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- (71) Applicant: ALBEMARLE CORPORATION [US/US];
451 Florida Street, Baton Rouge, LA 70801-1765 (US).
- (72) Inventors: MANIMARAN, Thanikavelu; 15011 Copping
Drive, Baton Rouge, LA 70810 (US). O'DAY, Joseph;
9048 Fox Gate Drive, Baton Rouge, LA 70809 (US).
- (74) Agent: HOEFLING, Marcy M.; ALBEMARLE COR-
PORATION, Law Department, 451 Florida Street, Baton
Rouge, LA 70801-1765 (US).

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[Continued on next page]

(54) Title: PROCESS FOR DISSOLVING OR EXTRACTING AT LEAST ONE PRECIOUS METAL FROM A SOURCE MATERIAL CONTAINING THE SAME

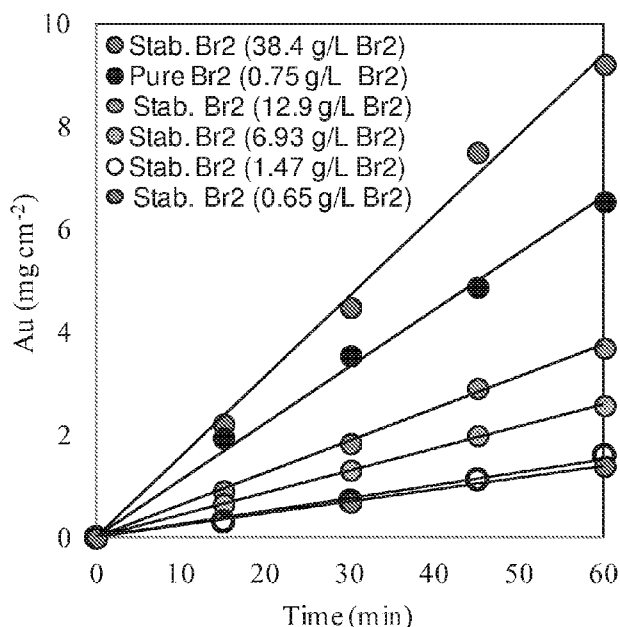


Figure 1 – Rates of Gold Dissolution at Various Bromine Concentrations

(57) Abstract: New and useful processes are provided for leaching precious metal from sources composed of or containing such metals. The leaching agents used are aqueous solutions of solvated alkali metal, alkaline earth metal, ammonium, and/or N-halosulfamate(s), and one or more alkali metal halides or alkaline earth metal halides, or ammonium halides. Compositions comprised of such aqueous solutions containing at least one precious metal in the form of a solute are also provided.



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PROCESS FOR DISSOLVING OR EXTRACTING AT LEAST ONE PRECIOUS METAL FROM A SOURCE MATERIAL CONTAINING THE SAME

TECHNICAL FIELD

[0001] This invention relates to hydrometallurgical processing involving extraction of at least one precious metal in a dissolved form from a source material containing such metal(s). At least one base metal may also be extracted from such source material.

BACKGROUND

[0002] Natural ores and mineral deposits have long been and continue to be an important source material for precious and base metals. Also, because of the rapid growth of the electronics industry, electronic wastes and scrap materials have become an ever-growing source for recovery and reuse of precious and base metals. Accordingly, attention has been focused over the years on ways of recovering precious metals, initially from ores and minerals and more recently from electronics waste and scrap materials as well as other waste or recycled products containing one or more precious metals.

[0003] Despite these continuing efforts some traditionally-used processes of different types remain in use even today. For example, gold is generally extracted from the ores by leaching with an alkaline cyanide solution. The major impetus to seek alternate lixiviants to cyanide arises from the environmental hazards posed by cyanide's toxicity. Care must be exercised to maintain cyanide solutions on the alkaline side in order to prevent the release of hydrogen cyanide gas. Also, leaching rates with alkaline cyanide solutions tend to be quite slow. For example, it has been reported that contact times in the range of ten to fifteen hours are common in extracting gold from ores using alkaline cyanide solutions.

[0004] A significant amount of literature has examined alternative extraction processes to cyanide for recovering gold as well as other precious metals from different ores. The alternate leaching agents include thiosulfate, thiourea, thiocyanate and halogens. Reagent decomposition and sulfur precipitation reduce the efficiency of the thio- reagents. Corrosivity and vapor loss have limited the use of elemental halogens, notably, Cl_2 and Br_2 . Use of DBDMH (1,3-dibromo-5,5-dimethylhydantoin) alleviated problems associated with vapor loss; however its low solubility in water (0.1 wt%) necessitated the need for larger quantities of aqueous solutions of the reagent, which makes controlling reagent dosage difficult.

[0005] In shipping and handling aqueous bromine compositions for various uses, especially for use in recovery of precious metals from ores at remote mining sites, the susceptibility of these compositions to freezing creates difficulties. Certain bromine compositions lack stability if subjected to a freeze/thaw cycle, and the susceptibility to freezing may also complicate packaging and shipping. Moreover, many known compositions have rather high freezing points, so that freezing can be a problem even at relatively moderate temperatures. In the case of DBDMH, low water solubility poses potential problems associated with precipitation or crystal formation in, or freezing of, aqueous systems containing DBDMH when used in cold climates.

[0006] In addition to ores and minerals, there are many suitable sources of precious and other metals that offer the opportunity for economical recovery. In fact, many such sources are richer than ores with respect to metal content for recovery. Gold is available from numerous scrap sources, including wastes from industrial uses, gold plated electronic circuit boards, and as an alloy with copper, zinc, silver, or tin in the karat gold used in jewelry. Platinum, palladium and other precious metals such as rhodium, osmium, and iridium are available from spent catalysts, as well as other industrial and/or jewelry scrap sources. However, as the prior art has shown, many efforts while workable, do not satisfy the requirements of less hazard, better economics, greater practicality, fewer material handling problems, reduced environmental concerns, and/or the like.

[0007] There is a need for improved hydrometallurgical processes for dissolving, leaching, and/or extracting precious and desirable base metals as well from a number of sources, thereby enabling recovery or isolation of such metals.

[0008] Further, it would be desirable to provide new leaching solutions from which precious leached metal(s) in suitable dissolved forms can be effectively and economically recovered. It would also be of advantage if a process could be found that is effective for the recovery of commercially useful base metals often associated with precious metals present in such source materials.

[0009] A novel method for recovery of precious and other metals by electrowinning, and the provision of novel electrolytic solutions useful in such electrowinning processes are also within the purview of this invention.

[0010] Still another objective of this invention is to provide a new way of regenerating used leachant solutions, i.e., solutions which have already been used to remove or extract one or more metals, preferably at least one precious metal, from its source material.

NON-LIMITING SUMMARY OF THE INVENTION

[0011] This invention is effective for recovery of precious metals such as gold, palladium, silver, rhodium, or the like in water soluble form from which these precious metals can be conveniently recovered in economically satisfying yields. If appropriate sources containing mixtures of these precious metals exist or become available, the present process technology is deemed capable of recovering such metals, while at the same time providing aqueous solutions or slurries from which other precious metals (*e.g.*, platinum, osmium, iridium or the like) and/or base metals may be recovered by this or other suitable processing. Accordingly, this invention provides the opportunity of effectively fulfilling the above referred to need for improved hydrometallurgical processes for dissolving, leaching, and/or extracting precious metals and desirably base metals as well from a number of suitable sources thereby enabling recovery and isolation of such metals. Additionally, this invention makes possible the utilization of various commercially-available products that are already being produced by a number of industrial concerns for uses unrelated to usage pursuant to this invention. In most cases, only one or two simple low-cost steps readily convert and adapt such products for effective use in the practice of this invention. Thus in such cases, only relatively inexpensive equipment can be used to effect such conversion and adaptation for effective usage.

[0012] Also, this invention provides effective ways of achieving the above advantages of providing new leaching solutions from which precious leached metal(s) in suitable dissolved forms can be effectively and economically recovered.

