had been biooxidized. The experiment was stopped and the mixture separated into a +600 μm fraction and a -600 μm fraction. Each fraction was ground to 95% minus 75 μm and then leached with a 500 ppm cyanide solution in a 96-hour bottle roll analysis. Activated carbon was added to the bottle roll test to absorb any dissolved gold.

[0188] The gold recovery of the -600 μm fraction was 83.7%. The -600 μm material had an increased head gold value of 8.87 ppm due to loss of pyrite weight. The coarse +600 μm fraction, on the other hand, had a gold recovery of 57% and a head gold value of 2.24 ppm. This indicated that the concentrate pyrite that was coated on the outside of the coarse rock had biooxidized faster than the coarse fraction of the rock.

Example 2

[0189] Another comparative test was made. In this example, the biooxidation rates of ore size fractions were compared. The ore, which was provided by the Ramrod Gold Corporation, was crushed to 1.9 cm. The -0.31 cm ore fraction was removed and used to form a concentrate. The ore sample had less than 2.7 g of gold per tonne of ore (2.7 ppm). The sample contained both arsenopyrite and pyrite. The concentrate was made by ball milling 5 Kg of the -0.31 cm ore until it passed -75 μm, the ball milled ore was then floated with Xanthate to form a pyrite concentrate. Before flotation clay was removed by settling with Na_2SiO_3 at 6 Kg/tonne of ore for 8 hours or more. The flotation was done in small batches of 500 g each in a laboratory Wemco flotation cell. Potassium Amyl Xanthate was used as a collector at a concentration of 100 g/tonne along with sodium sulfide at 1.5 Kg/tonne and Dowfroth D-200 at 50 g/tonne. The pyrite concentrate constituted 4.5% of the weight of the -0.31 cm ore fraction. However, this ore fraction contained over 80% of the gold and pyrite for the milled ore. The concentrate contained approximately 17.4% iron, 15.7% sulfur and approximately 40 ppm gold. The +0.31 cm ore contained 0.9% iron and 0.18% sulfur.

[0190] A sample of 140 g of this concentrate was coated onto 560 g of +0.31 cm coarse ore. The concentrate was added as a dry powder to the coarse ore. The mixture was then rotated in a small plastic drum at 30 rpm to spread the dry concentrate over the rock support. Liquid which contained 2,000 ppm ferric ion and 1% Nalco #7534 was sprayed

onto the mixture until all the concentrate was coated onto the rock. The pH of the liquid was maintained at 1.8. The amount of liquid used was estimated to be between 5 and 10 percent of the weight of the coarse ore and concentrate. The 700 g mixture of concentrate on coarse ore substrates was placed into a 7.62 cm column. The height of the ore after being placed in the column was approximately 12.7 cm. Air and liquid were introduced from the top of the column. The column of concentrate coated on coarse ore substrates was inoculated with about 10 ml of bacteria at an O.D. of 2.0 or about 8 x 10^9 bacteria per ml.

[0191] The bacteria were a mixed culture of Thiobacillus ferrooxidans, which were originally started with ATCC strains #19859 and 33020. The bacteria were grown in an acidic nutrient solution containing 5 g/l ammonium sulfate and 0.83 g/l magnesium sulfate heptahydrate. The pH of the solution was maintained in the range of 1.7 to 1.9 by adjustment with sulfuric acid (H_2SO_4). The solution also contained iron at 20 g/liter in the form of ferric and ferrous sulfate.

[0192] The bacteria were added to the top of the column after the pH was adjusted to pH 1.8. The liquid, introduced to the top of the column throughout the experiment had a pH of 1.8 with 0.2 x 9 K salts and 2,000 ppm ferric ion. The extent of iron oxidation was determined by analysis of the solution eluting off the column minus the iron introduced by the 2,000 ppm ferric feed.

[0193] This ore was low in sulfides having a concentration of less than 1% of its weight. By making a concentrate on the coarse rock at 20% by weight, the concentration of both the pyrite and gold could be increased by over tenfold. This increased the rate of biooxidation as seen in Figs. 6 and 7 over that for the whole ore. Not only did this process expose more of the pyrite to air and water but it also increased the amount of ferric ion and acid generated per unit volume of ore in the column model for a heap.

[0194] Fig. 6 shows the amount of oxidation as determined by percent iron leached for both the pyrite concentrate of this ore on +0.31 cm coarse ore and the whole ore itself. As the graph shows the concentrate process was biooxidized to about 40% in the first 30 days and over 65% in the first 60 days. Whereas the whole ore was only biooxidized to 24% in 84 days. The average daily biooxidation rates are shown in Fig. 7. The highest average daily rate of the coated concentrate was 1.8% per day compared to an average daily rate of only 0.5%. for the whole ore. As Fig. 7 illustrates, the coated concentrate sample did not take as long to begin biooxidizing the sample. This means that the coated concentrate process is more likely to achieve complete biooxidation in a reasonably short time.

[0195] Table 1 below shows the specific data points graphed in Figs. 6 and 7 for the concentrate on coarse ore process and for the whole ore process which was done for comparison.

[0196] After 68 days the concentrate coated on coarse ore column was taken down. The biooxidized material was separated into a plus 180 μm fraction and a minus 180 μm fraction. The weight of the fine material had increased from 140 g to 150 g. The total amount of iron removed from the system during the 68 days of biooxidation was 21.5 g which represents 46 g of pyrite. The weight of the coarse rock decreased by 54 g. This was believed to be due to breakdown of the rock to finer material due to the biooxidation process. The total weight after biooxidation was 656 g which was 44 g, less than the starting material. This fit well with the estimated 46 g of pyrite oxidized.

Table 1

Concentrate Process			Whole Ore Process		
# of Days	**% Fe leached**	**% Fe/day**	**# of days**	**% Fe Leached**	**% Fe/day**
0	0.0	0.00	0	0.0	0.00
9	8.4	0.93	13	0.2	0.01
16	18.5	1.44	21	2.5	0.29
20	25.5	1.76	28	5.1	0.38
23	31.0	1.82	35	8.6	0.50
28	37.5	1.30	42	11.7	0.44
33	41.7	0.84	49	13.8	0.29
37	46.1	1.10	56	15.9	0.31
43	51.8	0.95	62	18.4	0.42
51	60.7	1.11	70	21.5	0.39
58	66.7	0.86	77	23.1	0.23
65	70.9	0.60	84	24.3	0.16

[0197] Two samples of the -180 μm material and one sample of the +180 μm material were leached with cyanide. To leach the samples, bottle rolls were done for 96 hours, the leachant was maintained at 500 ppm cyanide. The +180 μm coarse ore support rock was ground to 95% -75 μm before doing the bottle roll. All bottle rolls were done with activated carbon in the leach solution.

[0198] Sulfide analysis of the minus 180 μm fraction after 68 days of biooxidation showed the sample still contained 8.8% sulfides which was 56% of the starting level. This was a lower percent oxidation than indicated by the iron leached off during the column experiment. The gold recovery increased to 84.3% for the high grade (38 ppm) - 180 μm fraction and 79.5% for the +180 μm low grade (3 ppm) fraction. This is a substantial increase from the 45.6% recovery of the unoxidized ore.

Example 3

[0199] A sample of 70 % minus 75 μm gold ore from a mine in the Dominican Republic was used to make a sulfide float concentrate. The ore sample was obtained from the tailing pile at the mine that had already been leached with cyanide. The ore sample still contained gold values of over 2 g per tonne which were occluded within the sulfides and not directly leachable by cyanide.

[0200] To form the sulfide concentrate, several kilograms of this sample were further ground to 95% minus 75 μm. The ground sample was then floated to form the sulfide concentrate. The flotation was done in small batches of 500 g each in a laboratory Wemco flotation cell. Before flotation, the ground ore sample was adjusted to a pulp density of 30%. The ore slurry was then mixed with 1.5 Kg/tonne sodium sulfide (Na_2S) for 5 minutes at pH 8.5. Then potassium amyl Xanthate was added as a collector at 100 g/tonne and mixed for 5 minutes. Next 50 g/tonne of Dowfroth D-200 was added and mixed for 5 minutes. Finally, air was introduced to produce a sulfide concentrate that contained 17.4% iron and 19.4% sulfide by weight and 14 g of gold per tonne of concentrate. A plurality of coated substrates were then made by coating 140 g of the sulfide concentrate onto 560 g of +0.31 cm to -0.62 cm granite rock. The concentrate was added as a dry powder to the granite rock. The mixture was then rotated in a small plastic drum at 30 rpm to spread the dry pyrite over the support material. A liquid which contained 2,000 ppm ferric ion and 1% Nalco #7534 agglomeration aid was sprayed on the mixture until all the sulfide concentrate was coated onto the wetted granite rock. The solution was maintained at a ph of 1.8. The coarse rock in this case had no iron or gold value. The rock, however, contained a small amount of mineral carbonate which tended to keep the pH high at first but also provided CO_2 as a carbon source for the bacteria.

[0201] The 700 g of concentrate coated rock was put into a column. A 0.2 x 9 K salts and 2,000 ppm ferric ion solution having a ph of 1.6 was introduced through the top of the column at a flow rate of about 300 ml/day. Then the column was inoculated with 10 ml of bacteria as in Example 2. After the pH of the concentrate coated rock substrate was adjusted to a pH of 1.8, the pH of the influent was set at 1.8. Air was also introduced through the top of the column.

[0202] Fig. 8 graphically illustrates the percent of biooxidation as determined by the percent of iron leached from the concentrate. The average daily percentage of biooxidation was calculated and is listed in Table 2 and is graphically illustrated in Fig. 9. The percentage biooxidation was determined by dividing the total iron removed by the total iron contained within the concentrate. The rate of biooxidation was slow to start as the pH was adjusted and the bacteria built up and adapted. However, after about two weeks the rate increased rapidly and reached a maximum after 30 days. By this time almost 50% of the total iron had been biooxidized. The process continued with a gradual slowdown as the remaining pyrite was consumed. At the end of 64 days nearly 97% of the iron had been biooxidized. Even with the concentrate almost completely biooxidized and the rate slowing down near the end of the process, the average daily rate was still near 1%/day. After 70 days the biooxidation was stopped. The biooxidized concentrate was separated into a plus 180 μm fraction and a minus 180 μm fraction. The weight of the biooxidized concentrate had decreased from 140 g to 115 g. The total amount of iron removed from the system during the 70 days of biooxidation was 25.9 g which represents 55.5 g of pyrite. The weight of the granite rock decreased by 98.8 g. This was believed to be due to a breakdown of the calcium carbonate in the rock by the acid as well as the breakdown of the rock to finer material. The total weight decreased by 123.3 g which was 67.8 g more than predicted by biooxidation of pyrite alone.

Table 2

Time in Days	% Bioox.	% Bioox./Day
5	2.590	0.288
15	10.270	1.100.
22	24.970	2.100
27	37.250	2.450
32	49.700	2.490
36	58.610	2.230
42	68.580	1.660
50	82.580	1.750
57	90.870	1.180

(continued)

Time in Days	% Bioox.	% Bioox./Day
64	96.820	0.850

[0203] The sample of -180 μm material was leached with 500 ppm cyanide in a bottle roll for 96 hours. The +180 μm granite rock was also leached with 500 ppm cyanide to determine how much gold could be stuck to the support rock in a process that used barren rock as a supporting substrate. Analysis of the -180 μm material showed it still contained 9.7% sulfide which indicated only about 50% oxidation.

[0204] Gold extraction was 77% from the -180 μm fraction. This gold was recovered from gold ore that had already been leached with cyanide, thus demonstrating that the process according to the present invention is even applicable to ores which heretofore have been considered waste. And while any recovery would be an improvement over the process currently practiced at the mine, the process according to the present invention was able to recover 77% of the gold in what was previously considered tailings.

[0205] Cyanide leaching of the granite support rock showed that it had picked up 0.15 ppm of gold which was 3.4% of the total gold.

Example 4

[0206] A sample of gold bearing refractory sulfide ore that had been crushed to 80% passing 0.62 cm was prepared for testing as support rock. The ore was from the Western States mine located in Nevada, and contained a high concentration of carbonate minerals in the form of limestone. The fine material (less than 0.31 cm) was removed in order to allow for good air flow. A four kilogram sample of the +0.31 cm to -0.62 cm rock was coated with one kilogram of a gold bearing pyrite concentrate provided by another mining company. The coating was formed by placing a the coarse ore substrates and dry concentrate into a small rotating drum and spraying the mixture with a liquid which contained 2,000 ppm ferric ion and 1% Nalco #7534 agglomeration aid until all the sulfide concentrate was coated onto the wetted granite rock.

[0207] Iron analysis of both samples showed that the concentrate contained 210 grams of iron and the four kilograms of support rock contained 42.8 grams of iron.

[0208] The five kilograms of coated ore substrates was placed in a 7.62 cm column. To start the biooxidation process, a solution having a pH of 1.3 and containing 2,000 ppm of ferric ions was passed through the column at about one liter per day. After seven days, the pH of solution leaving the column was below pH 2.5. At this point the column was inoculated with 10 ml of a culture of Thiobacillus ferrooxidans bacteria (as in Example 2) and the pH of the feed solution was raised to a pH of 1.8. After a total of fifteen days the column was generating acid at a pH of 1.7 and an Eh of 700 mV. The progress of the biooxidation process was followed by measuring the iron leaching off the column of concentrate coated nominal 0.62 cm ore. This data was compared with the data from an experiment using the same concentrate coated on a sample of barren rock. The rates of the leaching in both cases are compared in graph form in Figure 10. The fact that the Western States experiment was slightly faster suggests that the coarse ore support rock was also oxidizing to some extent.

[0209] The Western States column experiment ran for a total of 74 days and leached a total of 166 grams of iron out of the system or 66% of the total iron in both the concentrate and support rock. Most of the iron was leached from the concentrate, but some came from the support rock. The weight of the concentrate changed from 1,000 grams to 705.8 grams after biooxidation. The four kilograms of Western States coarse ore support rock decreased to 3695.5 grams, which corresponds to a loss of 304.5 grams or 7.6% of its weight after biooxidation. The decrease in weight of the coarse ore support rock was due to a combination of biooxidation of its pyrite, acid leaching of the carbonate in the ore, and physical abrasion of the ore.

[0210] The 705.8 grams of biooxidized concentrate, which was originally from another mine in Nevada, was tested for gold extraction using a cyanide bottle roll test. The gold recovery before biooxidation was 46%. After biooxidation it increased to 86%. This same gold recovery was achieved by biooxidizing the concentrate to the same extent on the gravel support material.

[0211] The acid consumption of the Western States ore was measured before and after its use as a support rock for biooxidation. The amount of sulfuric acid required to adjust the pH down to 2 before biooxidation was 31.4 g per 100 g ore. The amount of acid required to adjust the pH down to 2 after biooxidation was 11 g per 100 g ore. This would mean that about 20% of the weight of the support rock was acid neutralized during the 74 days of biooxidation. This was larger than the 7.6% loss in weight of the support rock. This may be due to a precipitate forming on the rock after biooxidation or sample to sample variation in the percent limestone.

