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(54) Title: METHOD AND PROCESS FOR THE ENHANCED LEACHING OF COPPER SULFIDE MINERALS CONTAINING CHALCOPYRITE

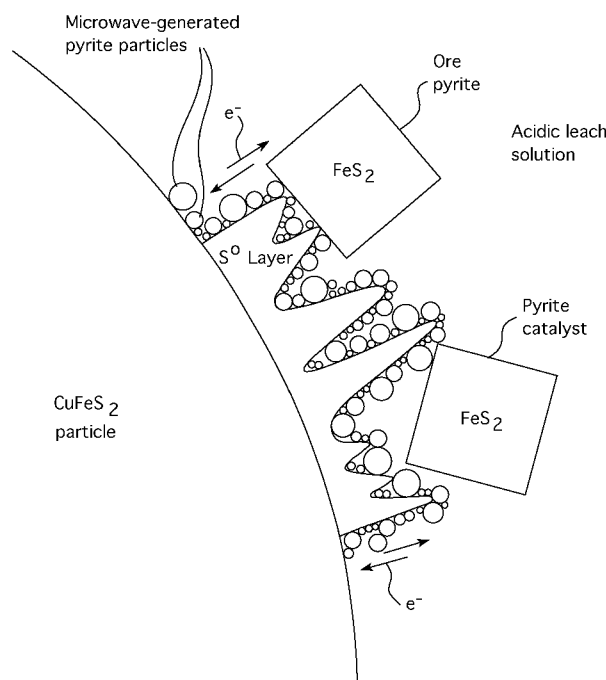


FIG. 4

(57) Abstract: A method of leaching a copper bearing sulfide mineral slurry containing chalcopyrite is described. The method comprises the steps of providing a slurry having chalcopyrite particles therein, exposing the slurry to an acidic leach solution, and chemically leaching copper from the slurry into the acidic leach solution in the presence of microwave irradiation. The microwave irradiation of the slurry takes place under process conditions whereby crystalline pyrite may be formed in-situ on surfaces of the chalcopyrite particles. Crystalline pyrite may be formed on surfaces of the chalcopyrite particles from amorphous phase pyrite. Leached copper is recovered from said acidic leach solution. A device for more efficiently leaching a copper bearing sulfide mineral slurry containing chalcopyrite is also described herein.

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METHOD AND PROCESS FOR THE ENHANCED LEACHING OF COPPER SULFIDE MINERALS CONTAINING CHALCOPYRITE

CROSS-REFERENCE TO RELATED APPLICATIONS

This international application claims the benefit of United States Provisional Patent Application No. 61/725,206 filed on November 12, 2012.

FIELD OF THE INVENTION

This invention relates to methods and systems for leaching metals from metal sulfide ores and concentrates and more particularly to methods and systems for microwave controlled formation of iron sulfides during leaching of metal values from sulfide ores and concentrates.

BACKGROUND OF THE INVENTION

This invention relates to the hydrometallurgical processing of sulfide ores for metals recovery. Chalcopyrite (CuFeS_2) is the primary copper-containing mineral found in the majority of the copper sulfide ores of commercial interest. Other copper-containing ore minerals of commercial interest include chalcocite (Cu_2S), bornite (Cu_5FeS_4), covellite (CuS), digenite (Cu_2S), enargite (Cu_3AsS_4), tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$), and tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$). Copper sulfide ores, aside from containing a variety of copper-containing minerals, will also contain a

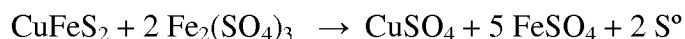
wide variety of gangue minerals including, but not limited to, silicates, pyrite (FeS_2) and pyrrhotite (FeS).

In the processing of metal sulfide ores, flotation is commonly and successfully used to effect a separation of the metal values from the gangue. However, separation of individual metal sulfides from each other can be a challenge, and the separation of copper-bearing sulfide minerals from pyrite by flotation remains a technical problem. It would be desirable to recover the copper by hydrometallurgical processes, such as leaching, without effecting a chemical or physical change in gangue minerals like pyrite.

It is also known from prior art that the dissolution of chalcopyrite is a slow process and that copper recoveries from chalcopyrite can be limited by surface passivation reactions that prevent complete mineral dissolution. The nature of the surface reactions that lead to passivation are not completely understood, but many researchers ascribe the hindered dissolution, at least partly, to the formation of a relatively impermeable layer of elemental sulfur on the chalcopyrite surface.

In U.S. Pat. No. 7,846,233 B2, a method for selectively leaching chalcopyrite includes using pyrite as a catalyst for improving copper recoveries and increasing chalcopyrite dissolution rates. The leaching is carried out in acidic ferric/ferrous sulfate solutions containing dissolved oxygen under redox conditions whereby the pyrite is not significantly oxidized. This enhancement in copper leaching rates has been attributed to galvanic interactions between pyrite and chalcopyrite particles present in the leach process. The prior art leach conditions lead to the formation of a porous sulfur layer, which facilitates rapid mass transport of copper from the

mineral surface to the leach solution. The overall mineral dissolution reaction, which is the sum of the anodic and cathodic half-cell reactions, can be described as:



The oxidative dissolution process is optimally carried out at temperatures which are below the melting point of elemental sulfur (S°), which is about 110 to 120 °C and at redox potentials which minimize the degree of sulfide oxidation to sulfate. However, it will be recognized by one skilled in the art that the reaction temperatures must be sufficiently high to produce rapid leaching of copper. Thus, prior art methods specify an optimum leach temperature of about 70-90 °C.

The kinetics of ferric ion reduction to ferrous ion has been shown by Majuste, et. al., in *Hydrometallurgy*, 113-114, 167-176 (2012) to be faster on pyrite surfaces than on chalcopyrite surfaces, when the leach conditions are such that there are no anodic reactions at the galvanically coupled pyrite surfaces. Thus, the dissolution of chalcopyrite will proceed faster when pyrite is galvanically coupled to chalcopyrite.

To maintain the galvanic couple as the leach reaction progresses, electron conduction must occur across the porous layer of elemental sulfur formed on the surfaces of the chalcopyrite particles. As the electrical resistivity of elemental sulfur is the highest of all known materials (i.e., approximately $10^{15} \Omega\text{-m}$), no explanation as to the mechanism by which the galvanic couple is maintained during the leaching reaction is provided in the method described in U.S. Pat. No. 7,846,233 B2.

In WO 2012/000090 A1, it is disclosed that pyrite from different sources could adversely affect the dissolution of chalcopyrite, and that the presence of silver is required to facilitate the

prior methods of catalytic dissolution of chalcopyrite described in U.S. Pat. No. 7,846,233 B2. It was postulated by Nazari, Dixon and Dreisinger in *Hydrometallurgy*, 113-114, 122-130, (2012) that minute amounts of silver ions may act to increase the electrical conductivity of both the pyrite surface and the elemental sulfur product layer. While the incorporation of silver ions may provide for improvements in copper dissolution kinetics and copper recoveries from chalcopyrite, the commercial viability of this approach is limited by the high cost of adding silver to the leaching system. Thus, there is a need for lower-cost approaches to initiating and maintaining high copper dissolution rates and copper recoveries during atmospheric leaching of copper-bearing sulfide minerals.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a Pourbaix Diagram (Eh vs. pH) for the system of species comprising FeS_2 , 100g $\text{H}_2\text{SO}_4/\text{L}$, in water at 80 °C, wherein the redox potential (Eh) scale is measured in volts (i.e., standard hydrogen electrode (SHE) reference), and all species concentrations are expressed as activities;

FIG. 2 shows a prior method of galvanic conduction between pyrite and chalcopyrite;

FIG. 3 shows a galvanic connection between pyrite and chalcopyrite using methods according to some embodiments of the invention;

FIG. 4 shows galvanic interactions which occur using methods described herein;

FIG. 5 shows a device for exposing copper sulfide-containing slurry to microwave irradiation according to one embodiment;

FIG. 6 shows a device for exposing copper sulfide-containing slurry to microwave irradiation according to yet another embodiment;

FIG. 7 shows a device for exposing copper sulfide-containing slurry to microwave irradiation according to yet another embodiment;

FIG. 8 shows a device for exposing copper sulfide-containing slurry to microwave irradiation according to further embodiments;

FIGS. 9-14 schematically illustrate various microwave signal profiles which may be used to irradiate copper sulfide-containing slurry according to some embodiments.