[0013] This invention provides the opportunity to accomplish still another desirable result referred to above, again in an efficient and a cost-effective manner. In this case, the desirable result is the possibility of providing ways of also recovering commercially useful base metals associated with the precious metals.

[0014] Provided by this invention is a process for extracting at least gold or palladium from a source material containing at least one said metal, the process comprising contacting said source material with an aqueous leaching solution comprising (A) water, (B) at least one solvated N-halosulfamate source, and (C) at least one solvated alkali metal halide and/or at least one solvated alkaline earth metal halide, and/or at least one solvated ammonium halide. In other words (C) is one of the following:

- 1) at least one solvated alkali metal halide;
- 2) at least one solvated ammonium halide;

- 3) at least one solvated alkaline earth metal halide;
- 4) at least one solvated alkali metal halide and at least one solvated ammonium halide;
- 5) at least one solvated alkali metal halide and at least one solvated alkaline earth metal halide;
- 6) at least one solvated ammonium halide and at least one solvated alkaline earth metal halide;
- 7) at least one solvated alkali metal halide, at least one solvated ammonium halide and at least one solvated alkaline earth metal halide.

[0015] During the above processes at least one precious metal is extracted into a dissolved form of at least one of said precious metals. It is also possible for at least one base metal to be extracted.

[0016] Individual or combinations of one or more alkali metal sulfamates, ammonium sulfamates, alkaline earth metal sulfamates and/or sulfamic acid in the solid state can be used as the source of the solvated N-halosulfamate in forming the aqueous leaching solutions of this invention. Preferred alkali metal sulfamates include sodium sulfamate; preferred combinations of alkali metal sulfamates include sodium sulfamate and potassium sulfamate. Typically, the alkali metal sulfamates are in solvated form.

[0017] Also provided by this invention is a composition comprising at least one precious metal in the form of a solute in an aqueous medium comprising at least one solvated N-halosulfamate source, and any one of the foregoing seven compositions of (C).

[0018] Also provided by this invention are a number of additional processes, including the following:

[0019] A process for producing an aqueous dissolving, leaching, or extracting solution containing at least one precious metal, the process comprising contacting a source of such precious metal with an aqueous leaching solution comprising (i) water, (ii) at least one solvated N-halosulfamate source, and (iii) at least one solvated alkali metal halide and/or at least one solvated alkaline earth metal halide and/or at least one solvated ammonium halide, whereby during the process at least one of said precious metals is extracted into a dissolved form of that precious metal. Preferably, (ii) is either at least one solvated N-bromosulfamate source, or at least one solvated N-bromosulfamate source and at least one solvated N-chlorosulfamate source. However, the N-halosulfamate source can be at least one solvated N-chlorosulfamate source or at least one solvated N-chlorosulfamate source

in combination with at least one solvated N-iodosulfamate source or at least one solvated N-fluorosulfamate source. Alternatively, (ii) can be or include at least one solvated N-iodosulfamate source or at least one solvated N-fluorosulfamate source. Other combinations can be at least one solvated N-bromosulfamate source and at least one solvated N-iodosulfamate source; at least one solvated N-bromosulfamate and at least one solvated N-fluorosulfamate; or at least one solvated N-iodosulfamate source and at least one solvated N-fluorosulfamate. Still further combinations can be at least one solvated N-bromosulfamate, at least one solvated N-chlorosulfamate, and at least one solvated N-iodosulfamate; at least one solvated N-bromosulfamate, at least one solvated N-chlorosulfamate, and at least one solvated N-fluorosulfamate; at least one solvated N-bromosulfamate, at least one solvated N-iodosulfamate, and at least one solvated N-fluorosulfamate; at least one solvated N-chlorosulfamate, at least one solvated N-iodosulfamate, and at least one solvated N-fluorosulfamate. Still further the combination can be at least one solvated N-bromosulfamate, at least one solvated N-chlorosulfamate, at least one solvated N-iodosulfamate, and at least one solvated N-fluorosulfamate.

[0020] The halogen atoms of (i) the halosulfamate source and of (ii) the alkali metal halides and/or (iii) the alkaline earth metal halides and/or (iv) the ammonium halides in the above processes and in the above compositions are preferably chlorine, bromine and/or iodine atoms, with bromine atoms alone or in combination with chlorine atoms being more preferred. It is possible for fluorine atoms to be present. When iodine and/or fluorine atoms are present, it is preferred that atoms of at least one other halogen are also present and that the total number of fluorine atoms is less than the total number of the other halogen atoms.

[0021] Preferred alkali metal halides and/or alkaline earth metal halides and/or ammonium halides, which are typically in solvated form, include

alkali metal bromides and/or ammonium bromides and/or alkaline earth metal bromides, and/or combinations of any two or all three of these;

alkali metal chlorides and/or ammonium chlorides and/or alkaline earth metal chlorides, and/or combinations of any two or all three of these; and

combinations comprising (a) at least one bromide selected from alkali metal bromides and/or ammonium bromides and/or alkaline earth metal bromides, and/or combinations of any two or all three of these, and (b) at least one chloride selected

from alkali metal chlorides and/or ammonium chlorides and/or alkaline earth metal chlorides, and/or combinations of any two or all three of these.

[0022] In some embodiments, the N-halosulfamate in the aqueous leaching solution comprises N-bromosulfamate, and the alkali metal halides and/or alkaline earth metal halides and/or ammonium halides comprise alkali metal bromides and/or ammonium bromides and/or alkaline earth metal bromides, and/or combinations of any two or all three of these, and the aqueous leaching solution is a bromine-containing solution that is chlorine-free, iodine-free, and fluorine-free, and also chloride-free, iodide-free, and fluoride-free.

[0023] In other embodiments, the N-halosulfamate in the aqueous leaching solution comprises N-bromosulfamate, and the alkali metal halides and/or alkaline earth metal halides and/or ammonium halides comprise combinations comprising (a) at least one bromide selected from alkali metal bromides and/or ammonium bromides and/or alkaline earth metal bromides, and/or combinations of any two or all three of these, and (b) at least one chloride selected from alkali metal chlorides and/or ammonium chlorides and/or alkaline earth metal chlorides, and/or combinations of any two or all three of these, and the aqueous leaching solution is a bromine- and chlorine-containing solution that is fluorine-free and iodine-free and also fluoride-free and iodide-free.

[0024] As used herein including the claims, the terms “dissolve”, “dissolving”, “dissolved”, *etc.*, “leach”, “leaching”, “leachant”, *etc.*, and “extract” (as a verb), “extracting”, “extract” (as a noun), *etc.*, are used interchangeably. It matters not whether the extracting or leaching solution is quiescent, under agitation, or passing over and/or through the precious metal-containing source material being treated. Naturally, at least a portion of the precious metal in the precious metal-containing source material should be capable of being contacted by the leaching (extracting) solution. In other words, at least a portion of the precious metal should be susceptible to leaching (extracting) by contact with the leaching (extracting) solution being used. When necessary, pretreatment such as grinding, milling or other forms of mechanical subdividing of the precious metal-containing source may be used to expose surfaces of precious metal in its source material for contact by the leaching (extracting) solution to be used. Alternatively, pretreatment with acids or the like may be used to achieve this same objective. Still other methods of rendering the precious metal in its own source material accessible to leaching (extraction) through contact by the leaching (extracting) solution are known and can be used if

necessary or desirable. In short, at least one precious metal in its source material used should be leachable (extractable).

[0025] Another way of achieving good leaching (extraction) of precious metal from its source material is to select a precious metal source material from which suitable amounts of precious metal can be leached (extracted) without any pretreatment to make this possible. It should of course be understood that this discussion about leaching (extraction) of precious metal, does not signify that the precious metal is to be leached (extracted) in solution as a free metal. This may possibly occur in some cases, but in other cases the precious metal leachant (extract) can be in the form of a complex or other chemical entity that is not simply pure dissolved precious metal in ionic form. The end result is in effect the same because, in either case, the precious metal in some kind of dissolved form is removed from the rest of the source material.