[0212] Several conclusions can be drawn from this test. First, a low pH biooxidation process can occur on the surface of a high carbonate ore. Second, with the +0.31 cm to -0.62 cm support material, the process of neutralization by the

pH 1.8 acid was slow enough that the carbonate in the ore was still not completely removed after 74 days. The process of slow acid neutralization is beneficial to the bacteria, because the neutralization of the limestone in the ore will provide needed CO_2 for the biooxidizing bacteria's carbon source. Third, the coarse ore support was benefited from the process because smaller nonfloatable sulfides in the Western State ore were biooxidized.

[0213] Based on the amount of neutralization that occurred in about 2 months of the +0.31 cm to -0.62 cm coarse ore support, a +0.62 cm to -1.9 cm coarse ore support rock would be best for a full scale process. With the larger coarse ore support, it will take 90 to 120 days in a heap biooxidation process to make the best use of the limestone neutralization and to biooxidize the smaller floatable sulfides in the coarse ore support rock. The time it takes to biooxidize the coating of sulfide spread on the outside of the coarse ore support is generally less than 90 days. Therefore, the coarse ore support may be used several times before it is ground up and floated to make a pyrite concentrate for biooxidation on the surface of a coarse ore support rock.

[0214] Prior to biooxidation, two attempts were made to produce a concentrate by flotation of the Western States ore. One method used only xanthate and produced only a small recovery of gold (less than 12%) into the pyrite concentrate. The tail from this flotation still contained 4.0 g Au/tonne. Extraction of the flotation tail with cyanide only recovered 17% of the gold remaining in the tail.

[0215] A second attempt at flotation used both kerosene to float off a carbon concentrate followed by xanthate to produce a pyrite concentrate. The combined weight of these concentrates accounted for 18 weight % of the ore, which was double the 7.4 weight % concentrate produced using only xanthate. The combined gold recovery for both concentrates increased to 53.8% of the gold. The tail from this flotation decreased to 2.12 g/tonne in gold. Extraction of the tail with cyanide recovered only 34.5% of the gold remaining in the tail after flotation of both concentrates.

[0216] The third attempt at flotation was done with the Western States ore after it had been used as a support rock for biooxidation in the present example. The +0.31 cm to -0.62 cm ore substrates were ground to -75 μm and then floated using xanthate as a collector. This formed a pyrite concentrate of 33.4 g Au/tonne and 7.9% of the original ore weight. The tail from this flotation contained 1.09 g Au/tonne. The recovery of the gold into the pyrite concentrate was 72.4%. Cyanide extraction of the 1.09 g/tonne tail recovered 48.7% of the gold to produce a final tail of 0.56 g/tonne.

[0217] The 33.4 g Au/tonne pyrite concentrate was biooxidized in a shake flask experiment. After biooxidation the cyanide extraction had increased to 99% gold recovery. This result showed that this concentrate was gold containing pyrite that could be biooxidized along with other concentrate in the coated substrate process.

[0218] As can be seen from the flotation results contained in Table 3 below, by floating the Western States ore after it was used as a support material for biooxidation, a high grade pyrite concentrate was more easily produced, and the flotation tail was less refractory to cyanide extraction. This may have been due to a chemical change to the pyrite during the 74 days in the high ferric and low pH conditions of biooxidation. Alternatively, the nonfloating sulfides may have been made less refractory by a combination of ferric and bacterial oxidation.

Table 3
Flotation Results

	1st Pyrite Float	2nd float	3rd after bioox. float
grinding	-75 μm	-75 μm	- 75 μm
reagents for flotation	Xanthate Dowfroth	Kerosene NaSiO3 Xanthate Dowfroth	NaS, CuSO4 Xanthate Dowfroth
Wt. % of pyrite conc.	7.4%	3.2%	7.9%
Wt. % of carbon conc.	-	14.8%	-
Total wt. % of cone.	7.4%	18.0%	7.9%
Grade of conc.	6.4g/t	26.4g/t	33.4g/t
% gold in conc.	11.3%	53.8%	72.4%
Gold in tail before CN	4.0g/t	2.12g/t	1.09g/t
Gold in tail after CN	3.32g/t	1.39g/t	0.56g/t
Gold recovery from leaching tail by CN	17.2%	34.5%	48.7%
Combined total recovery	26.4%	69.2%	85.4%
Head grade of sample tested	4.18g/t	3.77g/t	3.64g/t

Example 5

[0219] Two simultaneous bioleaching tests were set up to test the rate of biooxidation of a gold bearing ore pyrite

concentrate. The first test consisted of a column type experiment to simulate a heap leaching process and the second consisted of a shake flask experiment to simulate a stirred tank process.

[0220] The starting concentrate for both tests was obtained from the Jamestown mine in Tuolumne County, California. The mine is owned by Sonora Gold corporation and lies along the mother lode vein system. The concentrate was produced using a xanthate flotation process and contained 39.8% sulfides and 36.6% iron. The sulfide minerals within the concentrate primarily consisted of pyrite. Size analysis showed that over 76% of the concentrate particles were smaller than 75 μm. The concentrate had a high gold concentration (about 70 g per tonne of concentrate) and was known to be refractory to cyanide leaching.

[0221] The percentage of biooxidation in each of the tests was determined by analysis of the iron concentration in all solutions removed from the column or in the case of the flask experiment the concentration of iron in solution plus any iron solution removed.

[0222] A culture of Thiobacillus ferrooxidans was used to biooxidize the sulfide mineral concentrate in each of the tests. The culture of Thiobacillus ferrooxidans was originally started with ATCC strains 19859 and 33020. The culture was grown in an acidic nutrient solution having a pH of 1.7 to 1.9 and containing 5 g/l ammonium sulfate ($(NH_4)_2SO_4$), 0.833 g/l magnesium sulfate heptahydrate ($MgSO_4 \cdot 7H_2O$), and 20 g/l iron in the form of ferrous and ferric sulfate. The pH of the solution was adjusted to the above range using sulfuric acid (H_2SO_4).

[0223] Prior to application of the culture to the test samples, the mixed culture of sulfide mineral oxidizing bacteria was grown to a cell density of $4x10^9$ to $1x10^{10}$ cell per ml.

[0224] The column experiment was started by inoculating a 150 g sample of concentrate with about 10^8 cells per gram of concentrate. This was accomplished by adding three milliliters of bacteria at $5x10^9$ cells per milliliter to the 150 g sample of pyrite concentrate. The 150 g of pyrite concentrate suspension was then poured into a 7.62 cm by 1.83 meter column filled about halfway with 3 liters of .95 cm lava rock. The lava rock support material was chosen because it has a high surface area and it holds up well to the acid condition encountered during biooxidation.

[0225] During inoculation and subsequent solution additions, the pyrite concentrate did not wash out of the column. Most of the pyrite concentrate was held in the first 30 cm of the lava rock. Air and liquid were introduced through the top of the column. The bioleach solution was recirculated until the pH of the column was adjusted down to about 1.8. After biooxidation started within the column, a 0.2 x 9K salts solution having a pH of 1.8 and containing 2000 ppm of iron, primarily in the ferric form, was fed to the column. The 2,000 ppm of iron was subtracted from all analysis of iron in solution coming off of the column.

[0226] After 26 days of biooxidation, about 35% of the iron in the pyrite concentrate had been oxidized. At this point, the test was converted to a continuous process test by adding 3 g of new concentrate to the column every day. After 9 more days, the rate of pyrite addition was increased to 6 g per day.

[0227] The flask experiment was started at the same time as the column experiment. To start the experiment, a 50 g sample of the pyrite concentrate was inoculated with 1 milliliter of the bacteria culture. The pyrite concentrate was then added to 1 liter of 0.2 x 9K salts solution having a pH of 1.8 in a large shake flask. Not only was the concentrate inoculated with the same bacteria, but it was also inoculated at the same number of cells per gram.

[0228] Air was introduced to the bioleach solution by orbital shaking of the flask at about 250 rpm. Solution was removed from the flask from time to time to keep the ferric concentration from getting much higher than that in the column.

[0229] When the column experiment was converted to a continuous process on day 26, the flask experiment was also converted to a continuous test by adding 1 g of pyrite concentrate per day to the flask. After 9 more days, the amount of concentrate added was increased to 2 g per day.

[0230] After 58 days, the pyrite additions to both the flask and column experiments were stopped. Both the column and the flask were then allowed to biooxidize an additional 20 days. At this point, the concentrate in the column was about 76% oxidized and the concentrate in the flask was about 89% oxidized. The column was then leached for 10 days with thiourea to extract liberated gold. The thiourea only extracted about 30% of the gold. However, after 3 days of reverting back to additions of the 0.2 x 9K salts solution having a pH of 1.8 and containing 2,000 ppm of ferric iron, the Eh and the iron concentration of the column effluent increased. This indicated that the thiourea was not toxic to the bacteria and that thiourea extractions could be done from time to time without killing the bacteria.

[0231] Fig. 11 shows the amount of biooxidation versus time in days for both the column and flask concentrate bioleaching tests. The phrase "TU leach" in Fig. 8 stands for thiourea leach. The data used to prepare Fig. 8 is tabulated in Tables 4 and 5 at the end of this example.

[0232] As indicated above, the flask was meant to simulate a stirred tank process. When the flask test was converted to a continuous process by adding pyrite each day, it was meant to simulate a large scale process in which new pyrite is introduced on an intermittent basis to a rapidly biooxidizing tank containing a large amount of bacteria that have adapted to the ore. The daily addition of pyrite to the column was done to test the feasibility of a continuous process in which a concentrate of precious metal bearing sulfide minerals is continuously or intermittently added to the top of a heap comprised of biooxidizing concentrate distributed on a heap of support material such as lava rock.

[0233] As the above tests demonstrate, the rates of biooxidation were not significantly different between the column

and flask tests. The start of biooxidation was a little slower in the column test. This may have been due to about a 10 day lag time in adjusting the pH of the column down to 1.8. The rate of biooxidation in the column then picked up to be the same as the flask. Later in the experiment the rate began to slow down again. This may have been due to a lack of mixing of the fresh pyrite with the biooxidizing pyrite. However, the rates of biooxidation between the two tests were close enough to demonstrate the viability of the process according to the present invention. The viability of the present process is especially attractive in view of the much lower capital and operating costs of a heap process as compared to a stirred tank process.

Table 4 --Data From Column Biooxidation Test

Time in days	G. of iron added to column	Total g. of iron removed	% bioox. of pyrite based on iron	Conc. of iron in g./l
0	54.400	2.830	5.200	1.884
15	54.400	5.500	10.100	2.840
20	54.400	12.617	23.180	4.704
23	54.400	14.480	26.620	4.976
26	55.540	19.230	34.620	9.088
27	56.630	20.430	36.070	9.432
28	57.720	22.329	38.700	9.800
29	58.800	23.987	40.800	6.400
30	59.900	25.176	42.000	5.964
31	61.000	27.075	44.380	5.876
32	62.070	28.337	45.650	6.508
33	63.160	29.285	46.360	6.212
34	64.250	30.257	47.080	4.900
35	65.340	31.824	46.700	7.224
36	69.700	32.970	47.300	5.428
37	69.700	34.066	48.900	5.265
38	74.050	35.184	47.500	5.620
39	74.050	36.302	49.000	
40	76.230	37.420	49.100	5.120
41	78.410	38.425	49.000	5.000
42	80.590	39.453	48.900	5.024
43	82.760	40.744	49.200	5.536
44	84.940	42.172	49.600	5.808
45	89.300	43.602	48.800	5.964
46	89.300	45.032	50.400	
47	91.480	46.462	50.800	5.976
48	93.660	47.932	51.180	6.200
49	95.836	49.650	51.800	6.896
50	98.014	50.582	51.600	7.328
51	100.192	52.142	52.040	8.240
53	104.548	55.591	53.170	9.664
54	106.726	58.012	54.360	8.052
55	108.896	59.835	64.950	8.288
56	111.066	61.571	55.440	8.200
57	113.236	63.136	55.760	7.304
58	115.406	65.370	56.640	8.384
59	115.406	67.640	58.610	8.484
61	115.406	70.806	61.350	8.208
62	115.400	72.344	62.690	7.128
63	115.400	72.777	63.930	6.776
64	115.400	75.013	65.000	5.852
65	115.400	76.169	66.000	5.728

(continued)

Time in days	G. of iron added to column	Total g. of iron removed	% bioox. of pyrite based on iron	Conc. of iron in g./l
66	115.406	77.325	67.000	5.728
68	115.406	79.668	69.030	5.748
69	115.406	80.468	69.730	4.668
70	115.400	81.043	70.220	4.740
71	115.400	81.828	70.904	4.856
72	115.400	82.716	71.674	5.064
73	115.400	83.781	72.590	4.804
75	115.400	84.975	73.630	4.488
76	115.400	85.609	74.180	4.112
90	115.400	87.170	75.533	2.892
93	115.400	88.754	76.900	3.476

Table 5 --Flask Biooxidation Data

Time in days	Flask % bioox. by iron
0	4.930
15	18.890
21	29.850
26	37.400
28	39.790
36	45.370
44	46.890
47	52.310
49	54.510
51	58.380
54	62.010
56	62.630
58	65.400
63	72.110
69	81.410
72	83.300
75	89.440

Claims

1. A method of biotreating a solid material to remove an undesired compound using a nonstirred surface bioreactor, said method comprising the steps of:

a. coating the surface of a plurality of coarse substrates having a particle size greater than about 0.3 cm with a solid material to be biotreated and thereby forming a plurality of coated coarse substrates, said solid material to be biotreated having a particle size less than about 250 μm and containing an undesired compound;
b. forming a nonstirred surface reactor by stacking said plurality of coated coarse substrates into a heap or placing said plurality of coated coarse substrates into a tank, said reactor having a void volume greater than or equal to about 25 %;
c. inoculating said reactor with a microorganism capable of degrading the undesired compound in said solid material to thereby form a nonstirred surface bioreactor; and
d. biotreating said solid material in said bioreactor until said undesired compound in said solid material is degraded to a desired concentration.

2. A method according to claim 1, further comprising the steps of:

e. separating said biotreated solid material from said plurality of coarse substrates after said undesired compound has been degraded to said desired concentration; and
f. repeating steps a-d using said plurality of coarse substrates.

3. A method according to claim 1 or 2, wherein said undesired compound is an organic contaminant.

4. A method according to claim 3, wherein said solid material is soil.

5. A method according to claim 4, wherein said organic contaminant is at least one selected from the group consisting of waste oil, grease, jet fuel, diesel fuel, crude oil, benzene, toluene, ethylbenzene, xylene, polyaromatic hydrocarbons (PAH), polynuclear aromatics (PNAs), pentachlorophenol (PCP), polychlorinated biphenyls (PCBs), creosote, pesticides, 2,4,6,-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), N-methyl-N-2,4,6-tetranitroaniline, and nitrocellulose (NC).