DETAILED DESCRIPTION OF THE INVENTION

It is known from prior art that catalysts such as Cu° , Au° , MnO_2 , carbon, silver sulfide (Ag_2S), and pyrite can enhance the rate of copper dissolution from chalcopyrite and that the enhancement is attributable to galvanic coupling between the chalcopyrite surface and the catalyst. However, to maintain a galvanic couple with the catalyst, it is necessary that electron conduction occur across the elemental sulfur layer which forms around the chalcopyrite particles.

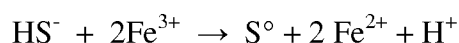
The resistivity of elemental sulfur is about $10^{15} \Omega\text{-m}$, while that of FeS_2 is about $3 \times 10^{-2} \Omega\text{-m}$, which amounts to a difference of about $10^{17} \Omega\text{-m}$. In the method of the present invention, microwave irradiation is used to promote the formation of a crystalline FeS_2 coating on the surface of the elemental sulfur layer to maintain galvanic contact between the catalyst and the sulfide mineral. The presence of a pyrite coating on the elemental sulfur layer thereby decreases the surface electrical resistivity of the sulfur coating by a factor of about $10^{17} \Omega\text{-m}$.

In the method of the present invention, the leaching of chalcopyrite, and other copper sulfides, is done under dissolution conditions wherein pyrite is thermodynamically stable. The redox potentials which satisfy this condition are readily obtained from Pourbaix diagrams, often referred to as Eh-pH diagrams. Referring to FIG. 1, the range of redox potentials over which pyrite is thermodynamically stable can be readily discerned as a function of pH. Similar diagrams can be prepared at any temperature and solution composition of interest using commercially available software or by calculation methods known to those skilled in the art. It will also be known to those skilled in the art that the Pourbaix diagrams provide approximate boundary conditions between the thermodynamically stable and thermodynamically unstable states. In this context, pyrite essentially becomes thermodynamically unstable wherein the surfaces of the pyrite particles react anodically. The voltage boundary conditions given in a Pourbaix diagram are understood to be approximate because of the existence of a reaction overpotential. Reaction overpotential refers to the voltage difference that exists between the thermodynamically determined potential and the potential at which a reaction is experimentally observable. In a galvanic cell, this means that the anodic surface is less negative (i.e., a lower electron activity) than thermodynamically expected due to electrochemical inefficiencies, and therefore more energy is required to drive the reaction.

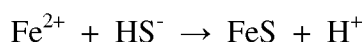
In prior methods of leaching chalcopyrite, and other copper sulfides, the production of pyrite as a reaction product has not been observed, particularly under conditions where FeS_2 is the thermodynamically stable iron-sulfur phase. This is because slow kinetics prevents any significant formation of the more thermodynamically preferred phase within the time scale of the leaching process. Under prior art conditions, the precursors required for pyrite formation (i.e., Fe^{2+} , HS^- , S^0 , and polysulfides such as S_n^{2-}) are produced during the course of the copper sulfide

dissolution, but kinetic factors prevent conversion to pyrite at timescales commensurate with the leaching processes. For example, it is well-known that the formation of pyrite is relatively slow at temperatures below 100 °C.

Elemental sulfur, polysulfides, and $\text{Fe}^{2+}/\text{Fe}^{3+}$ are all known constituents resulting from chalcopyrite dissolution in acidic ferric sulfate solutions. Prior art teaches that elemental sulfur can be produced by the oxidation of sulfide by ferric ion in the presence of oxygen:

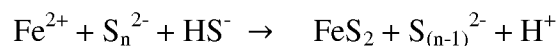


In a similar manner, a companion reaction takes place between ferrous ion and hydrogen sulfide:



In this case FeS is an amorphous phase and would not be electrically conductive, and hence would not be expected to aid in the dissolution of chalcopyrite through galvanic effects.

Without being limited to any particular theory, it is believed that with microwave irradiation, the formation of pyrite on the surface of elemental sulfur can be achieved in timescales commensurate with the copper sulfide dissolution reactions via the following reaction:



The formation of nano-scale and micro-scale FeS_2 crystallites on the surface of the elemental sulfur layers provides a mechanism for maintaining electron conduction across the elemental sulfur surface. Thus, by the inventive methods discussed herein it is possible to eliminate the need for silver addition as means for increasing the surface conductivity of elemental sulfur.

The present invention provides for the rapid dissolution of chalcopyrite by subjecting a leach slurry to microwave irradiation under typical leach conditions (i.e., temperature, pH and Eh), wherein pyrite is in the thermodynamically stable iron-sulfur phase. Without being held to any specific theory, it may be reasonably expected that the exposure of the leach slurry to microwave irradiation of 2.45 GHz reduces the time for pyrite formation through the crystallization of amorphous iron sulfides. Accordingly, microwave irradiation advantageously reduces the timescale of formation from days or weeks to minutes. It will be understood by those skilled in the art, that any microwave frequency and/or field intensity which produces the best intended results is within the scope of the present invention, and only routine experimentation is necessary to determine optimum levels of irradiation for a given slurry/process.

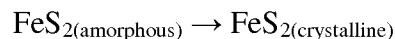
An added advantage of the present invention is the increased deportment of at least a portion of the iron and sulfur generated from chalcopyrite dissolution as FeS_2 . This catalyzed reaction thereby reduces the amount of catalytic pyrite that must be added from external sources. An additional advantage of the present invention is that the pyrite which is produced during the microwave irradiation comprises a very high surface area. This high surface area makes the pyrite a more efficient catalyst for the reduction of Fe^{3+} during chalcopyrite dissolution than catalysts taught in the prior art.

In the inventive method, the microwave irradiation is applied in such a way as to prevent excessive heating of the leach slurry and thereby prevent the generation of temperatures that would result in the melting of the S° layers surrounding the leaching chalcopyrite particles. Preferably, the power of the microwave device should be limited so as to prevent temperatures of the slurry from approaching 110 degrees C. The intensity of the incident irradiation energy

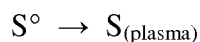
and/or the frequency of the microwaves may be varied as a function of time or applied intermittently as indicated in FIGS. 9-14. The microwaves may be pulsed at predetermined intervals, patterns, durations, or may be emitted and applied to slurry haphazardly. Other microwave frequencies which are only inefficiently absorbed by water may be used to reduce undesired heating of the mineral slurry.

Alternatively, cooling of the slurry can be provided to maintain the slurry temperature below the melting point of elemental sulfur. Pre-cooling of slurry (prior to leaching and/or microwave irradiation) may be done using one or more heat exchangers. Alternatively, cooling of slurry 115, 125, 135, 145 may be facilitated during leaching and/or microwave irradiation process through the use of internal cooling rods, fins, pipes, or other forms of heat exchangers. The aforementioned cooling devices may be positioned within, around, or adjacent to a tank 114, 124, 134, 144, or may otherwise be operatively connected to a leaching device 110, 120, 130, 140.

In some embodiments, a microwave frequency between about 1.6 and about 30 GHz (wavelengths between about 187mm and 10mm) may be utilized, wherein the intensity of the microwave is selected to be high enough to transform amorphous FeS_2 to stable crystalline phase FeS_2 , but low enough to avoid generating a sulfur plasma phase in the elemental sulfur layer which forms around the chalcopyrite particles during dissolution. In other words, any microwave frequency and intensity may be used to irradiate a copper-sulfate containing slurry alone or in combination with other microwave frequencies and intensities, so long as the following is satisfied:



wherein the following reactions do not occur:



For instance, microwaves used may incorporate intensities between 0.2 to 200 kW-s per gram of slurry, for example, between 2 and 30 kW-s per gram, so long as the above is satisfied. Higher and lower intensities are also envisaged. X-ray diffraction patterns can be used to differentiate between the amorphous FeS_2 and the crystal phases of FeS_2 . Electrical conductivity measurements show that crystalline FeS_2 has much better electrical conductivity properties than amorphous FeS_2 or elemental sulfur (S°). By converting amorphous FeS_2 to a stable crystalline phase, electron transfer between the pyrite and chalcopyrite is improved, which aids in the dissolution of chalcopyrite through the galvanic effect.