[0026] This invention involves two different types of leaching solutions. One is the dilute leaching solution used at the site of the precious metal recovery operation. The other is a concentrated solution such as are available commercially for uses other than that of the present invention or which may be produced on site of the precious metal recovery or may be produced elsewhere and in any such case, stored for usage as needed. There are a number of types of dilute aqueous solutions that may be formed and used pursuant to this invention that comprise at least one solvated N-halosulfamate and at least one solvated alkali metal halide, and/or at least one solvated ammonium halide, and/or at least one alkaline earth metal halide, where the halogen atoms are preferably Cl and/or Br and/or I, but may be or include F atoms. In all cases involving ions from one or more alkali metal halides, the atomic ratio of halogen from sulfamate(s) to total halide ions from alkali metal halide(s) and/or ammonium halide(s) and/or alkaline earth metal halide(s) is typically in the range of about 1:1 to about 1:20, and preferably in the range of about 1:1 to about 1:3. In all cases involving ions from one or more alkali metal halides, one or more ammonium halides and one or more alkaline earth metal halides, the atomic ratio of halide ions from sulfamate(s) to total halide ions from alkali metal halide(s), one or more ammonium halides and alkaline earth metal halide(s) is typically in the same ratios as given above. This is accomplished by suitably proportioning the total number of active halogen atoms from the halosulfamates to the total number of halide atoms from the alkali metal halide(s), ammonium halide(s) and the alkaline earth metal halides(s).

[0027] In the case of the concentrated solutions, the halogen atom ratios will be in the same ranges as given above for the dilute solutions.

[0028] The amount of N-halosulfamate in the concentrated and dilute solutions will vary depending upon a number of factors. In the case of the dilute solutions used in the leaching (extracting) operations, the active halogen concentration of dissolved N-halosulfamate can vary from as little as 0.5 grams/liter of water up to 100 grams per liter or even more depending upon the precious metal content of the precious metal source being used, the temperature of the solutions, the character of the precious metal source material, the particular leaching solution of this invention being used, the pretreatment if any and physical condition of the precious metal source being used, the amount of leaching solution being used, and the like. In any case where such factors have not been established, a few simple small scale trial experiments with different specified concentrations of the N-halosulfamate leaching solution of this invention should enable determination of desirable concentrations for use in a larger scale operation.

[0029] In the case of the more concentrated solutions, any suitable concentration can be used taking into consideration shipping costs, if any, are involved, storage space available for use, quantities of precious metal source material to be processed and projected rates of precious metal source material usage are among factors of interest.

[0030] In short therefore, solution concentrations are not critical but rather are readily developed from the information and Examples presented herein and application of common sense.

[0031] Leaching solutions of this invention to be used for recovery of precious metals from low grade ores should contain at least about 0.05 wt% preferably at least about 0.1 wt% of the leaching agent. Preferably the amount sufficient to leach gold from a leachable gold source and the amount required for leaching palladium from a leachable palladium source will be in about the same range of about 0.05 wt% to about 10 wt% of active bromine and more preferably in the range of about 0.05 wt% to about 5 wt%. Where the leaching solution is to be used for recovery of metal from such relatively high grade sources as jewelry scraps, karat gold, waste colloidal gold suspensions, and spent platinum metal catalysts, a stronger leaching solution is preferably used, for example, one containing between about 2 pounds and about 10 pounds of leaching agent per ton of solution or between about 1 and about 10 grams per liter. For purposes of this disclosure, a high grade source is one in which the metal to be recovered is present in a weight

proportion of greater than 1%, and the metal to be extracted is accessible to the leaching solution without the necessity of chemically degrading non-metallic contaminants.

[0032] Under the same operating conditions, the rate at which gold is dissolved in an extracting or leaching solution of this invention tends to be faster than the rate at which palladium dissolves in such solution. Therefore when extracting both gold and palladium from one or more suitable source materials, it is desirable to take into consideration the apparent slower rate of dissolution of palladium as compared to that of gold by providing sufficient time for a high quantity of palladium to go into solution. However, other factors should also be taken into consideration in this connection. For example, the total respective exposed areas of the respective precious metals in the source material(s) being employed is also of importance. In general, the greater the total surface area of the precious metal exposed to the extracting or leaching solution, the greater will be the amount of dissolution of that precious metal.

[0033] In systems containing both solvated bromine-containing and solvated chlorine-containing components, the bromine:chlorine atom ratio is preferably at least about 1:1. When the aqueous leaching solution contains in the range of about 0.01% to about 20% and preferably in the range of about 0.1% to about 5% by weight equivalent molecular bromine, the solution also contains in the range of about 0.01% to about 20% and preferably in the range of about 0.1% to about 5% by weight bromide ion, and in the range of about 0.01% to about 30% preferably in the range of about 0.1% to about 10% by weight total halide ion.

[0034] Another aspect of this invention is a process for extracting at least one precious metal, and/or a base metal from a source material containing said metal, the process comprising contacting said source material with an aqueous leaching solution containing a leaching agent comprising a solvated alkali metal halosulfamate, thereby producing an aqueous leachate-containing said metal in dissolved form. In this aspect, the alkali metal is preferably lithium, sodium, and/or potassium. Of these, sodium and/or potassium are more preferred. The halogen atoms of the alkali metal halosulfamate is preferably bromine, but chlorine, iodine, and/or fluorine may be the halogen atom. Thus, the following individual alkali metal halosulfamates, which are typically in solvated form, can be used:

sodium bromosulfamate, potassium bromosulfamate, lithium bromosulfamate;
sodium chlorosulfamate, potassium chlorosulfamate, lithium chlorosulfamate;

sodium iodosulfamate, potassium iodosulfamate, lithium iodosulfamate;
sodium fluorosulfamate, potassium fluorosulfamate, lithium fluorosulfamate.

Mixtures of any two or more of the foregoing 12 alkali metal halosulfamates can be used, as well. A preferred alkali metal halosulfamate is sodium bromosulfamate. A preferred mixture of alkali metal halosulfamates is a mixture of sodium bromosulfamate and sodium chlorosulfamate.

[0035] Further contemplated by the invention is a process for recovery of at least one precious metal, or a base metal in metallic form, the process comprising direct current electrolysis of an electrowinning solution containing at least one N-halosulfamate compound and anions comprising a metal complexed with halogens derived from the reaction of the N-halosulfamate compound with the metal whereby during the process the precious metal or base metal in metallic form is produced and electrodeposited. Deposition of a base metal separates it from the precious metal and thus provides a more concentrated form of the precious metal as well as the recoverable base metal.

[0036] Also included in the invention is a process for electrodeposition of a precious metal, or a base metal. The process comprises direct current electrolysis of an electrolytic solution containing (i) a dissolved N-halosulfamate source and anions comprising the metal complexed with halogens, especially bromine or bromine and chlorine atoms, whereby during the process the precious metal or the base metal are electrodeposited.

[0037] It will be appreciated that it is possible to prepare aqueous solvated solutions of N-halosulfamate by mixing with water (a) sulfamic acid and/or (b) one or more alkali metal halide salts, and/or one or more ammonium halide salts and/or one or more alkaline earth metal salts of sulfamic acid. The alkali metal halide, and/or alkaline earth metal halide and/or ammonium halide can be added before or after the addition of the sulfamic acid or salts thereof referred to in (a) or (b) above. Also, they may be added concurrently.

[0038] Also included in the invention is a process by which the N-halosulfamate can be pre-formed or generated *in-situ* by chemical or electrolytic oxidation of halides in presence of sulfamate. The source of sulfamate could be from used lixiviant or a used aqueous leaching solution so that an active lixiviant or an active aqueous leaching solution is regenerated. Some of the chemical oxidants for bromide oxidation include potassium peroxymonosulfate (Oxone[®]), sodium hypochlorite (bleach), chlorine, and trichloroisocyanuric acid (Trichlor).