6. A method according to claim 3, 4 or 5 wherein said plurality of coarse substrates are comprised of plastic.

7. A method according to claim 1 or 2, wherein said undesired compound is a sulfide mineral.

8. A method according to claim 7, wherein said solid material is coal.

9. A method according to claim 8, wherein said plurality of coarse substrates are comprised of coarse coal particles.

10. A method according to claim 7, wherein said solid material is a refractory sulfide ore.

11. A method according to claim 10, wherein said plurality of coarse substrates are comprised of coarse refractory sulfide ore particles.

12. A method according to claim 1, 2, 3, 4, 5, 7, 8, or 10, wherein said plurality of coarse substrates are comprised of at least one material selected from the group consisting of rock, lava rock, gravel, rock containing carbonate minerals, brick, cinder block, and slag.

13. A method according to any of claims 1-12, wherein the coarse substrates have a nominal particle size greater than or equal to about 0.6 cm and less than or equal to about 2.54 cm.

14. A method according to any of claims 1-13, wherein the amount of solid material coated onto said plurality of coarse substrates is from approximately 10% to approximately 30% by weight.

15. A method according to any of claims 1-14, wherein said solid material has a particle size that is greater than or equal to about 25 μm.

16. A method according to any of claims 1-14, wherein said solid material has a nominal particle size that is greater than or equal to 75 μm and less than or equal to 106 μm.

17. A method according to claim 1, wherein said biotreatment step comprises at least one of the following: supplying the bioreactor with nutrients necessary to sustain the growth of the microorganism, maintaining the moisture content of the bioreactor above a desired level, blowing air into the bioreactor through perforated pipes, maintaining the pH of the bioreactor within a predetermined range, and maintaining the temperature of the bioreactor within a predetermined range.

18. A method according to any of claims 1-17, wherein said solid material coating thickness on said plurality of substrates is less than about 1 mm.

19. A method according to any of claims 1-18, wherein said void volume is greater than or equal to about 35%.

20. A method according to any of claims 1-19, wherein no more than 5% by weight of said coarse substrates are less than 0.3 cm.

21. A method according to claim 1, wherein said solid material is a sulfide mineral concentrate comprised of fine metal

sulfide particles containing metal values of interest, said undesired compound is said fine metal sulfide particles, and wherein said biotreatment of said sulfide mineral concentrate coated on the surface of said substrates biooxidizes said fine metal sulfide particles until a desired amount of said fine metal sulfide particles in said sulfide mineral concentrate is biooxidized and the metal values of interest are liberated.

22. A method according to claim 21, wherein the nonstirred surface reactor is formed by stacking the plurality of concentrate coated coarse substrates into a heap and the method further comprises the steps of:

e. breaking the heap down after the fine metal sulfide particles coated on the surface of the plurality of coarse substrates are biooxidized by a desired amount;
f. separating the biooxidized fine metal sulfide particles from the plurality of coarse substrates; and
g. repeating steps a-d using the plurality of coarse substrates.

23. A method according to claim 21, wherein the nonstirred surface reactor is formed by placing the plurality of concentrate coated coarse substrates into a tank and the method further comprises the steps of:

e. separating the biooxidized fine metal sulfide particles from the plurality of coarse substrates; and
f. repeating steps a-d using the plurality of coarse substrates.

24. A method according to claim 21, wherein the plurality of coarse substrates comprise coarse ore particles that contain metal sulfide particles.

25. A method according to claim 24, further comprising the steps of:

e. separating the biooxidized fine metal sulfide particles from the plurality of coarse substrates after the metal sulfide particles coated on the surface of the plurality of coarse substrates are biooxidized by a desired amount;
f. grinding the plurality of coarse substrates to a particle size sufficient to permit the separation of metal sulfide particles therefrom;
g. producing a second sulfide mineral concentrate comprised of fine metal sulfide particles from the plurality of ground coarse substrates;
h. coating a second plurality of coarse substrates with the second concentrate;
i. forming a second heap using the second plurality of coated substrates; and
j. biooxidizing the second concentrate of fine metal sulfide particles.

26. A method according to claim 24 or 25, wherein the coarse ore particles also contain mineral carbonate.

27. A method according to claim 21, 22, or 23, wherein the material used for said plurality of coarse substrates is at least one material selected from the group consisting of lava rock, gravel, and rock containing mineral carbonate.

28. A method according to any of claims 21-27, wherein the metal values of interest are base metal values from the metal moiety of the metal sulfide particles.

29. A method according to claim 1 wherein said solid material is a sulfide mineral concentrate comprised of fine metal sulfide particles containing occluded precious metal values, said undesired compound is said fine metal sulfide particles, and wherein said biotreatment of said sulfide mineral concentrate coated on the surface of said coarse substrate biooxidizes said fine metal sulfide particles until a desired amount of said fine metal sulfide particles in said sulfide mineral concentrate is biooxidized and precious metal values are liberated, the process further comprising the steps of:

e. contacting the biooxidized fine metal sulfide particles with a precious metal lixiviant to thereby dissolve precious metal values from the biooxidized fine metal sulfide particles; and
f. recovering precious metal values from the lixiviant.

30. A method according to claim 29, wherein the nonstirred surface reactor is formed by stacking the plurality of concentrate coated coarse substrates into a heap and the method further comprises the steps of:

g. breaking the heap down after the fine metal sulfide particles coated on the surface of the plurality of coarse substrates are biooxidized by a desired amount; and

h. separating the biooxidized fine metal sulfide particles from the plurality of coarse substrates prior to contacting with the lixiviant.

31. A method according to claim 30, further comprising repeating steps a-f using the plurality of coarse substrates having been separated from the biooxidized fine metal sulfide particles.

32. A method according to claim 30 or 31, wherein the method of separating the biooxidized fine metal sulfide particles from the plurality of coarse substrates comprises placing the plurality of concentrate coated coarse substrates on a screen and then spraying with water.

33. A method according to claim 30 or 31, wherein the method of separating the biooxidized fine metal sulfide particles from the plurality of coarse substrates comprises tumbling the plurality of concentrate coated coarse substrates in a trommel.

34. A method according to claim 29, wherein the nonstirred surface reactor is formed by placing the plurality of concentrate coated coarse substrates into a tank and the method further comprises the step of:

g. separating the biooxidized fine metal sulfide particles from the plurality of coarse substrates prior to contacting with the lixiviant.

35. A method according to claim 34, further comprising repeating steps a-f using the plurality of coarse substrates having been separated from the biooxidized fine metal sulfide particles.

36. A method according to claim 34 or 35, wherein the method of separating the biooxidized fine metal sulfide particles from the plurality of coarse substrates comprises filling the tank with an aqueous solution and then rapidly draining the tank to thereby carry the biooxidized fine metal sulfide particles out of the tank in the aqueous solution.

37. A method according to claim 29, wherein the plurality of coarse substrates comprise coarse refractory sulfide ore particles having precious metal values occluded within metal sulfide particles.

38. A method according to claim 37, further comprising the steps of:

g. separating the biooxidized fine metal sulfide particles from the plurality of coarse substrates prior to contacting with the lixiviant;
h. grinding the plurality of coarse substrates to a particle size sufficient to permit the separation of the fine metal sulfide particles therefrom;
i. producing a second sulfide mineral concentrate comprised of fine metal sulfide particles from the plurality of ground coarse substrates;
j. coating a second plurality of coarse substrates with the second concentrate;
k. forming a second nonstirred surface reactor by stacking the second plurality of coated coarse substrates into a heap or placing the second plurality of coated coarse substrates into a tank;
l. biooxidizing the second concentrate of fine metal sulfide particles;
m. contacting the biooxidized second concentrate with the precious metal lixiviant to thereby dissolve precious metal values from the biooxidized second concentrate; and
n. recovering precious metal values dissolved from the second concentrate from the lixiviant.

39. A method according to claim 37, wherein the coarse refractory sulfide ore particles originate from the precious metal bearing refractory sulfide ore used to produce the concentrate.

40. A method according to claim 37, wherein the coarse refractory sulfide ore particles also contain mineral carbonate.

41. A method according to any of claims 29-36, wherein the material used for said plurality of coarse substrates is at least one material selected from the group consisting of lava rock, gravel, and rock containing mineral carbonate.

42. A method according to any of claims 29-41, wherein the lixiviant is selected from the group consisting of thiourea and cyanide.

43. A method according to any of claims 21-42, wherein the plurality of coarse substrates have a nominal particle size

greater than or equal to about 0.6 cm and less than or equal to about 2.5 cm.

44. A method according to any of claims 21-43, wherein the amount of concentrate coated onto the plurality of coarse substrates is from approximately 10% to approximately 30% by weight.

45. A method according to any of claims 21-44, wherein the sulfide mineral concentrate comprises at least about 20 weight % metal sulfide particles.

46. A method according to any of claims 21-44, wherein the sulfide mineral concentrate comprises at least about 40 weight % metal sulfide particles.

47. A method according to any of claims 21-44, wherein the sulfide mineral concentrate comprises at least about 70 weight % metal sulfide particles.

48. A method according to any of claims 21-44, wherein the sulfide mineral concentrate comprises between 40 and 80 weight % metal sulfide particles.

49. A method according to any of claims 21-48, wherein the concentrate has a particle size that is greater than about 25 μm.

50. A method according to any of claims 21-49, wherein the concentrate has a particle size that is less than about 106 μm.

51. A method according to any of claims 21-49, wherein the concentrate has a particle size of less than about 75 μm.

52. A method according to any of claims 21-51, wherein the precious metal recovered is at least one selected from the group consisting of silver, gold and platinum.

53. A method according to claim 1, wherein said solid material is a sulfide mineral concentrate comprised of fine metal sulfide particles containing metal values of interest, said undesired compound is said fine metal sulfide particles, and wherein said biotreatment of said sulfide mineral concentrate coated on the surface of said course substrates biooxidizes said fine metal sulfide particles thereby causing the production of a bioleachate off solution and the dissolution of the metal moiety of the metal sulfide particles, the method further comprising the step of:

e. recovering the desired metal values from the bioleachate off solution.

54. A method according to claim 53, wherein the concentrate of fine metal sulfide particles comprises particles of copper sulfide minerals and the metal recovered is copper.

55. A method according to claim 54, wherein the method of recovering copper from the bioleachate off solution comprises at least one process selected from the group consisting of solvent extraction, copper cementation, and electrowinning.

56. A method according to claim 53, wherein the concentrate of fine metal sulfide particles comprises zinc sulfide minerals and the metal recovered is zinc; or
wherein the concentrate of metal sulfide particles comprises nickel sulfide minerals and the metal recovered is nickel.

Patentansprüche

1. Ein Verfahren zur Biobehandlung eines festen Materials, um eine unerwünschte Verbindung unter Verwendung eines nicht-gerührten Oberflächenbioreaktors zu entfernen, wobei das Verfahren die Schritte umfasst:

a. Beschichten der Oberfläche einer Vielzahl von groben Substraten, die eine Teilchengröße haben, die größer als ungefähr 0.3 cm ist, mit einem festen Material, das biobehandelt werden soll, und dabei Bilden einer Vielzahl von beschichteten groben Substraten, wobei das feste Material, das biobehandelt werden soll, eine Teilchengröße von weniger als ungefähr 250 μm hat und eine unerwünschte Verbindung enthält;
b. Bilden eines nicht-gerührten Oberflächenreaktors durch Stapeln der Vielzahl von beschichteten groben Substraten zu einem Haufen oder durch Platzieren der Vielzahl von beschichteten groben Substraten in einen Behälter, wobei der Reaktor ein Hohlraumvolumen größer als oder gleich ungefähr 25% hat;

c. Impfen des Reaktors mit einem Mikroorganismus, der die unerwünschte Verbindung in dem festen Material vermindern kann, um dabei einen nicht-gerührten Oberflächenbioreaktor zu bilden;
d. Biobehandeln des festen Materials in dem Bioreaktor bis die unerwünschte Verbindung in dem festen Material auf eine gewünschte Konzentration vermindert ist.

2. Ein Verfahren gemäß Anspruch 1, das weiter die Schritte umfasst:

e. Trennen des biobehandelten festen Materials von der Vielzahl von groben Substraten nachdem die unerwünschte Verbindung auf die gewünschte Konzentration vermindert worden ist;
f. Wiederholen der Schritte a-d unter Verwendung einer Vielzahl von groben Substraten.

3. Ein Verfahren gemäß Anspruch 1 oder 2, wobei die unerwünschte Verbindung eine organische Verunreinigung ist.

4. Ein Verfahren gemäß Anspruch 3, wobei das feste Material Erde ist.

5. Ein Verfahren gemäß Anspruch 4, wobei die organische Verunreinigung mindestens eine ist, die aus der Gruppe, die aus Altöl, Schmiermittel, Düsentreibstoff, Diesel, Rohöl, Benzol, Toluol, Ethylbenzol, Xylen, polyaromatischen Kohlenwasserstoffen (PAH), polynuklearen Aromaten (PNAs), Pentachlorphenol (PCP), polychlorierten Biphenylen (PCBs), Creosot, Pestiziden, 2,4,6-Trinitrotoluol (TNT), Hexahydro-1,3,5-trinitro-1,3,5-triazin (RDX), Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocin (HMX), N-Methyl-N-2,4,6-tetranitroanilin und Nitrocellulose (NC) besteht, ausgewählt wird.

6. Ein Verfahren gemäß Anspruch 3, 4 oder 5, wobei die Vielzahl von groben Substraten Kunststoff umfassen.

7. Ein Verfahren gemäß Anspruch 1 oder 2, wobei die unerwünschte Verbindung ein Sulfidmineral ist.

8. Ein Verfahren gemäß Anspruch 7, wobei das feste Material Kohle ist.

9. Ein Verfahren gemäß Anspruch 8, wobei die Vielzahl von groben Substraten grobe Kohlepartikel umfassen.

10. Ein Verfahren gemäß Anspruch 7, wobei das feste Material ein feuerfestes Sulfiderz ist.

11. Ein Verfahren gemäß Anspruch 10, wobei die Vielzahl von groben Substraten grobe feuerfeste Sulfiderzteilchen umfassen.

12. Ein Verfahren gemäß Anspruch 1, 2, 3, 4, 5, 7, 8 oder 10, wobei die Vielzahl von groben Substraten mindestens ein Material umfassen, das aus der Gruppe, die aus Gestein, Lavagestein, Kies, Gestein, das Carbonatmineralien enthält, Ziegel, Schlackenbetonblock und Schlacke besteht, ausgewählt wird.