Turning back to FIG. 1, the shaded area between pH 0 and pH 3.5 which is bounded by borders A, B, and C represents conditions where FeS_2 is typically in the thermodynamically stable iron-sulfur phase and where FeS_2 formation is not inhibited by iron hydrolysis reactions. It will be understood that the boundaries may shift according to leach solution compositional effects such as reactant concentrations, product concentrations, and temperature. The shaded area between pH 2.5 and 3.5 represents regions where leaching reactions may begin to shut down and Fe^{3+} may precipitate.

FIG. 2 shows a prior method of galvanic conduction between pyrite and chalcopyrite. In this case the galvanic conduction occurs between pyrite inclusions within the chalcopyrite particles. It will be understood that not all chalcopyrite particles will contain pyrite inclusions, hence catalytic improvement is not optimal and will vary by particle size and between ore bodies in an unpredictable fashion.

FIG. 3 shows a galvanic conduction between pyrite and chalcopyrite using in-situ-formed pyrite via microwave irradiation according to some embodiments of the invention. The large-scale pyrite particles originate from the ore and the particle size distribution is comparable to the particle size distribution of the copper-containing mineral particles. Electron conduction between the copper sulfide particles and the large-scale pyrite particles is enabled when they make physical contact and there is a conductive coating on the elemental sulfur layer surrounding the chalcopyrite particles. The electron conduction within the surface conductive coating is promoted by the low electrical resistance of the pyrite nano-scale and micro-scale pyrite particles comprising the conductive surface coating.

FIG. 4 further shows galvanic interactions which occur using methods described herein. The microwave-generated pyrite crystallites form a conductive path between the chalcopyrite particle and the pyrite catalyst particles during the momentary periods wherein the pyrite catalyst particles make physically contact with the elemental sulfur layer surrounding the chalcopyrite particles. It will be understood that the microwave-generated pyrite crystallites also possess catalytic ability. The large surface area of the crystallites therefore accelerates the dissolution of the chalcopyrite particles by two separate mechanisms: a) increasing the surface electrical conduction of the S^0 surface layers surrounding the copper-containing particles, and b) and providing additional surface area for the catalyzed reduction of ferrous ion.

FIG. 5 shows a device 110 for exposing copper sulfide-containing slurry 115 to microwave irradiation 112a according to one embodiment. The device 110 shown comprises a pressurized or unpressurized tank 114 configured to hold copper sulfide-containing slurry 115 which is stirred or agitated. Agitation may be provided using an impeller 118 and a rotating drive shaft 119 or equivalent means. The impeller may also function to distribute microwave energy through the tank via reflector means provided on the impeller. For example, the impeller may comprise a polished stainless steel material or the like or otherwise provided with a reflective material to produce reflected microwaves 112b. One or more microwave devices 112 may be provided at various locations within or adjacent to the tank 114. For instance, as shown, two microwave devices 112 may be provided above air-exposed slurry 115. Each microwave device 112 provides microwaves 112a which penetrate partially into or completely through the slurry 115.

FIG. 6 shows a device 120 for exposing copper sulfide-containing slurry 125 to microwave irradiation 121a, 122a, 123a according to yet another embodiment. The device 120 shown comprises a pressurized or unpressurized tank 124 configured to hold copper sulfide-containing slurry 125 which is stirred or agitated. Agitation may be provided using an impeller 128 and a rotating drive shaft 129 or equivalent means. The impeller may also function to distribute one or more reflected microwaves 121b, 122b, 123b through the tank as previously discussed. As shown, one or more microwave devices 121, 122, 123 may be provided at various locations within or adjacent to the tank 124. For instance, as shown, a medium frequency microwave device 122 may be provided above air-exposed slurry 125, a low frequency microwave device 123 may be provided in a slip stream area 124c of the tank 124, and a high frequency microwave device 121 may be provided to a side area of the tank 124. While slip

stream area 124c may comprise a separate external tank operatively connected to the tank 124, it may alternatively form a chamber which is integral with tank 124 as shown. One or more false bottoms, interior chambers, dividing walls, or baffles 124a may define the slip stream area 124c. The dividing walls and baffles 124a may be fashioned from materials that allow them to function as wave guides, thereby directing the microwaves in a fashion to maximize their absorption in the slurry. For example, the one or more false bottoms, interior chambers, dividing walls, or baffles 124a may comprise a stainless steel reflective surface. Each microwave device 121, 122, 123 provides microwaves 121a, 122a, 123a which penetrate partially into or completely through the slurry 125. In instances where the microwave devices 121, 122, 123 are arranged at outer portions of the tank 124, one or more windows 126 of a passive/transmissive material may be utilized to form one or more portions of the tank 124. In this manner, microwaves 121a, 122a, 123a may be efficiently transmitted through the tank 124. Examples of microwave permeable materials may include, but are not limited to: microwave transmissive PTFE (polytetrafluoroethylene), glass, polyethylene, polypropylene, nylons, thermoplastic epoxies, copolymers of PTFE and polyolefins, glass-fiber reinforced polymers and plastics, nylon, hybrids and composites thereof, and other materials having very low dielectric constants and resilience to acidic compositions.

FIG. 7 shows another device 130 for exposing copper sulfide-containing slurry 135 to microwave irradiation 131a, 132a, 133a. The device 130 may be a vertically-oriented column tank 134 as shown. The tank 134 may be open air or configured for pressurization. The tank 134 may also be configured with control or manual valves (not shown) and be utilized in continuous or batch leaching systems. The tank 134 may have an inlet 137a on an upper, middle, or lower portion of the tank 134 and may have an outlet 137b on an upper, middle, or lower

portion of the tank 134. In the particular embodiment shown an upper inlet 137a is used in combination with a lower outlet 137b. In use, the slurry 135 cascades down the column and out the outlet 137b. Residence time within the tank 134 may be increased with transversely-extending baffles (not shown) to create a tortuous path for the slurry 135. Agitators or fluidized beds, though not shown, may also be incorporated with the tank 135. For example, while not shown, a bottom portion of the tank 134 may comprise an inlet 137a and a fluidized bed, and an upper portion of the tank 134 may comprise an outlet 137b, wherein the slurry flows upward around one or more lamellas, screens, or baffles. One or more microwave devices 131, 132, 133 may be provided at various locations within or adjacent to the tank 134. For instance, as shown, a low frequency microwave device 133, a medium frequency microwave device 132, and a high frequency microwave device 131 may be provided to a top portion of the tank 134 as shown, or the one or more microwave devices may be placed near upper portions of the tank 134. Alternatively, while not shown, one or more microwave devices 131, 132, 133 may be provided at various locations along the height of the tank 134. Each microwave device 131, 132, 133 provides microwaves 131a, 132a, 133a which penetrate partially into or completely through the slurry 135. The microwaves may be redistributed as reflected microwaves 131b, 132b, 133b throughout the tank 134 via one or more reflectors 139. In instances where the microwave devices 131, 132, 133 are arranged at outer portions of the tank 134 as shown in FIG. 7, one or more windows 136 of a passive/transmissive material may be utilized to form one or more portions of the tank 134. In this manner, microwaves 131a, 132a, 133a may be efficiently transmitted through the tank 134 to the slurry 135. While a single microwave permeable window 136 is shown, multiple windows 136 may be strategically located at various portions the tank 134. In a particular embodiment, the one or more reflectors may be replaced with a tank having

inner surfaces which are configured to reflect and/or guide microwaves throughout the slurry 135 contained within the tank 134.