[0039] Other embodiments, features, variants, and advantages will become apparent from the ensuing description and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0040] Figures 1-21 are graphs of, or relate to, experimental data, a more specific explanation or description of which accompanies or is provided with each Figure.

FURTHER DETAILED DESCRIPTION OF THE INVENTION

[0041] In its preferred embodiments this invention utilizes aqueous solutions comprising aqueous solutions of solvated N-bromosulfamates or aqueous solutions of combinations of solvated N-bromosulfamates and solvated N-chlorosulfamates and/or aqueous solutions of solvated N-iodosulfamates alone or in combination with either or both of solvated N-bromosulfamates alone or solvated N-bromosulfamates together with solvated N-chlorosulfamates in combination with solvated alkali metal halides and/or solvated alkaline earth metal halides. It is realized that if water is the sole solvent, the solvated substances can be referred to as “hydrated.”

[0042] This invention provides a number Groups of individual novel processes or compositions, including the following:

Group I - Processes

- [0043] 1) A process for extracting at least one precious metal from a source material containing at least one said metal, the process comprising contacting said source material with an aqueous leaching solution comprising (A) water, (B) at least one solvated N-bromosulfamate source, and (C) at least one solvated alkali metal halide, or at least one solvated alkaline earth metal halide, or at least one solvated ammonium halide, or any two or more of the foregoing solvated halides.
- 2) A process for extracting at least one precious metal from a source material containing at least one said metal, the process comprising contacting said source material with an aqueous leaching solution comprising (A) water, (B) at least one solvated N-bromosulfamate source, (C) at least one solvated alkali metal halide, or at least one solvated alkaline earth metal halide, or at least one solvated ammonium halide, or any two or more of the foregoing solvated halides, and (D) at least one solvated N-chlorosulfamate source. Preferably, (B) and (D) are proportioned such

that the active halogen atom ratio of solvated N-bromosulfamate source:solvated N-chlorosulfamate source is in the range of about 1:1 to 10:1.

- 3) A process for extracting at least one precious metal from a source material containing at least one said metal, the process comprising contacting said source material with an aqueous leaching solution comprising (A) water, (B) at least one solvated N-bromosulfamate source, and (C) at least one solvated potassium halide.
- 4) A process for extracting at least one precious metal from a source material containing at least one said metal, the process comprising contacting said source material with an aqueous leaching solution comprising (A) water, (B) at least one solvated N-bromosulfamate source, and (C) at least one solvated sodium halide and at least one solvated potassium halide.
- 5) A process for extracting at least one precious metal from a source material containing at least one said metal, the process comprising contacting said source material with an aqueous leaching solution comprising (A) water, (B) at least one solvated N-bromosulfamate source, and (C) at least one solvated sodium halide.
- 6) A process for extracting at least one precious metal from a source material containing at least one said metal, the process comprising contacting said source material with an aqueous leaching solution comprising (A) water, (B) at least one solvated N-bromosulfamate source, (C) at least one solvated sodium halide, and (D) at least one solvated N-chlorosulfamate source. Preferably, (B) and (D) are proportioned such that the active halogen atom ratio of solvated N-bromosulfamate source:solvated N-chlorosulfamate source is in the range of about 1:1 to 10:1.
- 7) A process for extracting at least one precious metal from a source material containing at least one said metal, the process comprising contacting said source material with an aqueous leaching solution comprising (A) water, (B) at least one solvated N-bromosulfamate source, (C) at least one solvated potassium halide, and (D) at least one solvated N-chlorosulfamate source. Preferably, (B) and (D) are proportioned such that the active halogen atom ratio of solvated N-bromosulfamate source:solvated N-chlorosulfamate source is in the range of about 1:1 to 10:1.
- 8) A process for extracting at least one precious metal from a source material containing at least one said metal, the process comprising contacting said source material with an aqueous leaching solution comprising (A) water, (B) at least one solvated N-bromosulfamate source, (C) at least one solvated sodium halide and at

least one solvated potassium halide, and (D) at least one solvated N-chlorosulfamate source. Preferably, (B) and (D) are proportioned such that the active halogen atom ratio of solvated N-bromosulfamate source:solvated N-chlorosulfamate source is in the range of about 1:1 to 10:1.

- 9) A process as in any of 1-8 wherein said aqueous leaching solution has a pH in the range of about 7.5 ± 0.5 or less.
- 10) A process as in 9) wherein said precious metal comprises gold, palladium, silver, or rhodium or any mixture of any two or more of these metals.
- 11) A process as in 10) wherein said precious metal comprises gold or palladium or a mixture thereof, and wherein said pH is in the range of about 4 to about 6.
- 12) A process as in 10) wherein said precious metal comprises silver or rhodium or a mixture thereof and wherein said pH is in the range of 1 or less.
- 13) A process as in 9) wherein the precious metal is gold or palladium or both, wherein the aqueous leaching solution has dissolved therein as a solution a precious metal selected from gold or palladium or both, and at least one dissolved metal other than gold or palladium, wherein (B) comprises at least one solvated N-bromosulfamate source, wherein (C) comprise solvated sodium bromide or solvated ammonium bromide or solvated alkaline earth metal bromide or a combination of any two or all three of these, and wherein the solution has a pH in the range of about 4 to about 6.

[0044] The use of one or more alkali metal iodides and/or one or more ammonium iodides and/or alkaline earth metal iodides as (C) in each of the above Group I processes is also within the scope of this invention. However, the bromides or chlorides, or both, are preferred halides because of their effectiveness and their lower cost as compared to iodides. As noted earlier herein, the fluorides may be used.

Group II - Compositions

- [0045] 1) A composition comprising at least one precious metal in the form of a solute in an aqueous medium, the composition comprising (A) water, (B) at least one solvated N-bromosulfamate source, and (C) at least one solvated alkali metal halide, or at least one solvated alkaline earth metal halide, or at least one solvated ammonium halide, or any two or more of the foregoing solvated halides.
- 2) A composition comprising at least one precious metal in the form of a solute in an aqueous medium, the composition comprising (A) water, (B) at least one solvated N-

bromosulfamate source, (C) at least one solvated alkali metal halide, or at least one solvated alkaline earth metal halide, or at least one solvated ammonium halide, or any two or more of the foregoing solvated halides, and (D) at least one solvated N-chlorosulfamate source. Preferably, (B) and (D) are proportioned such that the active halogen atom ratio of solvated N-bromosulfamate source:solvated N-chlorosulfamate source is in the range of about 1:1 to 10:1.

- 3) A composition comprising at least one precious metal in the form of a solute in an aqueous medium, the composition comprising (A) water, (B) at least one solvated N-bromosulfamate source, and (C) at least one solvated potassium halide.
- 4) A composition comprising at least one precious metal in the form of a solute in an aqueous medium, the composition comprising (A) water, (B) at least one solvated N-bromosulfamate source, and (C) at least one solvated sodium halide and at least one solvated potassium halide.
- 5) A composition comprising at least one precious metal in the form of a solute in an aqueous medium, the composition comprising (A) water, (B) at least one solvated N-bromosulfamate source, and (C) at least one solvated sodium halide.
- 6) A composition comprising at least one precious metal in the form of a solute in an aqueous medium, the composition comprising (A) water, (B) at least one solvated N-bromosulfamate source, (C) at least one solvated sodium halide, and (D) at least one solvated N-chlorosulfamate source. Preferably, (B) and (D) are proportioned such that the active halogen atom ratio of solvated N-bromosulfamate source:solvated N-chlorosulfamate source is in the range of about 1:1 to 10:1.
- 7) A composition comprising at least one precious metal in the form of a solute in an aqueous medium, the composition comprising (A) water, (B) at least one solvated N-bromosulfamate source, (C) at least one solvated potassium halide, and (D) at least one solvated N-chlorosulfamate source. Preferably, (B) and (D) are proportioned such that the active halogen atom ratio of solvated N-bromosulfamate source:solvated N-chlorosulfamate source is in the range of about 1:1 to 10:1.
- 8) A composition comprising at least one precious metal in the form of a solute in an aqueous medium, the composition comprising (A) water, (B) at least one solvated N-bromosulfamate source, (C) at least one solvated sodium halide and at least one solvated potassium halide, and (D) at least one solvated N-chlorosulfamate source. Preferably, (B) and (D) are proportioned such that the active halogen atom ratio of

solvated N-bromosulfamate source:solvated N-chlorosulfamate source is in the range of about 1:1 to 10:1.