13. Ein Verfahren gemäß einem der Ansprüche 1-12, wobei die groben Substrate eine nominale Teilchengröße haben, die größer als oder gleich ungefähr 0.6 cm und kleiner als oder gleich ungefähr 2.54 cm ist.

14. Ein Verfahren gemäß einem der Ansprüche 1-13, wobei die Menge an festem Material, das auf die Vielzahl von groben Substraten aufgetragen ist, ungefähr 10 bis ungefähr 30 Gew.-% ist.

15. Ein Verfahren gemäß einem der Ansprüche 1-14, wobei das feste Material eine Teilchengröße hat, die größer als oder gleich ungefähr 25 μm ist.

16. Ein Verfahren gemäß einem der Ansprüche 1-14, wobei das feste Material eine nominale Teilchengröße hat, die größer als oder gleich ungefähr 75 μm und kleiner als oder gleich 106 μm ist.

17. Ein Verfahren gemäß Anspruch 1, wobei der Biobehandlungsschritt mindestens eines der folgenden umfasst: Versorgen des Bioreaktors mit Nährstoffen, die notwendig sind, um das Wachstum der Mikroorganismen aufrechtzuerhalten, Halten des Feuchtigkeitsgehalts des Bioreaktors oberhalb eines gewünschten Niveaus, Einblasen von Luft in den Bioreaktor durch perforierte Rohre, Halten des pH des Bioreaktors innerhalb eines vorherbestimmten Bereichs und Halten der Temperatur des Bioreaktors innerhalb eines vorherbestimmten Bereichs.

18. Ein Verfahren gemäß einem der Ansprüche 1-17, wobei die Dicke der Beschichtung des festen Materials auf der

Vielzahl von Substraten geringer als ungefähr 1 mm ist.

19. Ein Verfahren gemäß einem der Ansprüche 1-18, wobei das Hohlraumvolumen größer als oder gleich ungefähr 35% ist.

20. Ein Verfahren gemäß einem der Ansprüche 1-19, wobei nicht mehr als 5 Gew.-% der groben Substrate kleiner als 0.3 cm sind.

21. Ein Verfahren gemäß Anspruch 1, wobei das feste Material ein Sulfidmineralkonzentrat ist, das feine Metallsulfidteilchen umfasst, die Metallwerte von Interesse enthalten, wobei die unerwünschte Verbindung die feinen Metallsulfidteilchen ist, und wobei die Biobehandlung des Sulfidmineralkonzentrats, das auf der Oberfläche der Substrate aufgetragen ist, die feinen Metallsulfidteilchen biooxidiert bis eine gewünschte Menge der feinen Metallsulfidteilchen in dem Sulfidmineralkonzentrat biooxidiert ist und die Metallwerte von Interesse freigesetzt sind.

22. Ein Verfahren gemäß Anspruch 21, wobei der nicht-gerührte Oberflächenreaktor durch Stapeln einer Vielzahl von Konzentrat-beschichteten, groben Substraten zu einem Haufen gebildet wird und das Verfahren weiter die Schritte umfasst:

e. Abbauen des Haufens nachdem die feinen Metallsulfidteilchen, die auf die Oberfläche der Vielzahl von groben Substraten aufgetragen sind, in einer gewünschten Menge biooxidiert worden sind;
f. Trennen der biooxidierten feinen Metallsulfidteilchen von der Vielzahl von groben Substraten; und
g. Wiederholen der Schritte a-d unter Verwendung der Vielzahl von groben Substraten.

23. Ein Verfahren gemäß Anspruch 21, wobei der nicht-gerührte Oberflächenreaktor durch Platzieren einer Vielzahl von Konzentrat-beschichteten, groben Substraten in einem Behälter gebildet wird und das Verfahren weiter die Schritte umfasst:

e. Trennen der biooxidierten feinen Metallsulfidteilchen von der Vielzahl von groben Substraten; und
f. Wiederholen der Schritte a-d unter Verwendung der Vielzahl von groben Substraten.

24. Ein Verfahren gemäß Anspruch 21, wobei die Vielzahl von groben Substraten grobe Erzteilchen, die Metallsulfidteilchen enthalten, umfasst.

25. Ein Verfahren gemäß Anspruch 24, das weiter die Schritte umfasst:

e. Trennen der biooxidierten feinen Metallsulfidteilchen von der Vielzahl von groben Substraten nachdem die Metallsulfidteilchen, die auf der Oberfläche der Vielzahl von groben Substraten aufgetragen sind, in einer gewünschten Menge biooxidiert sind;
f. Mahlen der Vielzahl von groben Substraten zu einer Teilchengröße, die ausreicht, um die Trennung der Metallsulfidteilchen davon zu ermöglichen;
g. Herstellen eines zweiten Sulfidmineralkonzentrats, das feine Metallsulfidteilchen umfasst, aus der Vielzahl der gemahlenen groben Substrate;
h. Beschichten einer zweiten Vielzahl von groben Substraten mit dem zweiten Konzentrat;
i. Bilden eines zweiten Haufens unter Verwendung der zweiten Vielzahl von beschichteten Substrate; und
j. Biooxidieren des zweiten Konzentrats von feinen Metallsulfidteilchen.

26. Ein Verfahren gemäß Anspruch 24 oder 25, wobei die groben Erzteilchen ebenfalls Mineralcarbonat enthalten.

27. Ein Verfahren gemäß Anspruch 21, 22 oder 23, wobei das für die Vielzahl von groben Substraten verwendete Material mindestens ein Material ist, das aus der Gruppe, die aus Lavagestein, Kies und Gestein, das Mineralcarbonat enthält, besteht, ausgewählt wird.

28. Ein Verfahren gemäß einem der Ansprüche 21-27, wobei die Metallwerte von Interesse Basismetallwerte der Metalleinheit der Metallsulfidteilchen sind.

29. Ein Verfahren gemäß Anspruch 1, wobei das feste Material ein Sulfidmineralkonzentrat ist, das feine Metallsulfidteilchen, die okkludierte Edelmetallwerte enthalten, umfasst, wobei die unerwünschte Verbindung die feinen Metallsulfidteilchen ist, und wobei die Biobehandlung des Sulfidmineralkonzentrats, das auf der Oberfläche des groben

Substrats aufgetragen ist, die feinen Metallsulfidteilchen biooxidiert bis eine gewünschte Menge der feinen Metallsulfidteilchen in dem Sulfidmineralkonzentrat biooxidiert worden ist und die Edelmetallwerte freigesetzt sind, wobei das Verfahren weiter die Schritte umfasst:

e. In-Kontakt-Bringen der biooxidierten feinen Metallsulfidteilchen mit einem Edelmetalllixiviant, um dabei Edelmetallwerte von den biooxidierten feinen Metallsulfidteilchen aufzulösen; und
f. Rückgewinnen der Edelmetallwerte von dem Lixiviant.

30. Ein Verfahren gemäß Anspruch 29, wobei der nicht-gerührte Oberflächenreaktor durch Stapeln der Vielzahl von Konzentrat-beschichteten, groben Substraten zu einem Haufen gebildet wird und das Verfahren weiter die Schritte umfasst:

g. Abbauen des Haufens nachdem die feinen Metallsulfidteilchen, die auf der Oberfläche der Vielzahl von groben Substraten aufgetragen sind, in einer gewünschten Menge biooxidiert sind; und
h. Trennen der biooxidierten feinen Metallsulfidteilchen von der Vielzahl von groben Substraten vor dem In-Kontakt-Bringen mit dem Lixiviant.

31. Ein Verfahren gemäß Anspruch 30, das weiter das Wiederholen der Schritte a-f unter Verwendung der Vielzahl von groben Substraten, die von den biooxidierten feinen Metallsulfidteilchen abgetrennt worden sind, umfasst.

32. Ein Verfahren gemäß Anspruch 30 oder 31, wobei das Verfahren des Trennens der biooxidierten feinen Metallsulfidteilchen von der Vielzahl von groben Substraten das Platzieren der Vielzahl von Konzentrat-beschichteten, groben Substraten auf einem Sieb und dann das Besprühen mit Wasser umfasst.

33. Ein Verfahren gemäß Anspruch 30 oder 31, wobei das Verfahren des Trennens der biooxidierten feinen Metallsulfidteilchen von der Vielzahl von groben Substraten das Rotieren der Vielzahl von Konzentrat-beschichteten groben Substraten in einer Trommel umfasst.

34. Ein Verfahren gemäß Anspruch 29, wobei der nicht-gerührte Oberflächenreaktor durch Platzieren der Vielzahl von Konzentrat-beschichteten groben Substrate in einen Behälter gebildet wird und das Verfahren weiter den Schritt umfasst:

g. Trennen der biooxidierten feinen Metallsulfidteilchen von der Vielzahl von groben Substraten vor dem In-Kontakt-Bringen mit dem Lixiviant.

35. Ein Verfahren gemäß Anspruch 34, das weiter das Wiederholen der Schritte a-f unter Verwendung der Vielzahl von groben Substraten, die von den biooxidierten feinen Metallsulfidteilchen abgetrennt worden sind, umfasst.

36. Ein Verfahren gemäß Anspruch 34 oder 35, wobei das Verfahren des Trennens der biooxidierten feinen Metallsulfidteilchen von der Vielzahl von groben Substraten das Befüllen des Behälters mit einer wässrigen Lösung und dann das schnelle Entleeren des Behälters umfasst, um dabei die biooxidierten feinen Metallsulfidteilchen aus dem Behälter in die wässrige Lösung zu bringen.

37. Ein Verfahren gemäß Anspruch 29, wobei die Vielzahl von groben Substraten grobe feuerfeste Sulfiderzteilchen, die Edelmetallwerte in den Metallsulfidteilchen okkludiert haben, umfasst.

38. Ein Verfahren gemäß Anspruch 37, das weiter die Schritte umfasst:

g. Trennen der biooxidierten feinen Metallsulfidteilchen von der Vielzahl von groben Substraten vor dem In-Kontakt-Bringen mit dem Lixiviant;
h. Mahlen der Vielzahl von groben Substraten zu einer Teilchengröße, die ausreicht, um die Abtrennung der feinen Metallsulfidteilchen davon zu ermöglichen;
i. Herstellen eines zweiten Sulfidmineralkonzentrats, das feine Metallsulfidteilchen umfasst, aus der Vielzahl der gemahlenen groben Substrate;
j. Beschichten einer zweiten Vielzahl von groben Substraten mit dem zweiten Konzentrat;
k. Bilden eines zweiten nicht-gerührten Oberflächenreaktors durch Stapeln der zweiten Vielzahl von beschichteten, groben Substraten zu einem Haufen oder durch Platzieren der zweiten Vielzahl von beschichteten, groben Substraten in einen Behälter;

l. Biooxidieren des zweiten Konzentrats von feinen Metallsulfidteilchen;
m. In-Kontakt-Bringen des biooxidierten zweiten Konzentrats mit dem Edelmetalllixiviant, um dabei die Edelmetallwerte von dem biooxidierten zweiten Konzentrat aufzulösen;
n. Rückgewinnen der Edelmetallwerte, die von dem zweiten Konzentrat gelöst sind, von dem Lixiviant.

39. Ein Verfahren gemäß Anspruch 37, wobei die groben feuerfesten Sulfiderzteilchen von dem Edelmetall herrühren, das feuerfestes Sulfiderz trägt, das verwendet wird, um das Konzentrat herzustellen.

40. Ein Verfahren gemäß Anspruch 37, wobei die groben feuerfesten Sulfiderzteilchen ebenfalls Mineralcarbonat enthalten.

41. Ein Verfahren gemäß einem der Ansprüche 29-36, wobei das für die Vielzahl von groben Substraten verwendete Material mindestens ein Material ist, das aus der Gruppe, die aus Lavagestein, Kies und Gestein, das Mineralcarbonat enthält, besteht, ausgewählt wird.

42. Ein Verfahren gemäß einem der Ansprüche 29-41, wobei das Lixiviant aus der Gruppe, die aus Thioharnstoff und Cyanid besteht, ausgewählt wird.

43. Ein Verfahren gemäß einem der Ansprüche 21-42, wobei die Vielzahl von groben Substraten eine nominale Teilchengröße hat, die größer als oder gleich ungefähr 0.6 cm und weniger als oder gleich ungefähr 2.5 cm ist.

44. Ein Verfahren gemäß einem der Ansprüche 21-43, wobei die Menge des Konzentrats, das auf die Vielzahl von groben Substraten aufgetragen ist, ungefähr 10 bis ungefähr 30 Gew.-% ist.

45. Ein Verfahren gemäß einem der Ansprüche 21-44, wobei das Sulfidmineralkonzentrat mindestens ungefähr 20 Gew.-% Metallsulfidteilchen umfasst.

46. Ein Verfahren gemäß einem der Ansprüche 21-44, wobei das Sulfidmineralkonzentrat mindestens ungefähr 40 Gew.-% Metallsulfidteilchen umfasst.

47. Ein Verfahren gemäß einem der Ansprüche 21-44, wobei das Sulfidmineralkonzentrat mindestens ungefähr 70 Gew.-% Metallsulfidteilchen umfasst.

48. Ein Verfahren gemäß einem der Ansprüche 21-44, wobei das Sulfidmineralkonzentrat mindestens zwischen 40 und 80 Gew.-% Metallsulfidteilchen umfasst.

49. Ein Verfahren gemäß einem der Ansprüche 21-48, wobei das Konzentrat eine Teilchengröße hat, die größer als ungefähr 25 μm ist.

50. Ein Verfahren gemäß einem der Ansprüche 21-49, wobei das Konzentrat eine Teilchengröße hat, die kleiner als ungefähr 106 μm ist.

51. Ein Verfahren gemäß einem der Ansprüche 21-49, wobei das Konzentrat eine Teilchengröße hat, die kleiner als ungefähr 75 μm ist.

52. Ein Verfahren gemäß einem der Ansprüche 21-51, wobei das zurückgewonnene Edelmetall mindestens eines ist, das aus der Gruppe, die aus Silber, Gold und Platin besteht, ausgewählt wird.

53. Ein Verfahren gemäß Anspruch 1, wobei das feste Material ein Sulfidmineralkonzentrat ist, das feine Metallsulfidteilchen, die Metallwerte von Interesse enthalten, umfasst, wobei die unerwünschte Verbindung die feinen Metallsulfidteilchen ist, und wobei die Biobehandlung des Sulfidmineralkonzentrats, das auf der Oberfläche der groben Substrate aufgetragen ist, die feinen Metallsulfidteilchen biooxidiert, wobei dabei die Herstellung einer Biolauge außerhalb der Lösung und die Auflösung der Metalleinheit der Metallsulfidteilchen verursacht wird, wobei das Verfahren weiter die Schritte umfasst:

e. Rückgewinnen der gewünschten Metallwerte von der Biolauge außerhalb der Lösung.