FIG. 8 shows a device 140 for exposing copper sulfide-containing slurry 145 to microwave irradiation 141a, 142a, 143a according to further embodiments. The device 140 may be a horizontally-oriented leach tank 144 with baffles 148 as shown. The baffles 148 are used to control slurry 145 flow and function as microwave guides to direct the microwave irradiation 141a, 142a, 143a to maximize the beneficial effects derived from *in situ* pyrite formation. The baffles 148 may comprise one or more reflectors 149 or reflective surfaces thereon to guide microwaves. The tank 144 may be open air or configured for pressurization. The tank 144 may also be configured with control or manual valves (not shown) and be utilized in continuous or batch leaching systems. The tank 144 may have an inlet 147a located at one portion of the tank 144 and may have an outlet 147b on another portion of the tank 144. In the particular embodiment shown an upper inlet 147a located at a first end of the tank 144 is used in combination with a lower outlet 147b located at an end of the tank 144 opposite to said first end. In use, the slurry 145 flows horizontally through the tank 144 and out the outlet 147b. Residence time within the tank 144 may be increased with longitudinal or transversely-extending baffles to create a tortuous path for the slurry 145. Agitators or fluidized beds, though not shown, may also be incorporated with the tank 145. In one particular embodiment the agitators are capable of reflecting and dispersing reflected microwaves 141b, 142b, 143b through the slurry 145 contained within the tank 144. One or more microwave devices 141, 142, 143 may be provided at various locations within or adjacent to the tank 144. For instance, as shown, a low frequency microwave device 143, a medium frequency microwave device 142, and a high frequency microwave device 141 may be provided along lower portions of the tank 144 as shown.

Alternatively, while not shown, the one or more microwave devices 141, 142, 143 may be provided at various side or upper regions of the tank 144. The location of each microwave device 141, 142, 143 may be staggered along the length of the tank 144 such that some alternate between upper and lower portions of the tank, thereby intermittently irradiating the slurry 145 as it traverses through the tank 145. Each microwave device 141, 142, 143 provides microwaves 141a, 142a, 143a which penetrate partially into or completely through the slurry 145. In instances where the microwave devices 141, 142, 143 are arranged at outer portions of the tank 144 as shown in FIG. 8, one or more windows 146 of a passive/transmissive material may be utilized to form one or more portions of the tank 144. In this manner, microwaves 141a, 142a, 143a may be efficiently transmitted through the tank 144 to the slurry 145. One or more reflective surfaces or baffles may be provided to reflect and guide the microwaves throughout the slurry contained within the tank and its various chambers. The reflective baffles also serve to direct the flow of the slurry throughout the tank to increase the residence time of the slurry within the tank and to control the microwave absorption by the reactants leading to more efficient production of pyrite particles.

FIGS. 9-14 schematically illustrate various methods of irradiating copper-sulfide containing slurry. Microwaves may be saw tooth, triangular (FIG. 9), square, or sinusoidal (FIG. 10). Multiple in-phase microwaves with similar frequency but different intensities may be applied to a slurry as suggested in FIG. 11. Multiple out-of-phase microwaves with different intensities and or wavelengths may be applied to copper sulfide containing slurries as suggested in FIG. 12. Microwaves may be activated at specific intervals thereby intermittently irradiating a slurry as graphically suggested in FIG. 13. As shown in FIG. 14, in some embodiments, microwave signals may vary uniquely as a function of time. Patterns of changing frequency,

intensity, and duration (e.g., MORSE code-type pulsing with varying on-off times) may be utilized for different compositions within the copper sulfide containing slurry. The exact irradiation dosage may be computer controlled by applying, internally, one or more temperature, pH, or voltage sensors to the devices 110, 120, 130, 140 described. In this manner, the galvanic process may be continually monitored and adjusted according to real-time process conditions.

All references disclosed herein are specifically incorporated by reference thereto.

While preferred embodiments of this invention have been described, it should be understood that changes and modifications can be made therein in accordance with ordinary skill in the art without departing from the invention in its broader aspects as defined in the following claims.

CLAIMS

What is claimed is:

1. A method of leaching a copper-bearing sulfide mineral slurry, comprising the steps of:
 - (a) providing a slurry having copper sulfide particles therein;
 - (b) exposing the slurry to an acidic leach solution;
 - (c) chemically leaching copper from the slurry into the acidic leach solution in the presence of microwave irradiation, under conditions whereby crystalline pyrite can be formed *in-situ*, on surfaces of the copper sulfide particles;
 - (d) generating microwaves at a predetermined frequency or intensity that is configured for forming crystalline pyrite on surfaces of the copper sulfide particles *in-situ*; and
 - (d) recovering leached copper from said acidic leach solution.
2. The method of claim 1, wherein step (c) is further performed under conditions whereby elemental sulfur (which may form surface passivation layer(s) on the copper sulfide particles as a result of exposure to the acidic leach solution), is prevented from entering a plasma phase.
3. The method of claim 2, further comprising forming crystalline pyrite on surfaces of the copper sulfide particles *in-situ* and/or converting amorphous pyrite to crystalline pyrite.
4. The method of claim 1, wherein step (b) comprises mixing the acidic leach solution with the slurry in a tank.

5. A method according to claim 4, wherein the tank comprises an agitation mechanism, a fluidization mechanism, or a mechanism for changing a residence time of the slurry in the tank.
6. The method of claim 4, wherein the tank comprises at least one microwave generating device which provides said microwave irradiation.
7. The method of claim 6, wherein the tank comprises multiple microwave generating devices.
8. The method of claim 1, wherein the microwave irradiation is provided intermittently.
9. The method of claim 1, wherein the microwave irradiation changes in intensity as a function of time.
9. The method of claim 1, wherein the microwave irradiation changes in frequency as a function of time.
10. The method of claim 1, wherein step (b) and/or step (c) is performed above atmospheric pressure.
11. The method of claim 1, further comprising adding catalytic pyrite to the slurry and acidic leach solution to instigate galvanic reactions.
12. The method of claim 1, wherein said copper sulfide particles comprises at least one of chalcopyrite (CuFeS_2), chalcocite (Cu_2S), bornite (Cu_5FeS_4), covellite (CuS), digenite (Cu_2S), enargite (Cu_3AsS_4), tennantite ($\text{Cu}_{12}\text{As}_4\text{S}_{13}$), or tetrahedrite ($\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$).

13. The method of claim 1, wherein the crystalline pyrite formed on the surfaces of the copper sulfide particles comprises micro- or nano-scale particles.

14. The method of claim 1, wherein the crystalline pyrite formed on the surfaces of the copper sulfide particles *in-situ*, is capable of catalyzing a reduction of Fe^{3+} (Ferrous iron) to Fe^{2+} (Ferric iron).

15. The method of claim 1, further comprising providing microwaves which have been optimized through the process of measuring microwave absorption for $\text{FeS}_{2(\text{Amorphous})}$ to maximize the conversion efficiency to $\text{FeS}_{2(\text{Crystalline})}$.

16. The method of claim 1, further comprising tuning one of a frequency or an intensity of said generated microwaves during leaching to maintain optimized formation of crystalline pyrite on surfaces of the copper sulfide particles *in-situ* and/or to maintain optimized copper leaching kinetics.

17. A device for leaching a copper bearing sulfide mineral slurry, comprising:

(a) a tank for providing a slurry having copper sulfide particles therein; and,

(b) at least one microwave generating device configured to irradiate the slurry during leaching; wherein the at least one microwave generating device is capable of producing microwaves at a predetermined frequency and intensity which are configured to facilitate *in-situ* crystalline pyrite formation on surfaces of the copper sulfide particles in the slurry.

18. The device of claim 17, wherein the at least one microwave generating device is further configured to produce microwaves which are configured to prevent elemental sulfur (which

may form surface passivation layer(s) on the copper sulfide particles), from entering a plasma phase.

19. The device of claim 17, wherein the tank is configured to withstand a mixture of acidic leach solution with the slurry in a tank.