- 9) A composition as in any of 1-8 wherein said aqueous leaching solution has a pH in the range of about 7.5 ± 0.5 or less.
- 10) A composition as in 9) wherein said precious metal comprises gold, palladium, silver, or rhodium or any mixture of any two or more of these metals.
- 11) A composition as in 10) wherein said precious metal comprises gold or palladium or a mixture thereof, and wherein said pH is in the range of about 4 to about 6.
- 12) A composition as in 10) wherein said precious metal comprises silver or rhodium or a mixture thereof and wherein said pH is in the range of 1 or less.
- 13) A composition as in 9) wherein the precious metal is gold or palladium or both, wherein the aqueous leaching solution has dissolved therein as a solution a precious metal selected from gold or palladium or both, and at least one dissolved metal other than gold or palladium, wherein (B) comprises at least one solvated N-bromosulfamate source, wherein (C) comprise solvated sodium bromide or solvated ammonium bromide or solvated alkaline earth metal bromide or a combination of any two or all three of these, and wherein the solution has a pH in the range of about 4 to about 6.

[0046] The use in each of the above compositions of (i) one or more alkali metal iodides and/or (ii) one or more alkaline earth metal iodides and/or (iii) one or more alkali metal fluorides and/or (iv) one or one alkaline earth metal fluorides is also within the practice of this invention. However, the bromides or chlorides, or both, are preferred halides because of their effectiveness and their lower cost as compared to iodides and fluorides.

Group III - Processes

[0047] I) A process for forming a water-soluble form of at least one precious metal, the process comprising:

- A) forming or obtaining a composition comprising an aqueous medium containing (i) at least one solvated N-halosulfamate compound which is totally in solution or is partially in solution and partially in the form of crystals or particles in said aqueous medium, and (ii) at least one solvated alkali metal halide, and/or at least one solvated ammonium halide and/or at least one solvated alkaline earth metal halide, or any two or more of the foregoing solvated halides;

- B) acidifying said composition with a mineral acid to form a lixiviant solution having a pH in the range of about 7.5 ± 0.5 or less, and optionally diluting said lixiviant solution with water to provide a diluted solution having a reduced active bromine content sufficient to leach the precious metal from its source; and
 - C) contacting the precious metal-containing a source material with said composition whereby a leachate (leached product) is formed containing in solution said at least one precious metal. Typically the leachate is recovered from the remainder of the so-processed composition (*i.e.*, that which is left after such recovery). When the source material additionally contains at least one base metal, optionally the leachate can also contain at least one base metal in solution.
- II) A process for forming a water-soluble form of at least one precious metal, the process comprising:
- A) forming or obtaining a composition comprising an aqueous medium containing (i) at least one solvated N-bromosulfamate compound and at least one solvated N-chlorosulfamate compound either or both of which are totally in solution or are partially in solution and partially in the form of crystals or particles in said aqueous medium, and (ii) at least one solvated alkali metal halide and/or at least one solvated ammonium halide and/or at least one solvated alkaline earth metal halide, or any two or more of the foregoing solvated halides;
 - B) acidifying said composition with a mineral acid to form a lixiviant solution having a pH in the range of about 7.5 ± 0.5 or less, and optionally diluting said lixiviant solution with water to provide a diluted solution having a reduced active bromine content sufficient to leach the precious metal from its source; and
 - C) contacting the precious metal-containing a source material with said composition whereby a leachate is formed containing said at least one precious metal in solution. Typically leachate is recovered from the remainder of the so-processed composition (*i.e.*, that which is left after such recovery). When the source material additionally contains at least one base metal, optionally the leachate can also contain at least one base metal in solution.
- III) A process for forming a water-soluble form of at least one precious metal, the process comprising:
- A) forming or obtaining a composition comprising an aqueous medium containing (i) at least one solvated N-bromosulfamate compound which is totally in solution or is

- partially in solution and partially in the form of crystals or particles in said aqueous medium, and (ii) at least one solvated potassium halide (preferably solvated sodium bromide or solvated potassium bromide or solvated ammonium bromide, or a mixture of any two or all three of these);
- B) acidifying said composition with a mineral acid to form a lixiviant solution having a pH in the range of about 7.5 ± 0.5 or less, and optionally diluting said lixiviant solution with water to provide a diluted solution having a reduced active bromine content sufficient to leach the precious metal from its source; and
- C) contacting the precious metal-containing a source material with said composition whereby a leachate is formed containing said at least one precious metal in solution. Typically leachate is recovered from the remainder of the so-processed composition (*i.e.*, that which is left after such recovery). When the source material additionally contains at least one base metal, optionally the leachate can also contain at least one base metal in solution.
- IV) A process for forming a water-soluble form of at least one precious metal, the process comprising:
- A) forming or obtaining a composition comprising an aqueous medium containing (i) at least one solvated N-bromosulfamate compound which is totally in solution or is partially in solution and partially in the form of crystals or particles in said aqueous medium, and (ii) at least one solvated sodium halide and at least one solvated potassium halide;
- B) acidifying said composition with a mineral acid to form a lixiviant solution having a pH in the range of about 7.5 ± 0.5 or less, and optionally diluting said lixiviant solution with water to provide a diluted solution having a reduced active bromine content sufficient to leach the precious metal from its source; and
- C) contacting the precious metal-containing a source material with said composition whereby a leachate is formed containing said at least one precious metal in solution. Typically leachate is recovered from the remainder of the so-processed composition (*i.e.*, that which is left after such recovery). When the source material additionally contains at least one base metal, optionally the leachate can also contain at least one base metal in solution.
- V) A process for forming a water-soluble form of at least one precious metal, the process comprising:

- A) forming or obtaining a composition comprising an aqueous medium containing (i) at least one solvated N-bromosulfamate compound which is totally in solution or is partially in solution and partially in the form of crystals or particles in said aqueous medium, and (ii) at least one solvated sodium halide;
 - B) acidifying said composition with a mineral acid to form a lixiviant solution having a pH in the range of about 7.5 ± 0.5 or less, and optionally diluting said lixiviant solution with water to provide a diluted solution having a reduced active bromine content sufficient to leach the precious metal from its source; and
 - C) contacting the precious metal-containing a source material with said composition whereby a leachate is formed containing said at least one precious metal in solution. Typically leachate is recovered from the remainder of the so-processed composition (*i.e.*, that which is left after such recovery). When the source material additionally contains at least one base metal, optionally the leachate can also contain at least one base metal in solution.
- VI) A process for forming a water-soluble form of at least one precious metal, the process comprising:
- A) forming or obtaining a composition comprising an aqueous medium (i) containing at least one solvated N-bromosulfamate compound and at least one solvated N-chlorosulfamate compound either or both of which are totally in solution or are partially in solution and partially in the form of crystals or particles in said aqueous medium, and (ii) at least one solvated potassium halide;
 - B) acidifying said composition with a mineral acid to form a lixiviant solution having a pH in the range of about 7.5 ± 0.5 or less, and optionally diluting said lixiviant solution with water to provide a diluted solution having a reduced active bromine content sufficient to leach the precious metal from its source; and
 - C) contacting the precious metal-containing a source material with said composition whereby a leachate is formed containing said at least one precious metal in solution. Typically leachate is recovered from the remainder of the so-processed composition (*i.e.*, that which is left after such recovery). When the source material additionally contains at least one base metal, optionally the leachate can also contain at least one base metal in solution.
- VII) A process for forming a water-soluble form of at least one precious metal, the process comprising:

- A) forming or obtaining a composition comprising an aqueous medium containing (i) at least one solvated N-bromosulfamate compound and at least one solvated N-chlorosulfamate compound which is totally in solution or is partially in solution and partially in the form of crystals or particles in said aqueous medium, and (ii) at least one solvated sodium halide and at least one solvated potassium halide;
 - B) acidifying said composition with a mineral acid to form a lixiviant solution having a pH in the range of about 7.5 ± 0.5 or less, and optionally diluting said lixiviant solution with water to provide a diluted solution having a reduced active bromine content sufficient to leach the precious metal from its source; and
 - C) contacting the precious metal-containing a source material with said composition whereby the leachate is formed containing said at least one precious metal in solution. Typically leachate is recovered from the remainder of the so-processed composition (*i.e.*, that which is left after such recovery). When the source material additionally contains at least one base metal, optionally the leachate can also contain at least one base metal in solution.
- VIII) A process for forming a water-soluble form of at least one precious metal, the process comprising:
- A) forming or obtaining a composition comprising an aqueous medium containing (i) at least one solvated N-bromosulfamate compound and at least one solvated N-chlorosulfamate compound which is totally in solution or is partially in solution and partially in the form of crystals or particles in said aqueous medium, and (ii) at least one solvated sodium halide;
 - B) acidifying said composition with a mineral acid to form a lixiviant solution having a pH in the range of about 7.5 ± 0.5 or less, and optionally diluting said lixiviant solution with water to provide a diluted solution having a reduced active bromine content sufficient to leach the precious metal from its source; and
 - C) contacting the precious metal-containing a source material with said composition whereby a leachate is formed containing said at least one precious metal in solution. Typically leachate is recovered from the remainder of the so-processed composition (*i.e.*, that which is left after such recovery). When the source material additionally contains at least one base metal, optionally the leachate can also contain at least one base metal in solution.

- IX) A process as in any of I) - VIII) wherein said precious metal comprises gold, palladium, silver, or rhodium or any mixture of any two or more of these metals.
- X) A process as in IX) wherein said precious metal comprises gold or palladium or a mixture thereof, and wherein said pH is in the range of about 4 to about 6.
- XI) A process as in IX) wherein said precious metal comprises silver or rhodium or a mixture thereof and wherein said pH is in the range of 1 or less.
- XII) A process as in IX) wherein the precious metal is gold or palladium or both, wherein the aqueous leaching solution has dissolved therein as a solution a precious metal selected from gold or palladium or both, and at least one dissolved metal other than gold or palladium, wherein (B) comprises at least one solvated N-bromosulfamate source, wherein (C) comprise solvated sodium bromide or solvated ammonium bromide or solvated alkaline earth metal bromide or a combination of any two or all three of these, and wherein the solution has a pH in the range of about 4 to about 6.

[0048] In each of processes of Group III, Nos. IV)–VIII) above, (C) can be only “at least one solvated ammonium halide”, or can include “at least one solvated ammonium halide”.

[0049] The use in each of the above compositions of (a) one or more alkali metal iodides and/or (b) one or more alkaline earth metal iodides and/or (c) one or more alkali metal fluorides and/or (d) one or one alkaline earth metal fluorides is also within the practice of this invention. However, the bromides or chlorides, or both, are preferred halides because of their effectiveness and their lower cost as compared to iodides and fluorides.

[0050] Of the various aqueous lixiviant or extracting solutions of this invention, the most preferred aqueous solutions comprise water containing solvated sodium bromosulfamate and solvated sodium bromide. These solutions have shown the best overall performance and product characteristics. These solutions are sometimes referred to hereinafter as “Stabilized Bromine” in recognition of the enhanced stability characteristics which they possess.

[0051] Still another embodiment of this invention is a process for dissolving at least one precious metal from a material containing or composed of at least one said precious metal in leachable form and optionally at least one base metal in leachable form, and/or leaching at least one said precious metal in leachable form from a source material comprising at least one precious metal, the process comprising the steps of:

- A) forming or obtaining (*i.e.*, providing) a composition comprising (i) an aqueous medium containing (i) at least one solvated N-halosulfamate compound which is totally in solution or is partially in solution and partially in the form of crystals or particles in said aqueous medium, and (ii) at least one solvated alkali metal halide, and/or at least one solvated ammonium halide and/or at least one solvated alkaline earth metal halide (preferably where the halogen of said halosulfamate compound and of said metal halide being, independently, bromine, chlorine, or iodine, or a combination of at least two thereof, but which may be fluorine);
- B) acidifying said composition with a mineral acid to form a lixiviant solution having a pH in the range of about 7.5 ± 0.5 or less (preferably a pH in the range of about 4 to about 6 for gold and/or palladium, and preferably a pH in the range of about 1 or less for silver and/or rhodium), and optionally diluting said lixiviant solution with water to provide a diluted lixiviant solution having a reduced active bromine content sufficient to leach the precious metal from its source; and
- C) contacting said material or source material with said lixiviant solution or diluted lixiviant solution whereby a leachate is formed containing said at least one precious metal and optionally at least one base metal; and
- D) recovering leachate from the remainder of the so-processed composition (*i.e.*, that which is left after such recovery).

[0052] Temperatures used in the leaching (extraction) operations of this invention can vary provided that under the pressure conditions at which the process is conducted, the leaching solution contains enough liquid water to enable leaching to occur. Desirably, however, temperatures of the leaching solution when in use are in the range of about ambient room temperature to about 60°C. Pressures may be atmospheric, autogenous, sub-atmospheric, or super-atmospheric. Atmospheric or autogenous pressures are usually preferred.

[0053] Because the metal leaching processes of the invention may be carried out without the use of any cyanide, it offers significant advantages from the standpoint of both safety and environmental protection. This translates into major cost advantages, since elaborate cyanide disposal facilities and procedures may be entirely eliminated.

[0054] Typically, the extraction or leaching operation will be conducted using a contact time long enough to ensure that at least most of the extractable metal has been leached into the leaching solution. Thus, time is not a critical parameter – any suitable contact time

may be used. It is to be noted however, that on the basis of experimental studies conducted to date, N-halosulfamates attack the precious metal source materials to extract the metal therefrom at rates which may be substantially enhanced in comparison to those achieved in cyanide extraction processes. Thus, for example, within a period of 2 to 4 hours, contact with a leaching solution of this invention may typically provide substantial leaching of ores which require a greater number of hours for leaching with cyanide solutions.

[0055] The leaching processes of this invention enable recovery of the precious metals from refractory ores and ores containing sulfide minerals and carbonaceous material. The processes are deemed capable of providing improved rates of leaching such ores as compared to cyanide-based processing. While oxidative treatment of sulfide-containing or carbonaceous ores generally remains necessary, the oxidizing power of the leaching agents used pursuant to this invention is such that it may be used for this purpose as well. Generally, an acidic solution of the leaching agent is used for both oxidative pre-leaching and leaching of the precious metal from such ores, while either an acidic or basic solution of the leaching agent is used for recovery of the metal from the ore after oxidation and removal of sulfides and excess carbonaceous material.

[0056] The process technology of this invention makes possible the recovery of metal values from gold ores and other precious metal ores. Moreover, leaching using the leaching solutions of this invention is effective and advantageous for secondary recovery of precious metals from other source materials such as jewelry scraps, spent colloidal gold suspensions, gold plating from electronic circuit boards, spent platinum metal catalysts and the like. Further in accordance with the invention, the solvated N-halosulfamate source together with one or more solvated alkali metal halides and/or one or more alkaline earth metal halides may be utilized for leaching of the various base metals, particularly those which form halide complex anions such as aluminum, magnesium, chromium, iron, cobalt, nickel, copper, tin, bismuth, antimony, cadmium, lead, zinc, indium, gallium and arsenic.