54. Ein Verfahren gemäß Anspruch 53, wobei das Konzentrat der feinen Metallsulfidteilchen Kupfersulfidmineralien-

teilchen umfasst und das zurückgewonnene Metall Kupfer ist.

55. Ein Verfahren gemäß Anspruch 54, wobei das Verfahren der Kupferrückgewinnung von der Biolauge außerhalb der Lösung mindestens ein Verfahren umfasst, das aus der Gruppe, die aus Lösungsmittelextraktion, Kupferzementierung und Elektrogewinnung besteht, ausgewählt wird.

56. Ein Verfahren gemäß Anspruch 53, wobei das Konzentrat der feinen Metallsulfidteilchen Zinksulfidmineralien umfasst und das zurückgewonnene Metall Zink ist; oder
wobei das Konzentrat der Metallsulfidteilchen Nickelsulfidmineralien umfasst und das zurückgewonnene Metall Nickel ist.

Revendications

1. Procédé de traitement biologique d'un matériau solide pour éliminer un composé non souhaité, utilisant un bioréacteur de surface non agité, ledit procédé comprenant les étapes consistant à :

a. revêtir la surface d'une pluralité de substrats grossiers ayant une granulométrie supérieure à environ 0,3 cm avec un matériau solide devant être traité biologiquement en formant ainsi une pluralité de substrats grossiers revêtus, ledit matériau solide devant être traité biologiquement ayant une granulométrie inférieure à environ 250 μm et contenant un composé non souhaité ;
b. former un réacteur de surface non agité en empilant en tas ladite pluralité de substrat grossiers revêtus ou en plaçant ladite pluralité de substrats grossiers revêtus dans un réservoir, ledit réacteur ayant un volume de vide supérieur ou égal à environ 25 % ;
c. inoculer ledit réacteur avec un micro-organisme capable de dégrader le composé non souhaité dans ledit matériau solide de façon à former ainsi un bioréacteur de surface non agité ; et
d. traiter biologiquement ledit matériau solide dans ledit bioréacteur jusqu'à ce que ledit composé non souhaité dans ledit matériau solide soit dégradé à une concentration souhaitée.

2. Procédé selon la revendication 1, comprenant en outre les étapes consistant à :

e. séparer ledit matériau solide traité biologiquement de ladite pluralité de substrats grossiers après que ledit composé non souhaité ait été dégradé à ladite concentration souhaitée ; et
f. répéter les étapes a-d en utilisant ladite pluralité de substrats grossiers.

3. Procédé selon la revendication 1 ou 2, dans lequel ledit composé non souhaité est un contaminant organique.

4. Procédé selon la revendication 3, dans lequel ledit matériau solide est du sol.

5. Procédé selon la revendication 4, dans lequel ledit contaminant organique est au moins un composé choisi dans le groupe constitué par l'huile usée, la graisse, le carburant d'avion, le carburant diésel, le pétrole brut, le benzène, le toluène, l'éthylbenzène, le xylène, les hydrocarbures polyaromatiques (PAH), les aromatiques polynucléaires (PNA), le pentachlorophénol (PCP), les biphényles polychlorés (PCB), la créosote, les pesticides, le 2,4,6-trinitrotoluène (TNT), l'hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), l'octahydro-1,3,5,7-tétranitro-1,3,5,7-tétrazocine (HMX), la N-méthyl-N-2,4,6-tétranitroaniline, et la nitrocellulose (NC).

6. Procédé selon la revendication 3, 4 ou 5, dans lequel ladite pluralité de substrats grossiers est composée de matière plastique.

7. Procédé selon la revendication 1 ou 2, dans lequel ledit composé non souhaité est un minéral de type sulfureux.

8. Procédé selon la revendication 7, dans lequel ledit matériau solide est le charbon.

9. Procédé selon la revendication 8, dans lequel ladite pluralité de substrats grossiers est composée de particules de charbon grossières.

10. Procédé selon la revendication 7, dans lequel ledit matériau solide est un minerai de sulfure réfractaire.

11. Procédé selon la revendication 10, dans lequel ladite pluralité de substrats grossiers est constituée de particules grossières de minerai de sulfure réfractaire.

12. Procédé selon la revendication 1, 2, 3, 4, 5, 7, 8 ou 10, dans lequel ladite pluralité de substrats grossiers est composée d'au moins un matériau choisi dans le groupe constitué par la roche, la roche de lave, le gravier, la roche contenant des minéraux à base de carbonate, la brique, le bloc de mâchefer, et le laitier.

13. Procédé selon l'une quelconque des revendications 1 à 12, dans lequel les substrats grossiers ont une granulométrie nominale supérieure ou égale à environ 0,6 cm et inférieure ou égale à environ 2,54 cm.

14. Procédé selon l'une quelconque des revendications 1 à 13, dans lequel la quantité de matériau solide dont est revêtue ladite pluralité de substrats grossiers est d'environ 10 % à environ 30 % en poids.

15. Procédé selon l'une quelconque des revendications 1 à 14, dans lequel ledit matériau solide a une granulométrie qui est supérieure ou égale à environ 25 μm.

16. Procédé selon l'une quelconque des revendications 1 à 14, dans lequel ledit matériau solide a une granulométrie nominale qui est supérieure ou égale à 75 μm et inférieure ou égale à 106 μm.

17. Procédé selon la revendication 1, dans lequel ladite étape de traitement biologique comprend au moins l'une des opérations suivantes : fourniture au bioréacteur de nutriments nécessaires pour soutenir la croissance du micro-organisme, maintien de la teneur en humidité du bioréacteur au-delà d'une valeur souhaitée, insufflation d'air dans le bioréacteur par l'intermédiaire de tuyaux perforés, maintien du pH du bioréacteur à l'intérieur d'une plage prédéterminée, et maintien de la température du bioréacteur à l'intérieur d'une plage prédéterminée.

18. Procédé selon l'une quelconque des revendications 1 à 17, dans lequel ladite épaisseur de revêtement de matériau solide sur ladite pluralité de substrats est inférieure à environ 1 mm.

19. Procédé selon l'une quelconque des revendications 1 à 18, dans lequel ledit volume de vide est supérieur ou égal à environ 35 %.

20. Procédé selon l'une quelconque des revendications 1 à 19, dans lequel au plus 5 % en poids desdits substrats grossiers font moins de 0,3 cm.

21. Procédé selon la revendication 1, dans lequel ledit matériau solide est un concentré de minéral sulfureux constitué de fines particules de sulfure métallique contenant des valeurs de métaux intéressants, ledit composé non souhaité est constitué desdites fines particules de sulfure métallique, et dans lequel ledit traitement biologique dudit concentré de minéral sulfureux dont est revêtue la surface desdits substrats oxyde biologiquement lesdites fines particules de sulfure métallique jusqu'à ce qu'une quantité souhaitée desdites fines particules de sulfure métallique dans ledit concentré de minéral sulfureux soit oxydée biologiquement et que les métaux de valeur intéressants soient libérés.

22. Procédé selon la revendication 21, dans lequel le réacteur de surface non agité est formé par empilement en tas de la pluralité de substrats grossiers revêtus de concentré et le procédé comprend en outre les étapes consistant à :

e. démolir le tas après que les fines particules de sulfure métallique dont est revêtue la surface de la pluralité de substrats grossiers ont été oxydées biologiquement en une quantité souhaitée ;
f. séparer les fines particules de sulfure métallique oxydées biologiquement de la pluralité de substrats grossiers ; et
g. répéter les étapes a-d en utilisant la pluralité de substrats grossiers.

23. Procédé selon la revendication 21, dans lequel le réacteur de surface non agité est formé par disposition de la pluralité de substrats grossiers revêtus de concentré dans un réservoir et le procédé comprend en outre les étapes consistant à :

e. séparer les fines particules de sulfure métallique oxydées biologiquement de la pluralité de substrats grossiers ; et
f. répéter les étapes a-d en utilisant la pluralité de substrats grossiers.

24. Procédé selon la revendication 21, dans lequel la pluralité de substrats grossiers comprend des particules de minerai grossières qui contiennent des particules de sulfure métallique.

25. Procédé selon la revendication 24, comprenant en outre les étapes consistant à :

e. séparer les fines particules de sulfure métallique oxydées biologiquement de la pluralité de substrats grossiers après que les particules de sulfure métallique dont est revêtue la surface de la pluralité de substrats grossiers aient été oxydées biologiquement d'une quantité souhaitée ;
f. broyer la pluralité de substrats grossiers à une granulométrie suffisante pour permettre la séparation de particules de sulfure métallique à partir de ceux-ci ;
g. produire un deuxième concentré de minéral sulfureux composé de fines particules de sulfure métallique à partir de la pluralité de substrats grossiers broyés ;
h. revêtir une deuxième pluralité de substrats grossiers avec le deuxième concentré ;
i. former un deuxième tas en utilisant la deuxième pluralité de substrats grossiers ; et
j. oxyder biologiquement le deuxième concentré de fines particules de sulfure métallique.

26. Procédé selon la revendication 24 ou 25, dans lequel les particules de minerai grossières contiennent aussi un carbonate minéral.

27. Procédé selon la revendication 21, 22 ou 23, dans lequel le matériau utilisé pour ladite pluralité de substrats grossiers est au moins un matériau choisi dans le groupe constitué par la roche de lave, le gravier, et la roche contenant un carbonate minéral.

28. Procédé selon l'une quelconque des revendications 21 à 27, dans lequel les valeurs de métaux intéressants sont les métaux de valeur de base provenant de la partie métal des particules de sulfure métallique.

29. Procédé selon la revendication 1, dans lequel ledit matériau solide est un concentré de minéral sulfureux composé de fines particules de sulfure métallique contenant des valeurs de métaux précieux occlus, le composé non souhaité est constitué des fines particules de sulfure métallique et dans lequel ledit traitement biologique dudit concentré de minéral sulfureux dont est revêtue la surface dudit substrat grossier oxyde biologiquement lesdites fines particules de sulfure métallique jusqu'à ce qu'une quantité souhaitée desdites fines particules de sulfure métallique dans ledit concentré de minéral sulfureux soit oxydée biologiquement et que les valeurs de métaux précieux soient libérés, le procédé comprenant en outre les étapes consistant à :

e. mettre en contact les fines particules de sulfure métallique oxydées biologiquement avec un agent de lixiviation de métaux précieux de façon à dissoudre ainsi les valeurs de métaux précieux à partir des fines particules de sulfure métallique oxydées biologiquement ; et
f. récupérer les valeurs de métaux précieux à partir de l'agent de lixiviation.

30. Procédé selon la revendication 29, dans lequel le réacteur de surface non agité est formé par empilement en tas de la pluralité de substrats grossiers revêtus de concentré et le procédé comprend en outre les étapes consistant à :

g. démolir le tas après que les fines particules de sulfure métallique dont est revêtue la surface de la pluralité de substrats grossiers aient été oxydées biologiquement d'une quantité souhaitée ; et
h. séparer les fines particules de sulfure métallique oxydées biologiquement de la pluralité de substrats grossiers avant mise en contact avec l'agent de lixiviation.

31. Procédé selon la revendication 30, comprenant en outre la répétition des étapes a-f par utilisation de la pluralité de substrats grossiers ayant été séparés des fines particules de sulfure métallique oxydées biologiquement.

32. Procédé selon la revendication 30 ou 31, dans lequel le procédé de séparation des fines particules de sulfure métallique oxydées biologiquement de la pluralité de substrats grossiers comprend la disposition de la pluralité de substrats grossiers revêtus de concentré sur un tamis et ensuite arrosage avec de l'eau.

33. Procédé selon la revendication 30 ou 31, dans lequel le procédé de séparation des fines particules de sulfure métallique oxydées biologiquement de la pluralité de substrats grossiers comprend le tonnelage de la pluralité de substrats grossiers revêtus de concentré dans un trommel.

34. Procédé selon la revendication 29, dans lequel le réacteur de surface non agité est formé par disposition de la pluralité de substrats grossiers revêtus de concentré dans un réservoir et le procédé comprend en outre l'étape consistant à :

g. séparer les fines particules de sulfure métallique oxydées biologiquement de la pluralité de substrats grossiers avant la mise en contact avec l'agent de lixiviation.

35. Procédé selon la revendication 34, comprenant en outre la répétition des étapes a-f par utilisation de la pluralité de substrats grossiers ayant été séparés des fines particules de sulfure métallique oxydées biologiquement.

36. Procédé selon la revendication 34 ou 35, dans lequel le procédé de séparation des fines particules de sulfure métallique oxydées biologiquement de la pluralité de substrats grossiers comprend le remplissage du réservoir avec une solution aqueuse et ensuite la vidange rapide du réservoir de façon à transporter ainsi les fines particules de sulfure métallique oxydées biologiquement hors du réservoir dans la solution aqueuse.

37. Procédé selon la revendication 29, dans lequel la pluralité de substrats grossiers comprend des particules grossières de minerai de sulfure réfractaire ayant des valeurs de métaux précieux occlus à l'intérieur des particules de sulfure métallique.

38. Procédé selon la revendication 37, comprenant en outre les étapes consistant à :

g. séparer les fines particules de sulfure métallique oxydées biologiquement de la pluralité de substrats grossiers avant la mise en contact avec ledit agent de lixiviation ;
h. broyer la pluralité de substrats grossiers à une granulométrie suffisante pour permettre la séparation des fines particules de sulfure métallique d'avec ceux-ci ;
i. produire un deuxième concentré de minéral sulfureux constitué de fines particules de sulfure métallique à partir de la pluralité de substrats grossiers broyés ;
j. revêtir une deuxième pluralité de substrats grossiers avec le deuxième concentré ;
k. former un deuxième réacteur de surface non agité en empilant en tas la deuxième pluralité de substrats grossiers revêtus ou en plaçant la deuxième pluralité de substrats grossiers revêtus dans un réservoir ;
l. oxyder biologiquement le deuxième concentré de fines particules de sulfure métallique ;
m. mettre en contact le deuxième concentré oxydé biologiquement avec l'agent de lixiviation de métaux précieux de façon à dissoudre ainsi les valeurs de métaux précieux à partir du deuxième concentré oxydé biologiquement ; et
n. récupérer les valeurs de métaux précieux dissous par l'agent de lixiviation à partir du deuxième concentré.

39. Procédé selon la revendication 37, dans lequel les particules de minerai de sulfure réfractaire grossières proviennent du minerai sulfureux réfractaire, porteur des métaux précieux, utilisé pour produire le concentré.

40. Procédé selon la revendication 37, dans lequel les particules de minerai sulfureux réfractaire grossières contiennent aussi un carbonate minéral.

41. Procédé selon l'une quelconque des revendications 29 à 36, dans lequel le matériau utilisé pour ladite pluralité de substrats grossiers est au moins un matériau choisi dans le groupe constitué par la roche de lave, le gravier, et la roche contenant un carbonate minéral.