20. The device of claim 17, wherein the tank comprises a window comprising a microwave-permeable material.

21. The device of claim 17, wherein the tank comprises an agitation mechanism, a fluidization mechanism, or a mechanism for changing residence time of the slurry in the tank.

22. The device of claim 21, wherein the agitation mechanism comprises an impeller, the fluidization mechanism comprises a fluidized bed, and the mechanism for changing residence time comprises a false bottom, interior chamber, dividing wall, baffle, lamella, screen, slip stream area, or tortuous path.

23. The device of claim 17, wherein the at least one microwave generating device is configured to irradiate slurry in the tank intermittently.

24. The device of claim 17, wherein at least one microwave generating device is configured to irradiate slurry in the tank with different frequencies.

25. The device of claim 17, wherein the at least one microwave generating device is configured to irradiate slurry in the tank at various intensities.

26. The device of claim 17, wherein the at least one microwave generating device comprises a plurality of microwave generating devices.

27. The device of claim 26, wherein a plurality of microwave generating devices are configured to emit different microwave signals in any one of intensity, frequency, or continuity.

28. The device of claim 17, wherein the tank comprises a cooling system to cool the slurry prior to or during leaching, particularly during microwave irradiation.

29. The device of claim 28 wherein said cooling system comprises a heat exchanger, a cooling fin, a cooling pipe, or a cooling rod protruding into the tank.

30. The device of claim 17, wherein the device comprises at least one reflector within the tank, which may be provided on a wall, a baffle, or an impellor.

31. The device of claim 17, wherein said at least one microwave generating device further comprises means for adjusting a frequency or intensity of said generated microwaves during leaching to maintain optimized formation of crystalline pyrite on surfaces of the copper sulfide particles *in-situ* and/or optimized copper leaching.

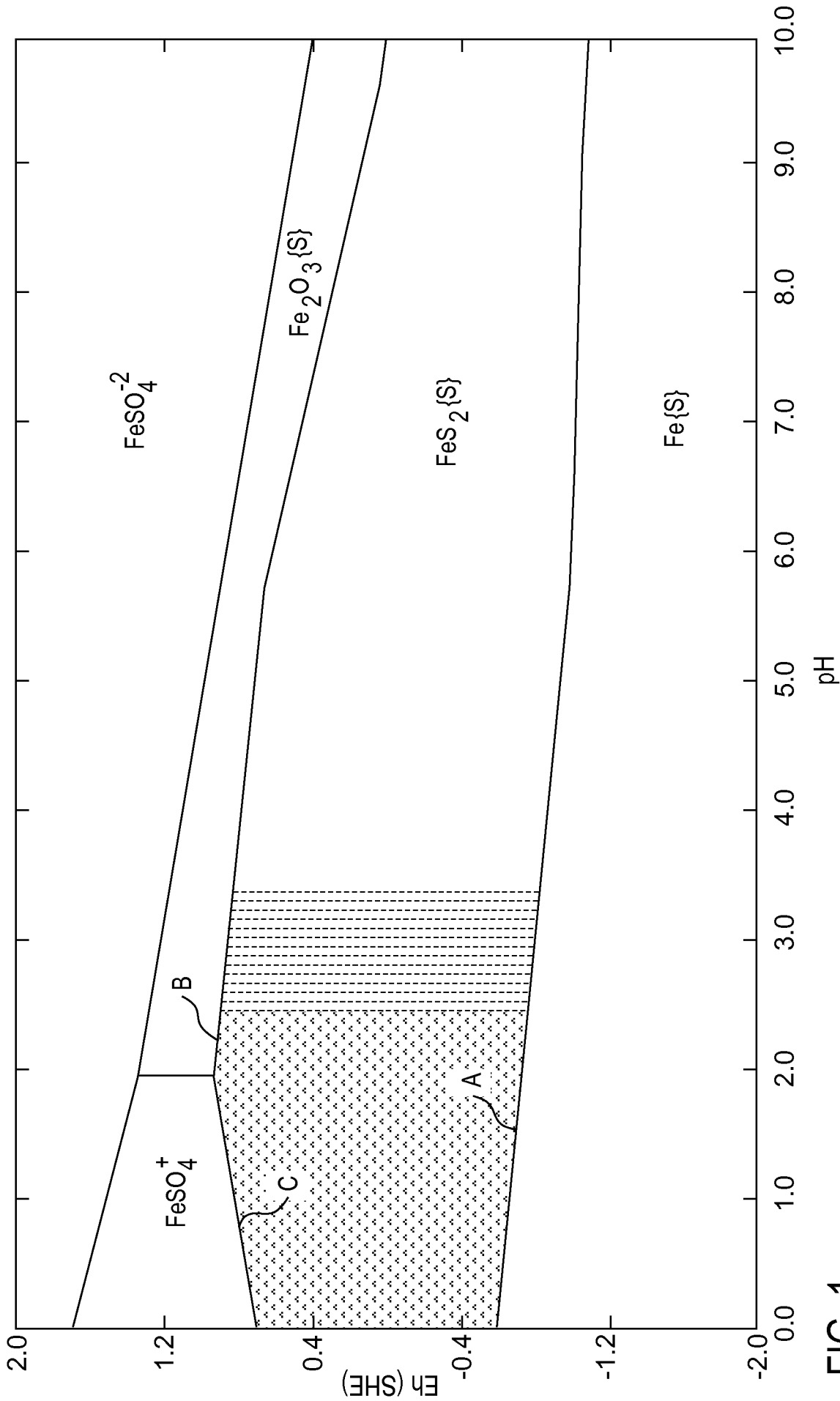


FIG. 1

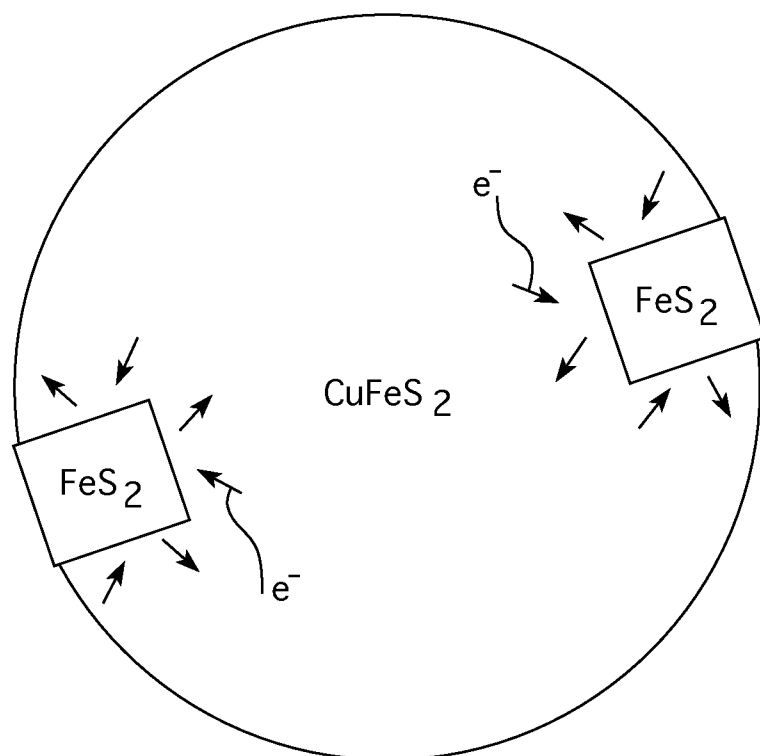


FIG. 2 (PRIOR ART)