[0057] Precious metals of particular interest in the practice of this invention include gold, palladium, silver, rhodium, platinum, osmium, iridium, and the like. Some of these metals may be co-extracted in very small amounts along with other more highly recoverable precious metals. Such other metals may remain as precipitates or in slurry form after recovery of the dissolved forms (*e.g.*, complexes, *etc.*) of, for example, gold,

palladium, silver, and/or rhodium. In short, the processes of this invention have the potential of concentrating these other precious metals in solid form so that they may be recovered and isolated by other processing procedures.

[0058] Without being bound by theory, it appears reasonable to suggest that the solvated N-halosulfamate source(s) used may react with the with at least one precious metal in the source material to form an anion comprising the precious metal complexed with halogen, and that this complex anion has sufficient stability to remain in the leaching solution. Whatever the mechanism, the processes of this invention provide effective methods for recovery of the precious metal(s) while optionally enabling recovery of at least one base metal as well, because of its separation or ready separability from the precious metal complex or other chemical entity form.

[0059] As noted above, another embodiment of this invention is a process which comprises preforming or generating *in situ* at least one N-halosulfamate by chemically or by electrolytically oxidizing at least one halide source in presence of at least one sulfamate source such as sulfamic acid or a water soluble salt of sulfamic acid. In a further embodiment, the source of sulfamate can be a previously used lixiviant solution whereby the residual active lixiviant is regenerated either chemically or electrolytically. Some of the chemical oxidants for use in forming and/or regenerating N-halosulfamate include Oxone (potassium peroxymonosulfate), bleach (sodium hypochlorite), chlorine and Trichlor (trichloroisocyanuric acid). The mixing of such oxidants with water can be conducted at any temperature in which the water remains in the liquid state *e.g.*, typically at ambient room temperatures or at temperatures up to about 60°C. Conventional forms of agitation can be used in forming such solutions.

[0060] As noted above, an advantageous feature of this invention is that concentrated aqueous solutions developed and produced commercially for uses not related to the present invention (*e.g.*, biocidal uses) are available commercially in the form of concentrated aqueous solutions. Simple operations can readily convert most of such solutions into solutions adapted, and highly effective, for use pursuant to this invention.

[0061] One such group of concentrated solutions comprising N-bromosulfamate and N-chlorosulfamate together with alkali metal halides are available from Albemarle Corporation. These solutions are Stabrom[®] 909 biocide, Stabrom[®] Plus biocide and Maxxis[®] biocide.

[0062] Albemarle Corporation reports that:

- Stabrom[®] 909 biocide is a clear yellow to clear orange liquid having a total halogen content expressed as Br₂ of 14.5-15.9 wt%, a pH of 12.4-14.0, and a specific gravity at 20°C/20°C of 1.295-1.370. It has a freezing point of approximately 0°C and a boiling point of approximately 106°C, and has complete solubility in water.
- Stabrom[®] Plus biocide is a clear yellow to clear orange liquid having a total halogen content expressed as Br₂ of 17.3-19.1 wt%, a pH of 12.4-14.0, and a density of 1.35-1.45 g/mL at 25°C. It has a freezing point of approximately 2°C, a boiling point of approximately 106°C, and is completely soluble in water.
- Maxxis[®] biocide is a clear yellow to clear orange liquid having a total halogen content expressed as Br₂ of 19.7-21.7 wt%, a pH of 12.4-14.0, and a density of 1.4-1.55 g/mL at 25°C. It has a freezing point of approximately 7°C (as a summer formulation), and -1°C (as a winter formulation), a boiling point of approximately 106°C, and is completely soluble in water.

[0063] The pH levels given above for the Albemarle Corporation products result from use of at least one suitable base of the manufacture of the product. Such bases are typically alkali metal hydroxides, although other bases can be used, non-limiting examples of which include alkali metal oxides, alkali metal carbonates, alkali metal bicarbonates, or their alkaline earth counterparts, and the like.

[0064] As can be appreciated therefore, the components in the above commercial Albemarle Corporation products include a number of other components due to reaction in water among the ingredients used in producing the products. For example, NaOH is present in Stabrom[®] 909 biocide and Stabrom[®] Plus biocide whereas NaOH and KOH are present in the Maxxis[®] biocide formulations. To adjust the pH more base may be used but in most cases a suitable amount of an acid such as H₂SO₄, HCl or HBr or the like, can be used to reduce the pH of the concentrated solution or preferably the pH of the more dilute aqueous solution for use in the leaching solution just prior to its use in a leaching operation. Conveniently the base is used as a pre-formed water solution for addition to the concentrated solution as received from Albemarle Corporation. This ensures that the storage life of the remaining concentrated solution will remain high.

[0065] Another commercial source of suitable biocidal solutions that may be employed in the practice of this invention are available from Enviro Tech Chemical Services, Inc. Two such products containing, *inter alia*, solvated N-bromosulfamate and N-

chlorosulfamate are available as BromMax[®] 10.2 and BromMax[®] 7.1 biocide solutions. It has been reported by Enviro Tech Chemical Services, Inc. that these are registered biocides (No. 63838-3) and are covered by U.S. Patent Nos. 7,045,153 and reference is also made to 7,455,859.

[0066] The composition of the BromMax biocides as specified by the supplier in its Material Safety Data Sheet are as follows:

Ingredients	CAS No.	Approximate %
Sodium N-bromosulfamate	1004542-84-0	11-21%
Sodium Hydroxide	1310-73-2	1-5%
Sodium Chloride	7647-14-5	3-13%
Water	7732-18-5	Balance

[0067] The properties of the BromMax biocides as specified by the supplier given in its Material Safety Data Sheet the composition of these products as follows:

Form:	Liquid	
Color:	Golden	
Water Solubility:	Complete	
Density:	10.7-11.0 lbs./gal. @ 68°F	
Specific Gravity:	1.28-1.32 @ 68°F	ASTM D-1298
Viscosity	N/A	ASTM D-2983
pH (Neat)	> 13	ASTM E-70
Freeze Point:	< 32°F	ASTM D-1177
Flash Point:	None (PMCC)	ASTM D-93
Voc Content %	None	EPA Method 24

[0068] The pH of the aqueous leaching solutions used in the practice of this invention can be readily adjusted if necessary to achieve optimum extraction or leaching conditions to the particular precious metal source being treated. For example, when using highly basic solutions, such as are available in the marketplace for biocidal usage, addition of mineral acids (*e.g.*, sulfuric acid, hydrobromic acid, hydrochloric acid, nitric acid, phosphoric acid, or the like with H₂SO₄, HBr, and HCl being preferred) to reduce the pH is a convenient way of accomplishing pH adjustment. It is desirable to add the quantity of the acid to the aqueous leaching solution prior to contacting the solution with the precious

metal source which is in a suitable subdivided form. In forming the aqueous leaching solution, (1) the acid can be added to the precious metal source, (2) the precious metal source can be added to the acid, or (3) both the acid and the precious metal source can be fed concurrently into the extraction vessel. Precious metal sources which have extraction characteristics similar to gold can be effectively extracted or leached at pH levels in the range of about 7.5 ± 0.5 or less, e.g., in the range of above about 1 to about 8, typically in the range of about 2 to about 7.5 ± 0.5 . In some cases pH levels in the range of about 4 to about 7 or about 4 to about 8 are more preferred. Continuous addition of such acids during the extraction or leaching operation is usually preferred. In any given situation, a few simple pilot tests with a given proposed aqueous leaching solution, a given precious metal source, and a selected acid to achieve optimum extraction at a given temperature will suffice.

[0069] For pre-leaching and oxidative treatment of carbonaceous ores, it is preferred that the treating solution be acidic. The acidic solution should contain at least about 0.05%, preferably at least about 0.1% by weight of the leaching agent. The pH is preferably in the range of about 1 to about 7. Acids which may be used in the acidic leaching solution include hydrochloric acid, hydrobromic acid, phosphoric acid, nitric acid, sulfuric acid, and like mineral acids.