42. Procédé selon l'une quelconque des revendications 29 à 41, dans lequel l'agent de lixiviation est choisi dans le groupe constitué par la thiourée et le cyanure.

43. Procédé selon l'une quelconque des revendications 21 à 42, dans lequel la pluralité de substrats grossiers a une granulométrie nominale supérieure ou égale à environ 0,6 cm et inférieure ou égale à environ 2,5 cm.

44. Procédé selon l'une quelconque des revendications 21 à 43, dans lequel la quantité de concentré dont est revêtue la pluralité de substrats grossiers est d'environ 10 % à environ 30 % en poids.

45. Procédé selon l'une quelconque des revendications 21 à 44, dans lequel le concentré de minéral sulfureux comprend au moins environ 20 % en poids de particules de sulfure métallique.

46. Procédé selon l'une quelconque des revendications 21 à 44, dans lequel le concentré de minéral sulfureux comprend au moins environ 40 % en poids de particules de sulfure métallique.

47. Procédé selon l'une quelconque des revendications 21 à 44, dans lequel le concentré de minéral sulfureux comprend au moins environ 70 % en poids de particules de sulfure métallique.

48. Procédé selon l'une quelconque des revendications 21 à 44, dans lequel le concentré de minéral sulfureux comprend entre 40 et 80 % en poids de particules de sulfure métallique.

49. Procédé selon l'une quelconque des revendications 21 à 48, dans lequel le concentré a une granulométrie qui est supérieure à environ 25 μm.

50. Procédé selon l'une quelconque des revendications 21 à 49, dans lequel le concentré a une granulométrie qui est inférieure à environ 106 μm.

51. Procédé selon l'une quelconque des revendications 21 à 49, dans lequel le concentré a une granulométrie qui est inférieure à environ 75 μm.

52. Procédé selon l'une quelconque des revendications 21 à 51, dans lequel le métal précieux récupéré est au moins un métal choisi dans le groupe constitué par l'argent, l'or et le platine.

53. Procédé selon la revendication 1, dans lequel ledit matériau solide est un concentré de minéral sulfureux composé de fines particules de sulfure métallique contenant des valeurs de métaux d'intérêt, ledit composé non souhaité est constitué desdites fines particules de sulfure métallique, et dans lequel ledit traitement biologique dudit concentré de minéral sulfureux dont est revêtue la surface desdits substrats grossiers oxyde biologiquement lesdites fines particules de sulfure métallique en engendrant ainsi la production d'une solution secondaire de lixiviat biologique et la dissolution de la partie métal des particules de sulfure métallique, le procédé comprenant en outre l'étape consistant à :

e. récupérer les valeurs de métaux d'intérêt à partir de la solution secondaire de lixiviat biologique.

54. Procédé selon la revendication 53, dans lequel le concentré de fines particules de sulfure métallique comprend des particules de minéraux sulfureux de cuivre et le métal récupéré est le cuivre.

55. Procédé selon la revendication 54, dans lequel le procédé de récupération du cuivre à partir de la solution secondaire de lixiviat biologique comprend au moins un procédé choisi dans le groupe constitué par une extraction au solvant, une cémentation du cuivre, et une extraction électrolytique.

56. Procédé selon la revendication 53, dans lequel le concentré de fines particules de sulfure métallique comprend des minéraux à base de sulfure de zinc et le métal récupéré est le zinc ; ou bien
dans lequel le concentré de fines particules de sulfure métallique comprend des minéraux à base de sulfure de nickel et le métal récupéré est le nickel.

FIG. 1.

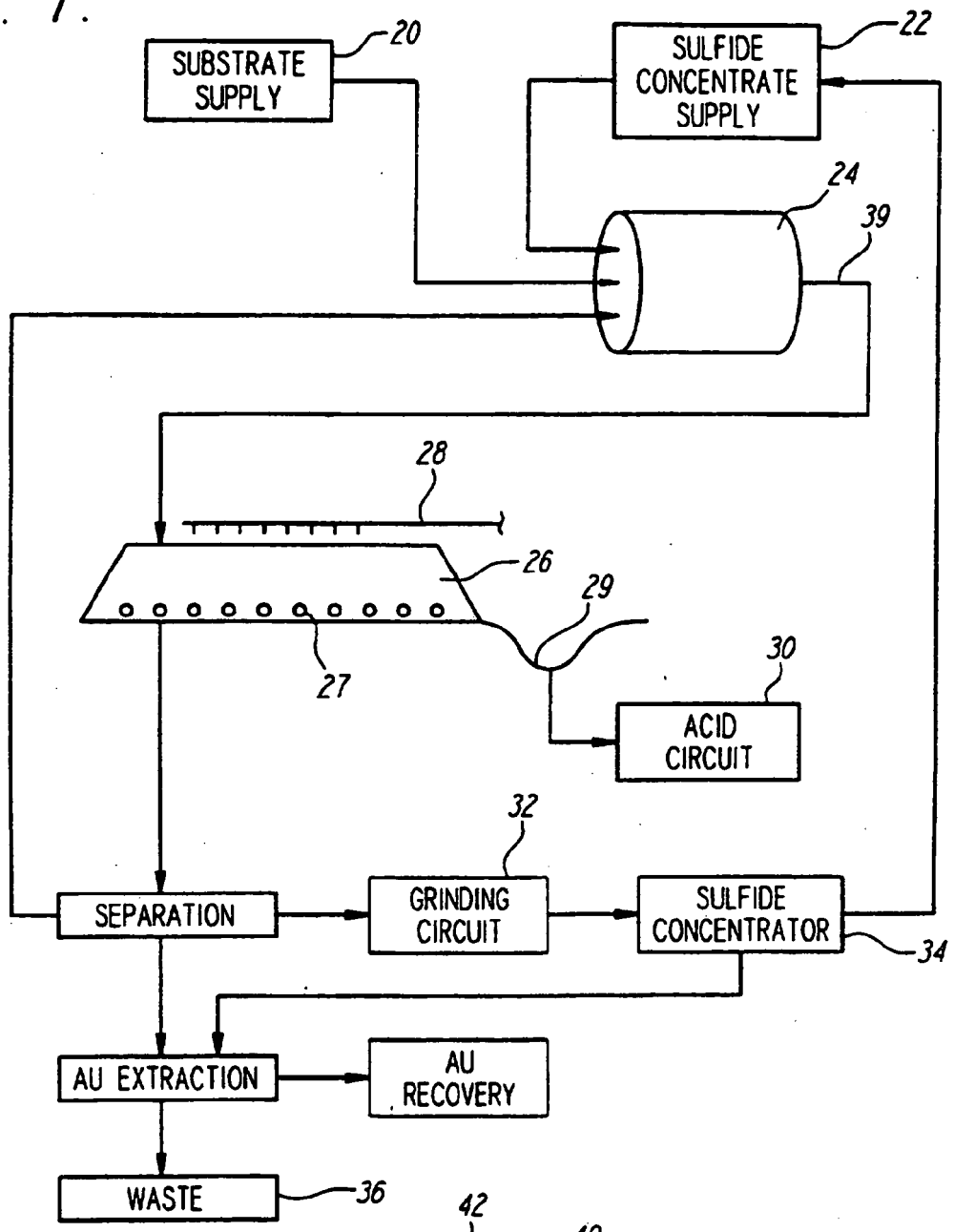
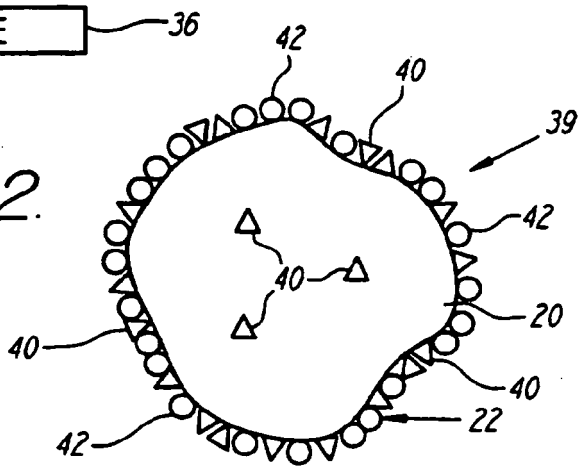

SUBSTRATE SUPPLY
20
SULFIDE CONCENTRATE SUPPLY
22
24
39
28
26
29
27
30
ACID CIRCUIT
32
SEPARATION
GRINDING CIRCUIT
SULFIDE CONCENTRATOR
34
AU EXTRACTION
AU RECOVERY
WASTE
36

FIG. 2.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40

FIG. 3.

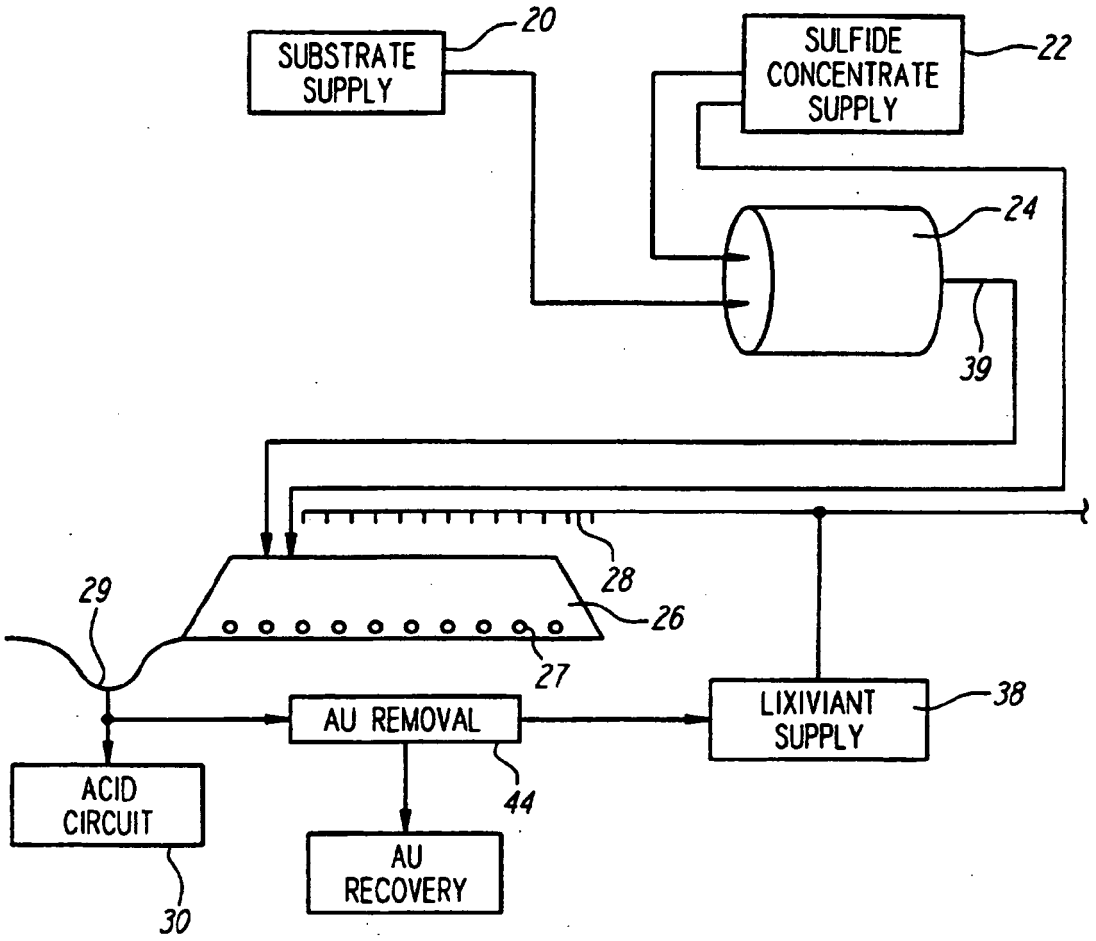

SUBSTRATE SUPPLY
20
SULFIDE CONCENTRATE SUPPLY
22
24
39
28
29
26
27
AU REMOVAL
LIXIVIANT SUPPLY
38
ACID CIRCUIT
44
AU RECOVERY
30

FIG. 4.

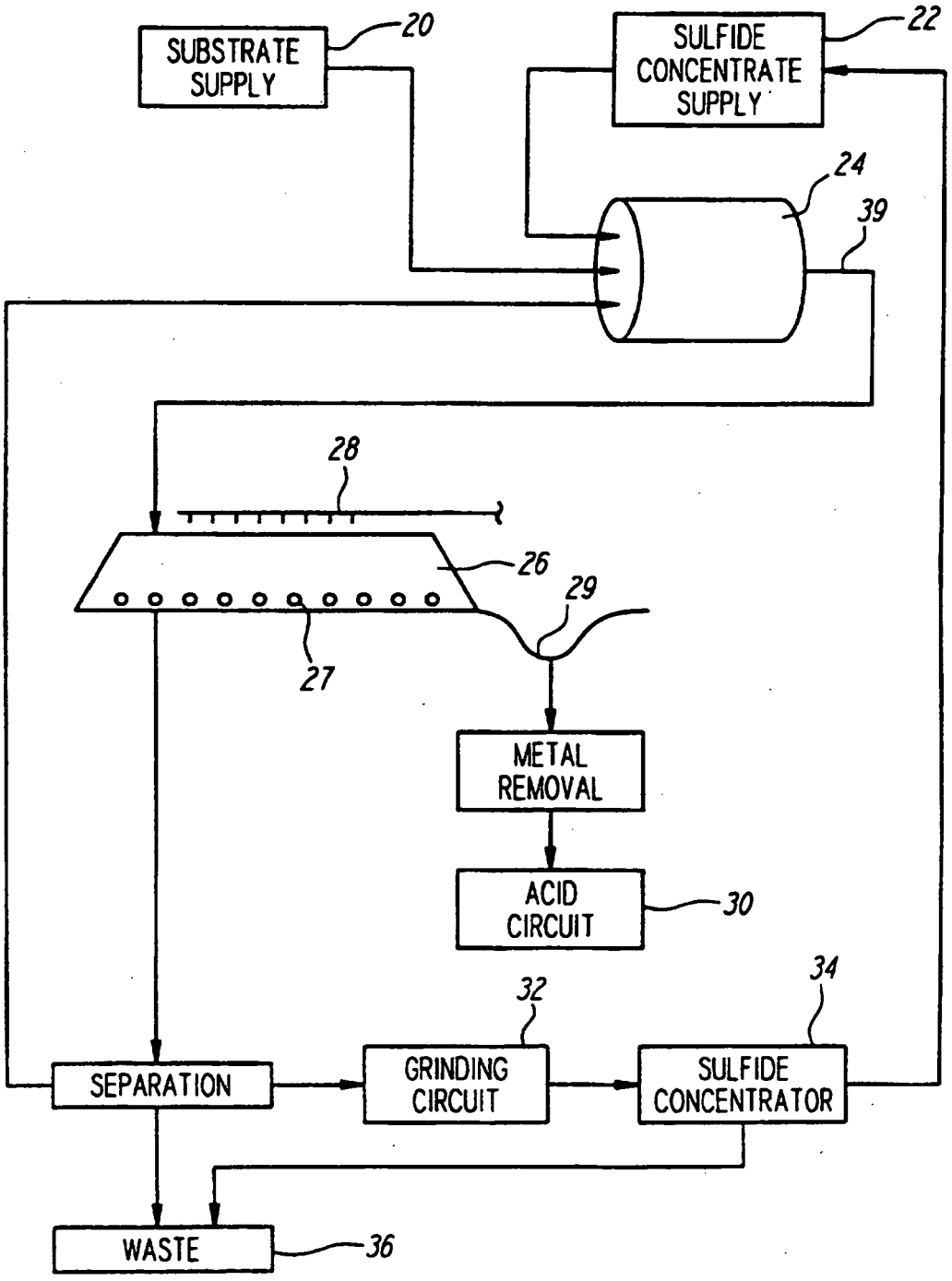

SUBSTRATE SUPPLY
20
SULFIDE CONCENTRATE SUPPLY
22
24
39
28
26
29
27
METAL REMOVAL
ACID CIRCUIT
30
32
34
SEPARATION
GRINDING CIRCUIT
SULFIDE CONCENTRATOR
WASTE
36

FIG. 5.