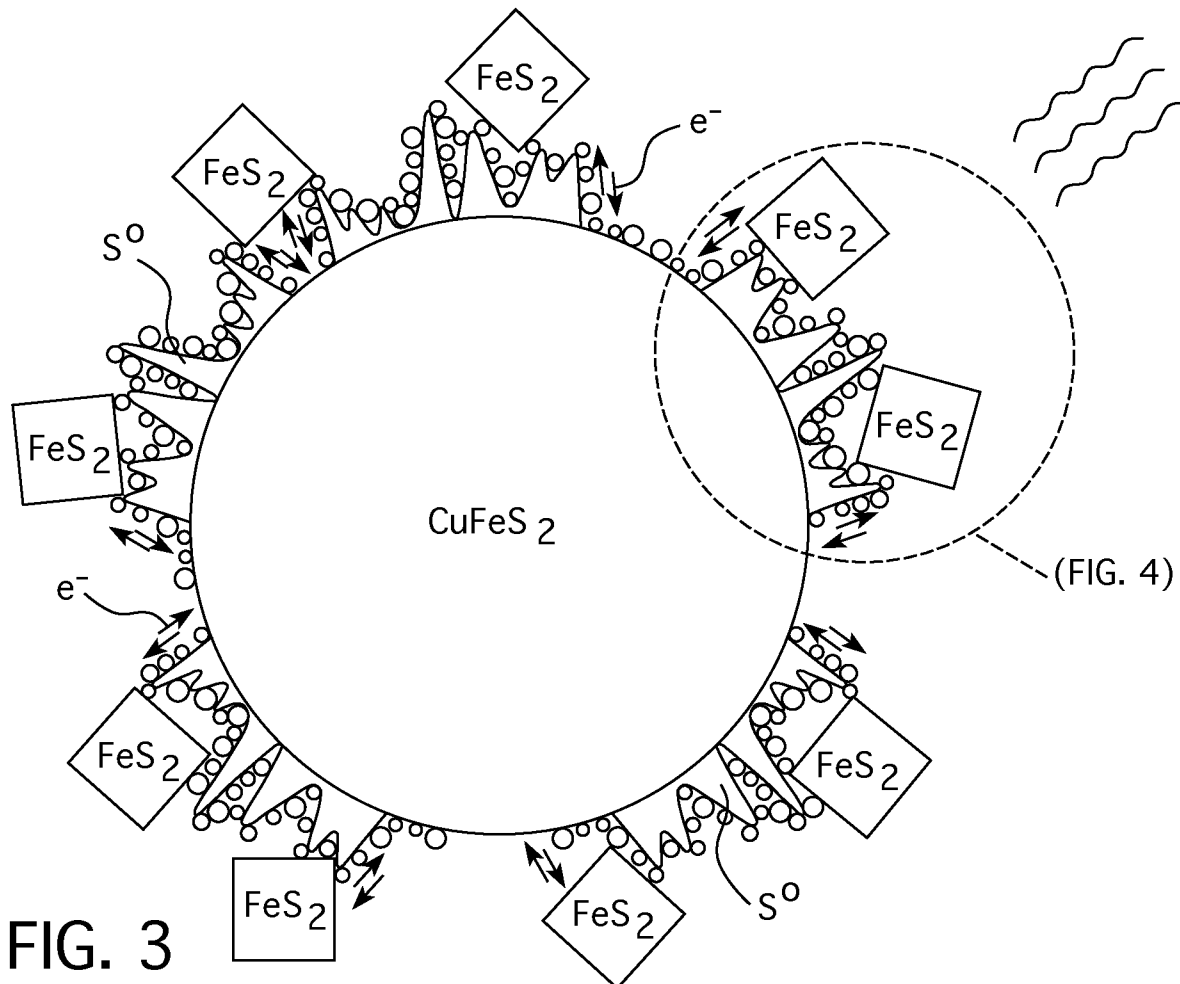


FIG. 3

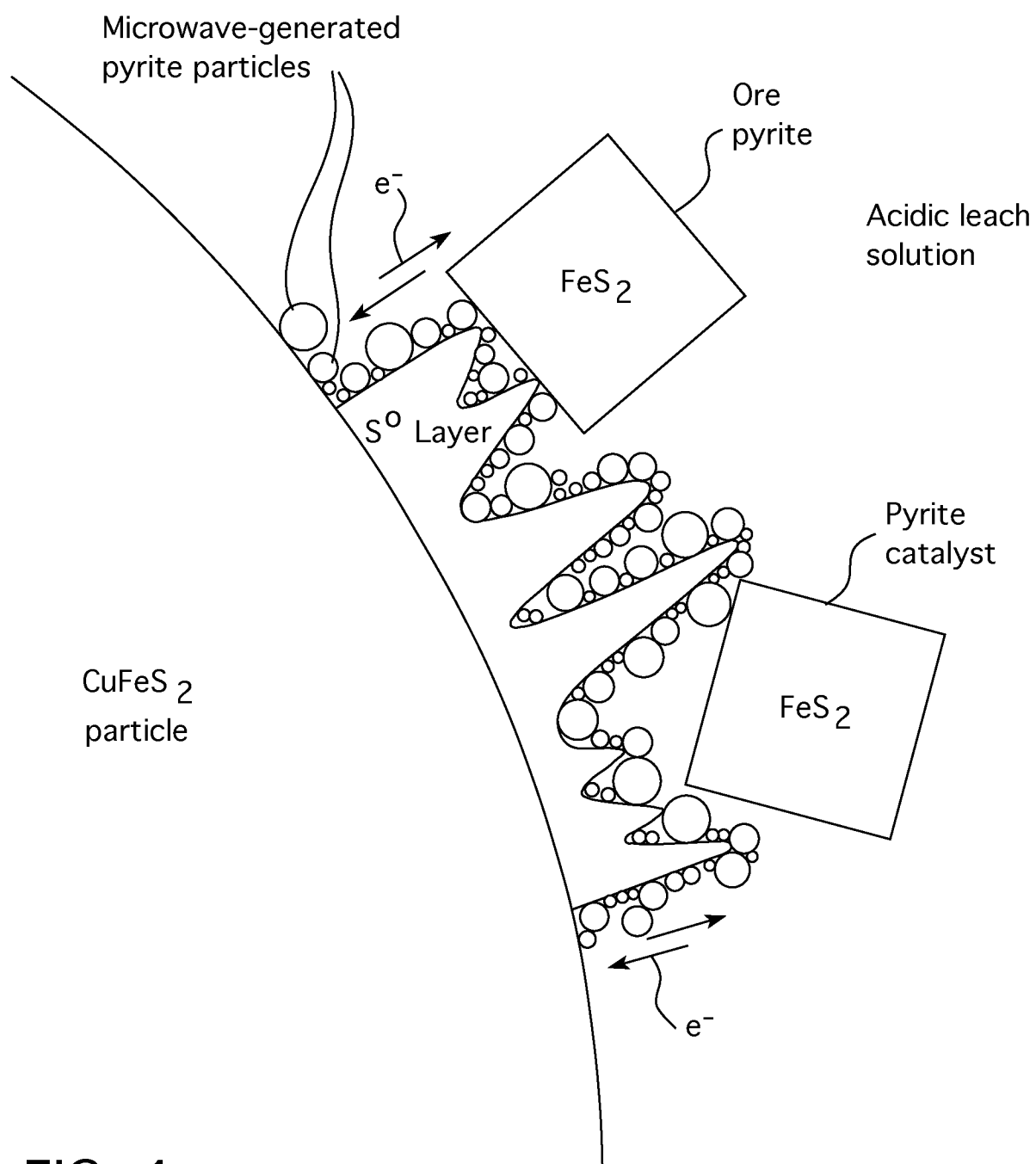


FIG. 4

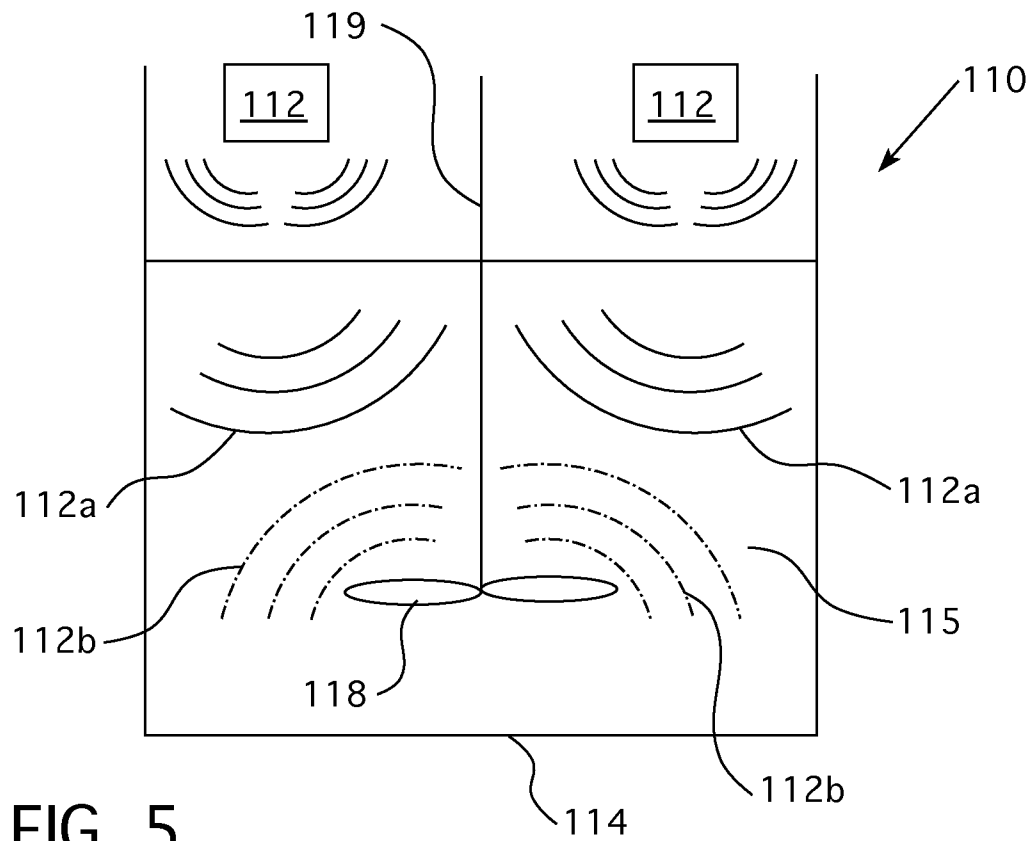


FIG. 5

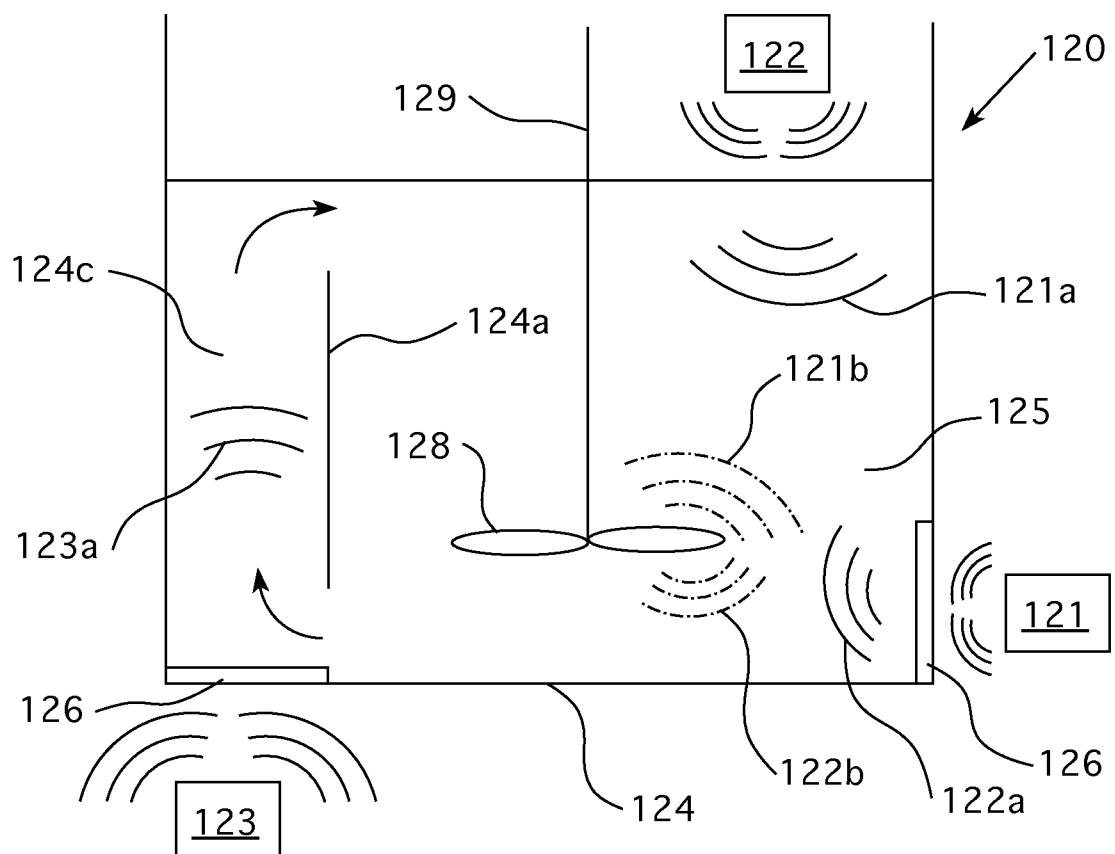


FIG. 6

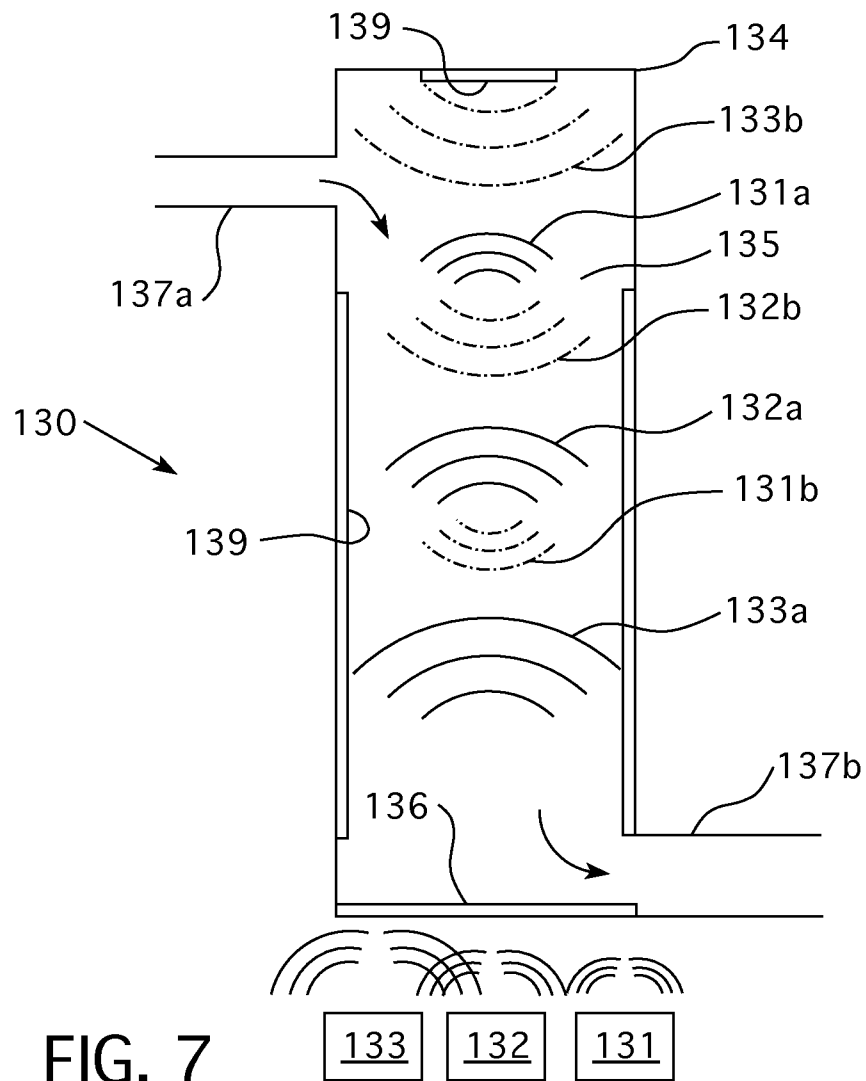


FIG. 7

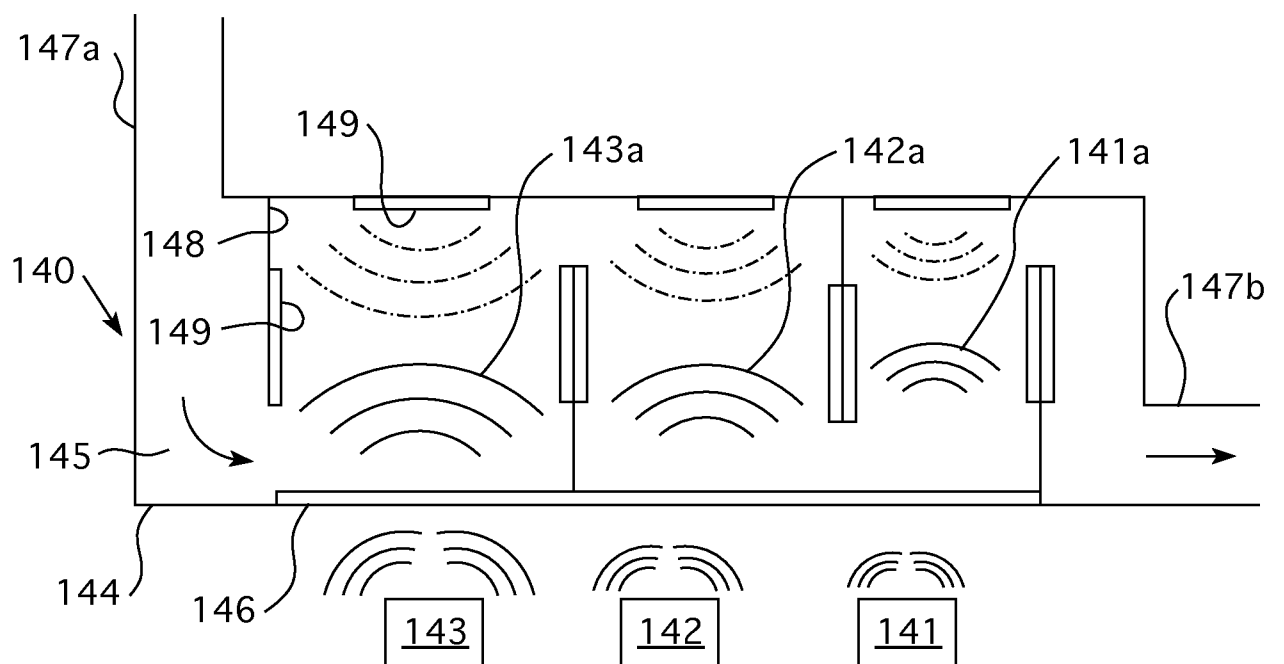


FIG. 8

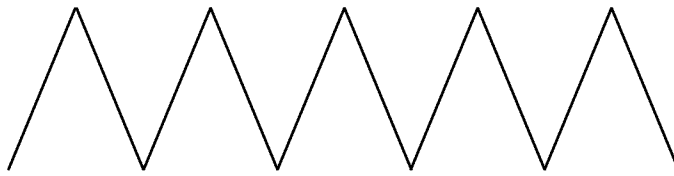


FIG. 9

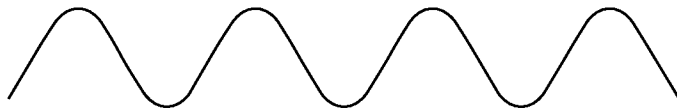


FIG. 10

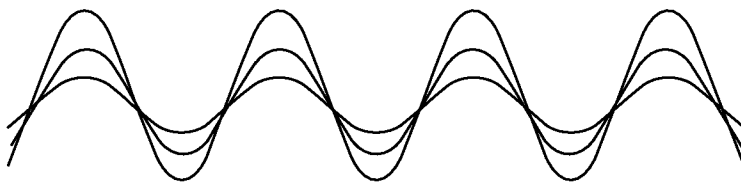


FIG. 11

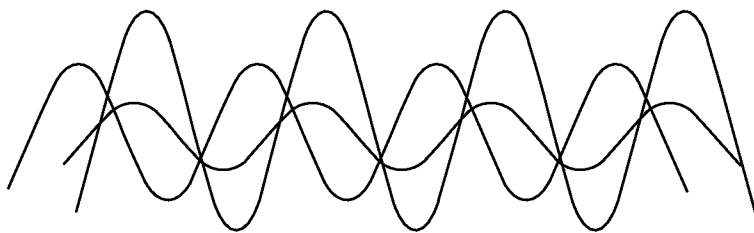


FIG. 12

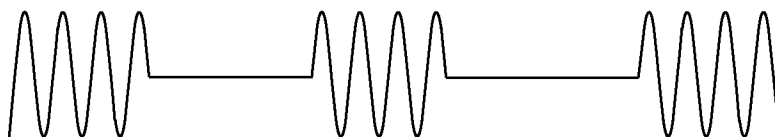


FIG. 13

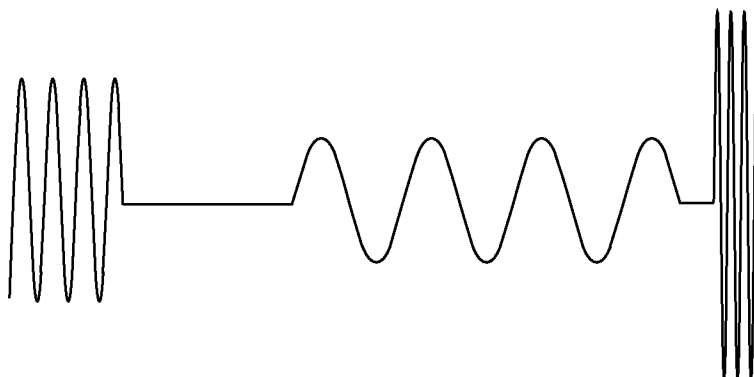


FIG. 14

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 13/69433

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C22B 3/08, 15/00, 3/04; C25C 1/12 (2014.01)

USPC - 75/373, 753, 411; 205/568

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

USPC -- 75/373, 753, 411; 205/568

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PubWEST (USPT,PGPB,JPAB,EPAB); Google

Search Terms: Leaching copper microwave crystalline pyrite acid copper sulfide chalcopryite chalcocite bornite in situ energy radiation waves frequency intensity surface particles nanoparticles nanocrystals extraction recovery metal slurry ore

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 7,846,233 B2 (Dixon et al.) 07 Dec 2010 (07.12.2010), entire document especially Abstract, col 4, ln 23-45, claim 34	1-31
A	WO 2012/000090 A1 (Dixon et al.) 05 Jan 2012 (05.01.2012), entire document especially Abstract, claim 1	1-31
A	US 7,850,759 B2 (Roy et al.) 14 Dec 2010 (14.12.2010), entire document especially abstract, claim 1	1-31
A	US 2012/0043314 A1 (Liubakka et al.) 23 Feb 2012 (23.02.2012), entire document	1-31
A	WO 2012/098783 A1 (Manabe) 26 July 2012 (26.01.2012), entire document	1-31
A	US 7,678,172 B2 (Batterham et al.) 16 Mar 2010 (16.03.2010), entire document	1-31
A	US 2012/0103827 A1 (Ruonala et al.) 03 May 2012 (03.05.2012), entire document	1-31

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

24 February 2014 (24.02.2014)

Date of mailing of the international search report

17 MAR 2014

Name and mailing address of the ISA/US

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P.O. Box 1450, Alexandria, Virginia 22313-1450

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