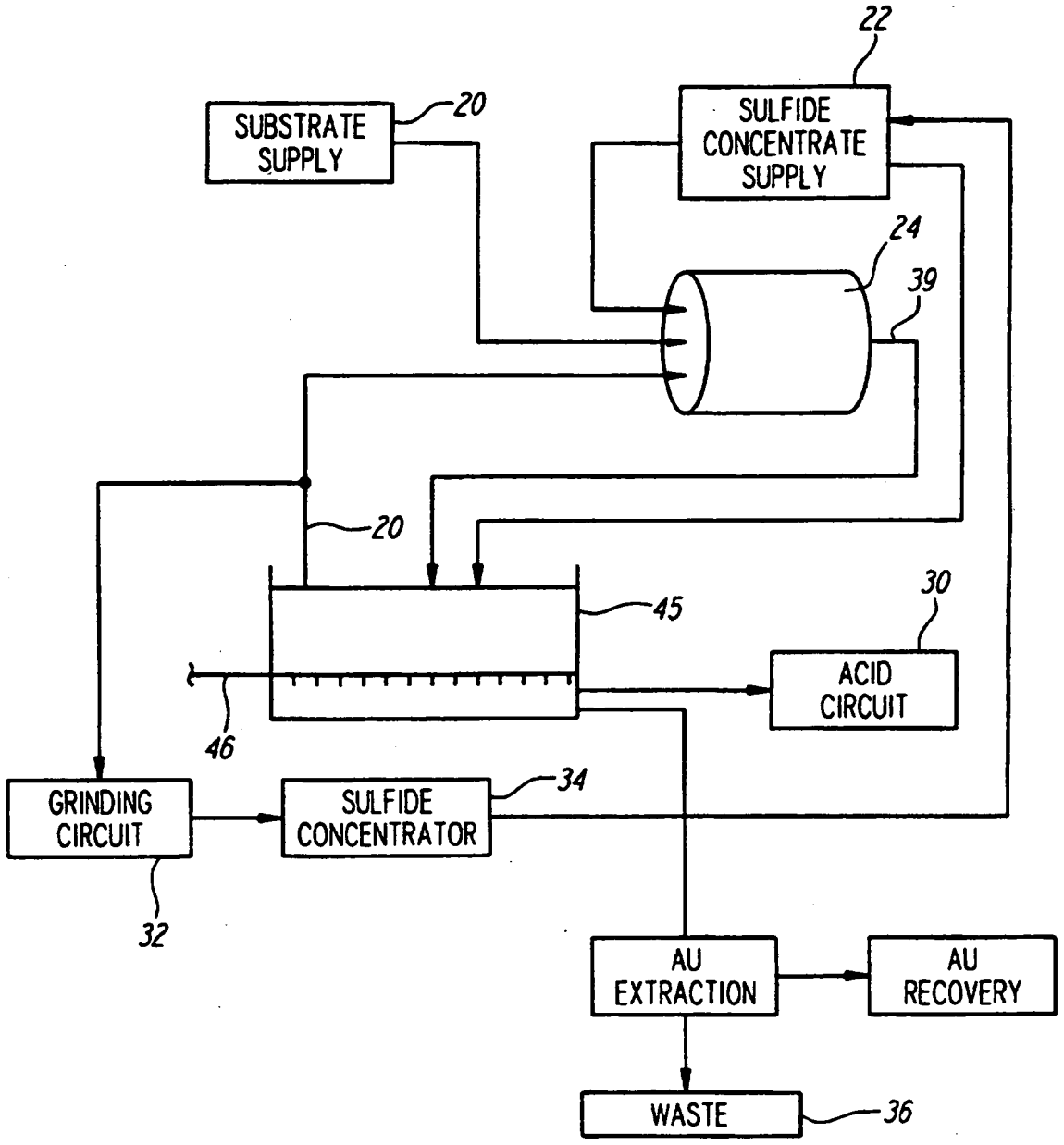

22
SUBSTRATE SUPPLY
20
SULFIDE CONCENTRATE SUPPLY
24
39
20
45
30
ACID CIRCUIT
46
GRINDING CIRCUIT
SULFIDE CONCENTRATOR
34
32
AU EXTRACTION
AU RECOVERY
WASTE
36

FIG. 6.

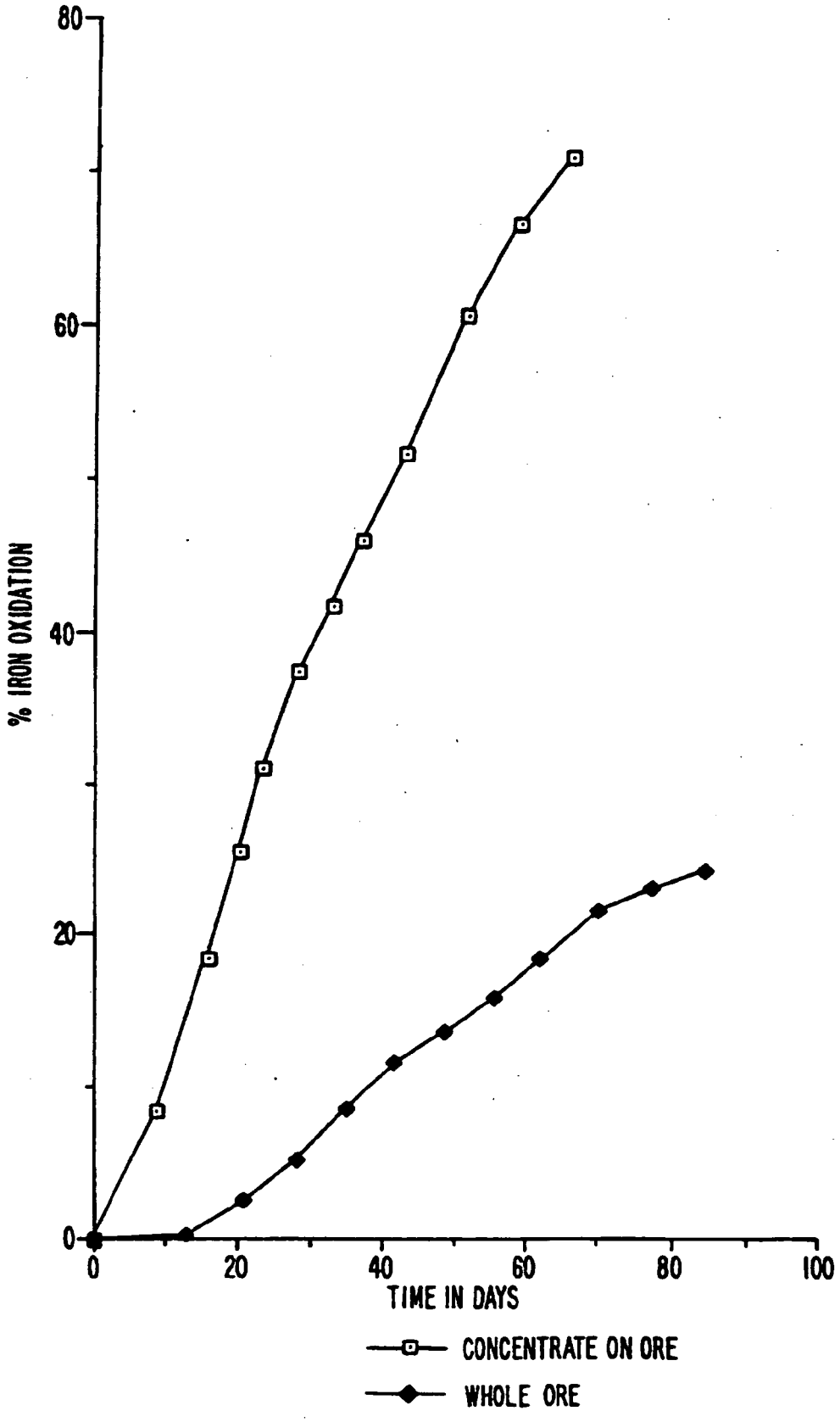

80
60
40
20
0
% IRON OXIDATION
0
20
40
60
80
100
TIME IN DAYS
CONCENTRATE ON ORE
WHOLE ORE

FIG. 7.

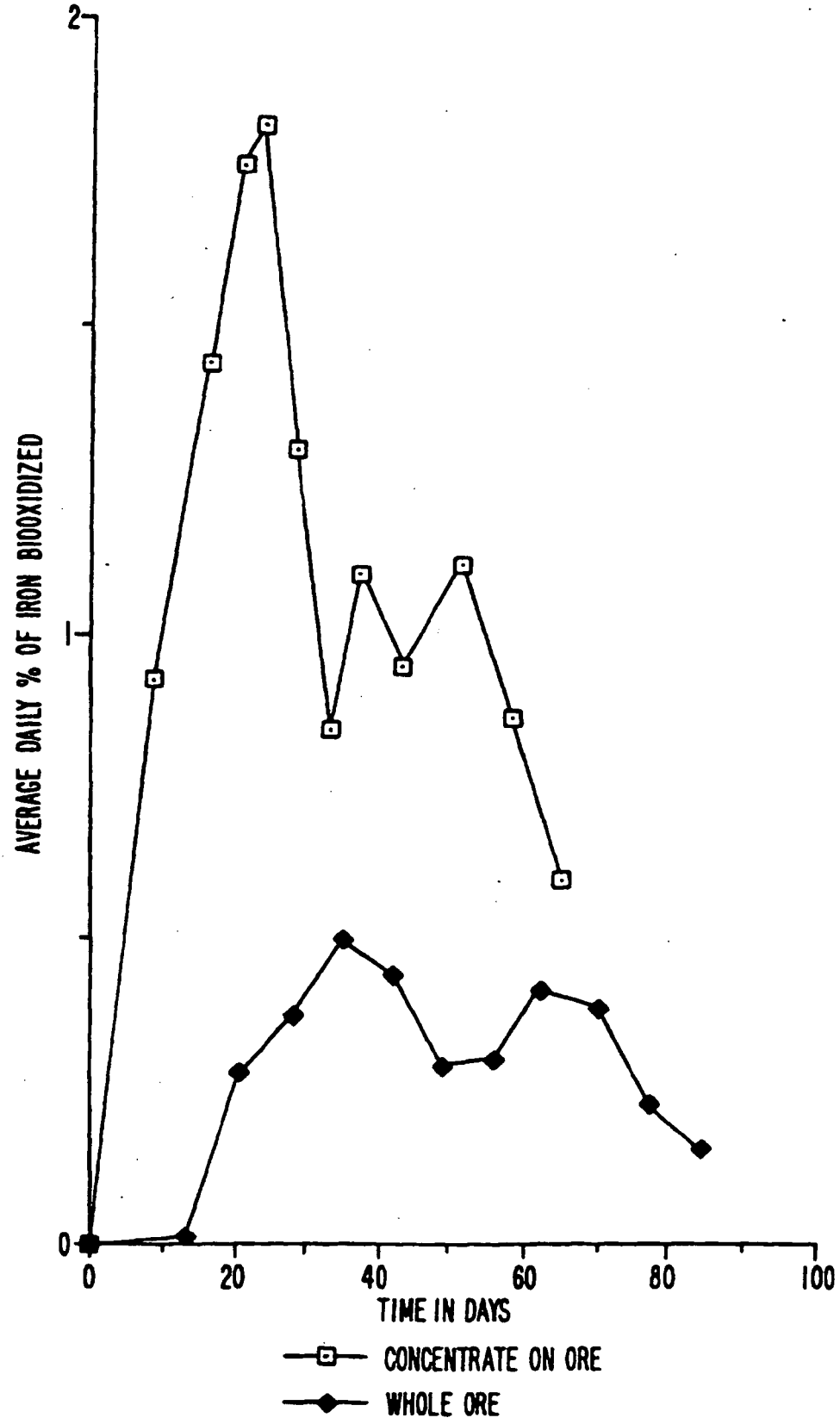

AVERAGE DAILY % OF IRON BIOOXIDIZED
2
1
0
0
20
40
60
80
100
TIME IN DAYS
CONCENTRATE ON ORE
WHOLE ORE

FIG. 8.

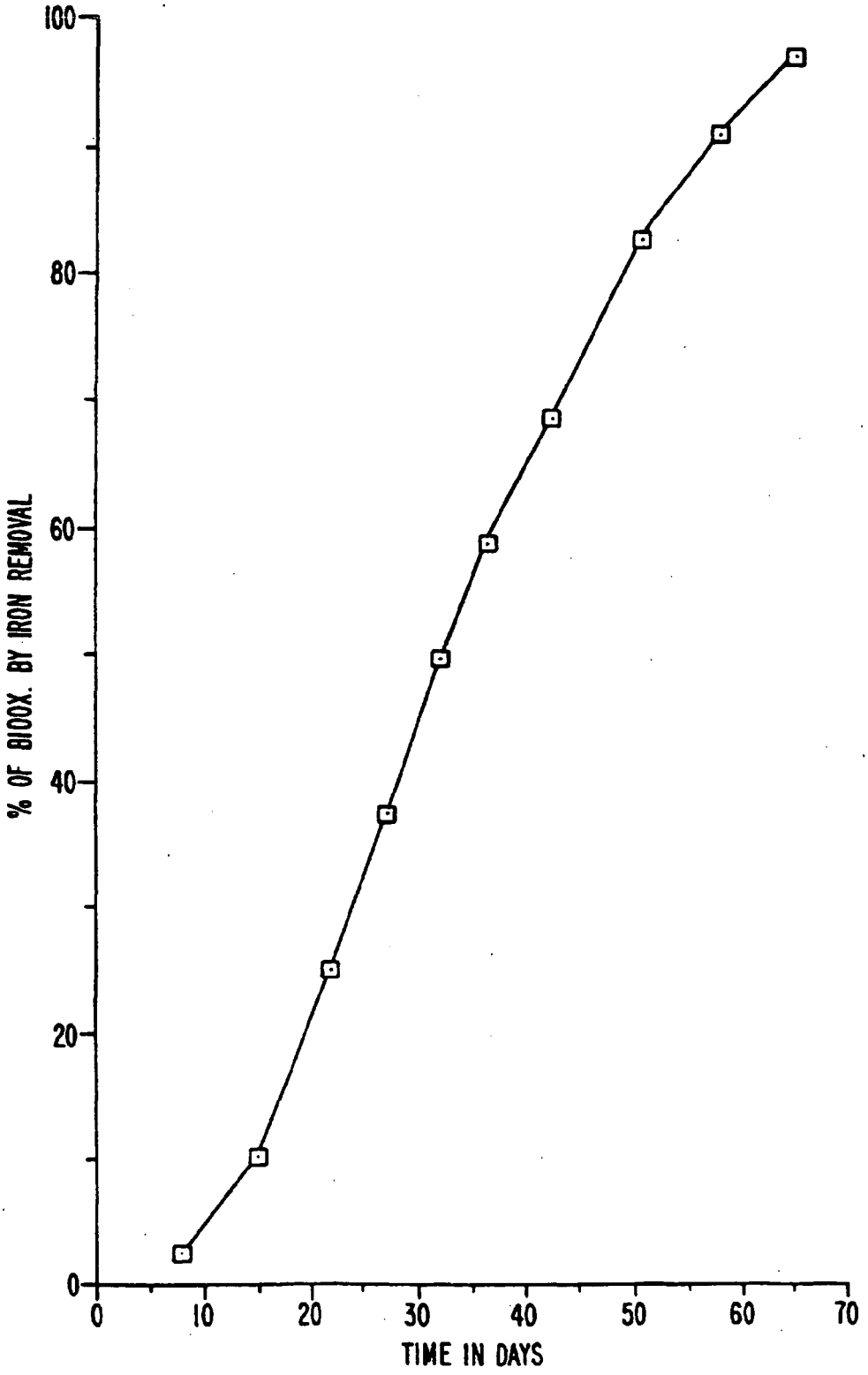

100
80
60
40
20
0
% OF BIOOX. BY IRON REMOVAL
0
10
20
30
40
50
60
70
TIME IN DAYS

FIG. 9.

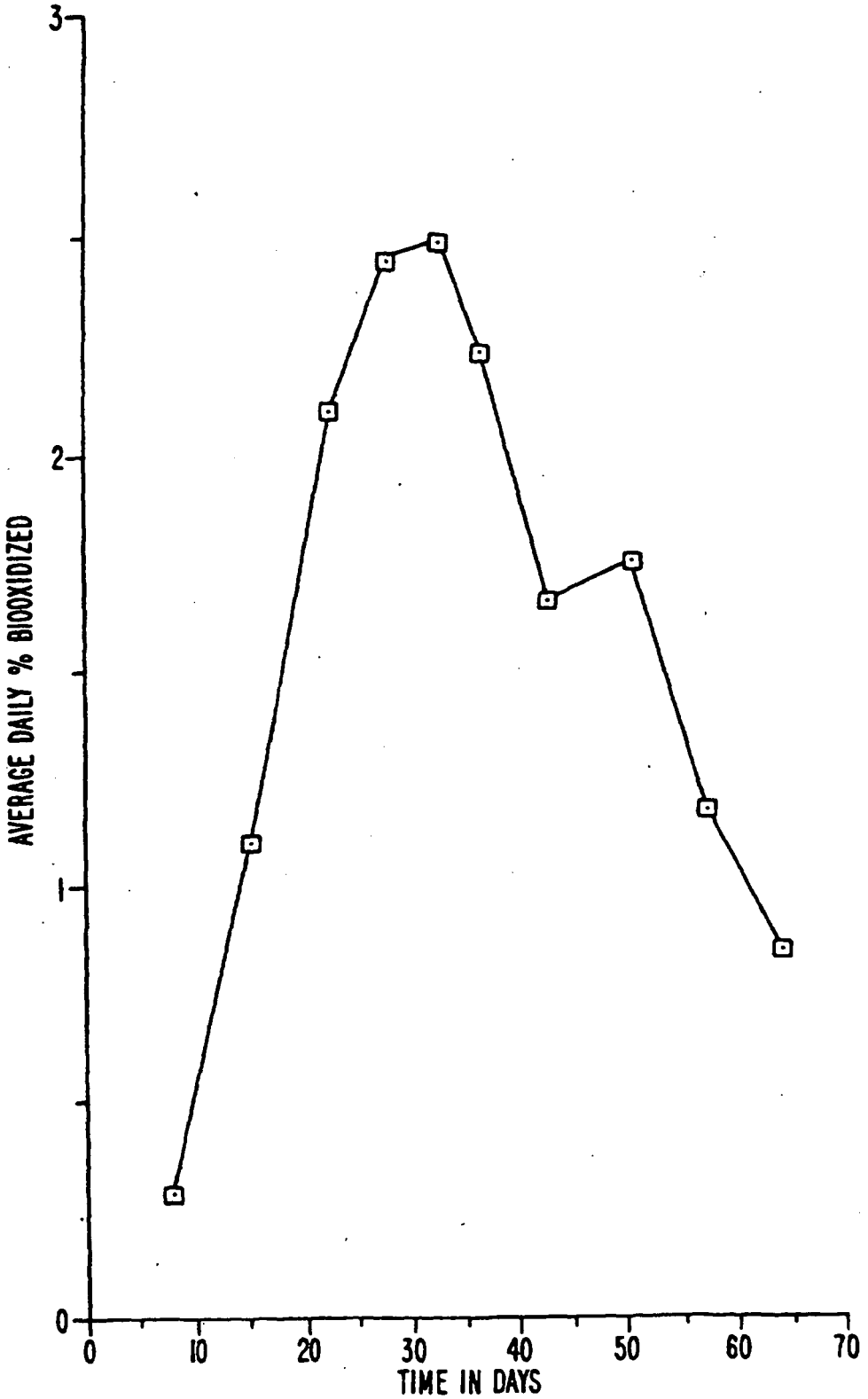

AVERAGE DAILY % BIOOXIDIZED
0
1
2
3
0
10
20
30
40
50
60
70
TIME IN DAYS

FIG. 10.

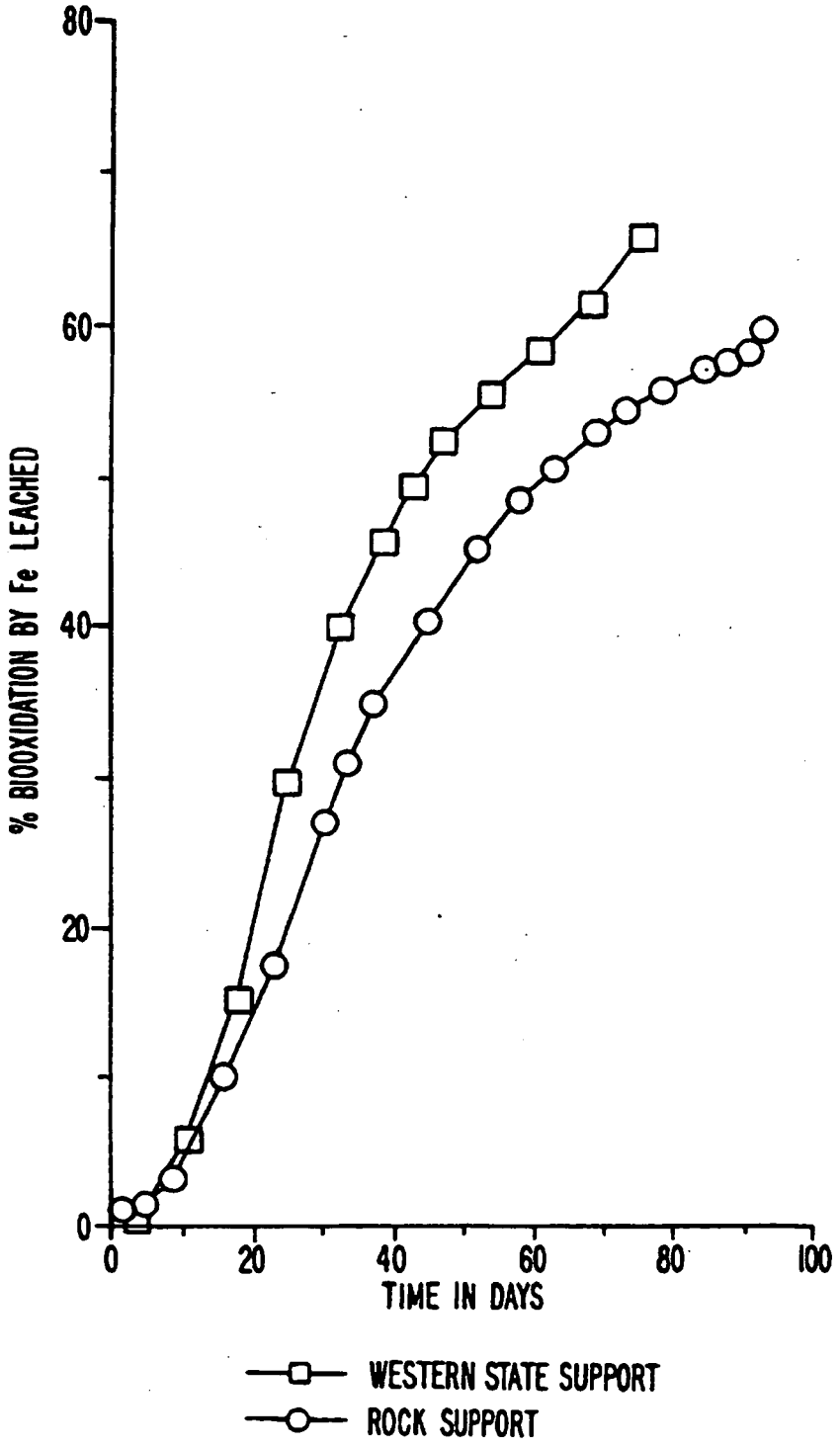
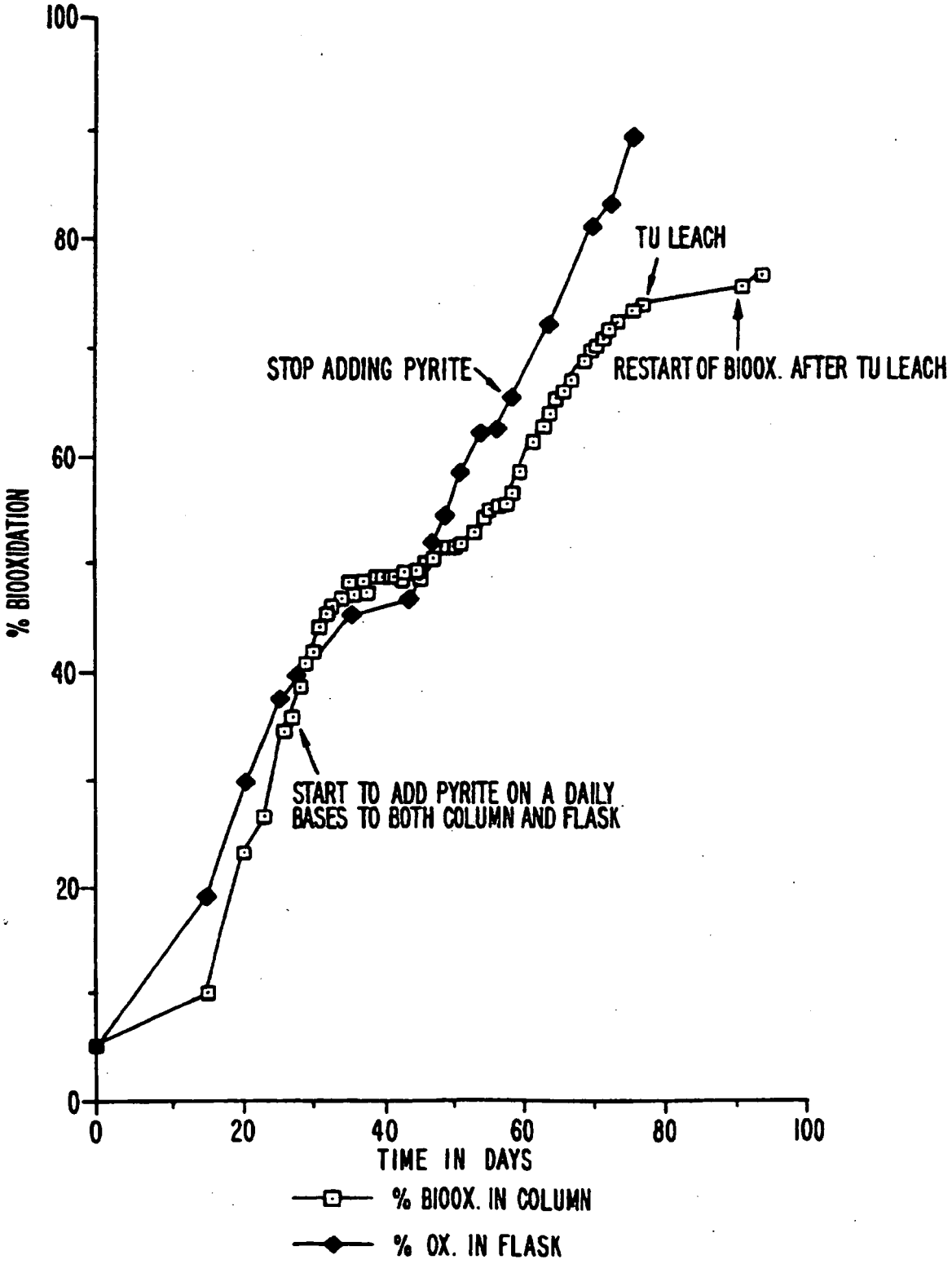

80
60
40
20
0
% BIOOXIDATION BY Fe LEACHED
0
20
40
60
80
100
TIME IN DAYS
WESTERN STATE SUPPORT
ROCK SUPPORT

FIG. 11.


100
80
60
40
20
0
% BIOOXIDATION
0
20
40
60
80
100
TIME IN DAYS
TU LEACH
STOP ADDING PYRITE
RESTART OF BIOOX. AFTER TU LEACH
START TO ADD PYRITE ON A DAILY BASES TO BOTH COLUMN AND FLASK
% BIOOX. IN COLUMN
% OX. IN FLASK

REFERENCES CITED IN THE DESCRIPTION

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