[0070] The metal source material may be contacted with the leaching solution in any conventional fashion, for example, by causing the leaching solution to percolate through a mass of ore or other sources material. For use in this leaching technique, the ore is initially crushed, typically to a particle size of less than 25 millimeters, and the particulate mass is placed on impermeable surfaces such as liners, sheeting or pads prior to initiating percolation of the leaching solution through the crushed source material.

[0071] Alternatively, the ore may be subjected to vat leaching or agitation leaching. In vat leaching, the ore is crushed, again typically to a particle size of less than 25 mm, and agglomerated, for example, with lime or cement. Leaching solution is passed through a bed of particulate ore contained within a leaching vessel. The solution may be passed either upwardly or downwardly through the bed of material; or the leaching solution and ore can be moved countercurrently through a continuous or cascade leaching system.

[0072] In agitation leaching, the ore is typically ground to a finer particle size, for example, to a size in which 50% by weight or more passes through a standard 200 mesh sieve. Thereafter, a leaching slurry is formed by suspending a source material in the

leaching solution. Leaching rates are enhanced by agitating the leaching slurry to promote mass transfer from the solid source material to the leaching solution. However, while agitation is desirable, excessive shearing action is undesirable. Therefore, typically a propeller type agitator is used.

[0073] In leaching of ore, the ore is contacted with leaching solution in relative proportions equivalent to at least about 2 preferably at least about 5 pounds of N-halosulfamate source per ton of ore. For maximum productivity in slurry leaching, the solids content of the leaching slurry should not be greater than about 40% by weight. Leaching may be carried out at any temperature above ambient, but is preferably conducted at a temperature of between about 70° and about 140° F., *i.e.*, between about 20° and about 60°C. At temperatures in the aforesaid range, leaching proceeds very rapidly. In slurry leaching, complete and quantitative recovery of the precious metal from ore may be accomplished within a contact time of one to two hours, or even less.

[0074] For oxidative pre-leaching of carbonaceous or sulfide bearing ore, the conditions employed are generally comparable to those used for leaching. For treatment of high grade ores, or in the case of secondary recovery, the pre-leaching oxidative treatment step is not normally necessary.

[0075] To recover the metal from the leachate, various techniques may be utilized. In some instances, particularly in the case of secondary recovery from a metal-rich source material, the leachate may be subjected directly to electrowinning or precipitation. In electrowinning, the metal to be recovered is preferably recovered on a cathode of the same metal. Alternatively, an inert cathode may be used. Conventional inert anode materials, current densities, temperatures and other conditions conventionally appropriate for the particular metal to be recovered are utilized in the electrowinning process. In one advantageous application, the electrolytic system comprises a steel wool cathode and an ion exchange membrane for dividing the anodic and cathodic zones.

[0076] Where the leachate contains a precious metal, it is often feasible to recover it by contacting the leachate with a metal less noble than the leached metal, thereby precipitating the leached metal in metallic form. In the case of gold, precipitation may be carried out by methods known to the art, for example, in a Merrill-Crowe apparatus using zinc as the precipitating agent. In a preferred commercial technique, the leachate is contacted with zinc shavings or zinc powder in the presence of lead acetate, the lead acetate typically being provided as a coating on the surface of the zinc. In a still further

alternative recovery method, the leachate may be contacted with an ion exchange resin effective for separating anionic precious metal complexes from aqueous solutions. Typical of these are the 3200 to 4200 series of resins selective for silver and gold as sold by Rohm & Haas. The metal may then be recovered from the resin pyrolytically.

[0077] Where the leachate is derived from ore, particularly where it is obtained by leaching of refractory or other low grade ore, it is normally desirable to concentrate the metal before attempting to recover it in metallic form. A preferred method for concentrating the metal is by adsorption of halometal complex salts from the leachate onto activated carbon, followed by redissolution in a desorptive leaching solution. In accordance with the process of the invention, the desorbing agent contained in the desorption solution may comprise a solvated N-halosulfamate or cyanide, and the metal may ultimately be recovered from the desorbate by precipitation or electrowinning. Conventional cyanide desorption solutions comprise alkaline mixtures of alcohol, typically ethanol and water. Where the metal is redissolved in a solvated N-halosulfamate solution, the concentrated desorption solution is preferably substantially saturated with respect to solvated N-halosulfamate, and the desorbate contains 5 to 30 grams per liter of the desorbed metal. It is also preferred that the desorption solution be either alkaline in a pH range of about 7.5 to about 9.5, or acid in a pH range of between about 1 and about 5. Desorptive leaching of the metal from the activated carbon is preferably carried out at a temperature of between about 30°C and about 95°C at atmospheric pressure.

[0078] A desirable way of recovering precious metal(s) from the aqueous leaching (extraction) solution is to contact this solution with a suitable adsorption agent such as activated carbon or an adsorbent resin. Examples of suitable adsorbent resins are Dowex-21k resin and Reilex 425 ion exchange resin. The contacting may be effected in various ways such as stirring the adsorption agent in a body of the aqueous leaching solution and recovering the resultant metal-containing particles by a mechanical separation procedure such as filtration, centrifugation, decantation, or the like. Alternatively, the aqueous leaching solution can be passed through a bed of the adsorption agent whereby a bed of particles of adsorbed precious metal-containing product is formed for further treatment such as incinerating or smelting the carbon or resin particles to recover the precious metal(s). Alternatively, the precious metal may be recovered from the adsorptive resins by extraction of the precious metal-laden particles by contacting the adsorbent with an eluting

solution containing an eluant such as hydrochloric acid or acidified thiourea. Other methods known to the art *e.g.*, pyrolysis, may also be used for these recovery operations.

[0079] To regenerate the used aqueous lixivant solutions, chemical oxidation with sodium hypochlorite solution, trichloroisocyanuric acid, or potassium peroxymonopersulfate converts the bromide in the used solution to bromine and thus should also be effective for oxidizing the other halides to halogens. Thus these reagents regenerate at least N-bromosulfamate for reuse.

[0080] Electrowinning of the precious metal or base metal from a solvated N-halosulfamate solution comprises a useful method for recovery of such metals. Generally, the electrolytic solution used for electrowinning contains between about 5 and about 30 grams per liter, preferably at least about 15 grams per liter, of the desired metal in the form of halometal complex anions, and is substantially saturated with respect to solvated N-halosulfamate. When the electrowinning solution is acidic, it preferably has a pH of between about 4 and about 6. Where it is alkaline, it preferably has a pH of between about 7.5 and about 9. Application of a direct current through the solution breaks down the metal halide complex anions at the anode, resulting in the formation of free metal ions which are attracted to the cathode where they are reduced and the metal is deposited. The selection of anode and cathode materials, current density, electrode spacing, temperature and other conditions is governed by conventional practice for electrowinning of the particular metal involved. Thus, for example, in the case of gold electrowinning is preferably carried out at a temperature of not greater than about 140° F (52° C.), a current density of approximately 0.25 amps./ft.², a voltage of 1.9 to 2.1 volts, and an electrode spacing of not greater than about 2". As noted above, after electrowinning is complete, the spent electrolytic solution may be replenished with leaching agent, pH-adjusted as necessary, and recycled for leaching of additional source material.

[0081] Further in accordance with the invention, electrolytic solutions of the type described above in connection with electrowinning can be used for other electrodeposition processes, including electrorefining and electroplating. In electrorefining, the anode comprises the metal to be purified, and the electrolytic solution contains solvated N-halosulfamate and halogen complex anions of the metal which is to be deposited at the cathode as direct current is applied. In some instances, the metal to be refined is deposited at the cathode, while in other instances an impurity is deposited at the cathode while the metal to be refined is collected in the form of a sludge or mud as the anode disintegrates.

For example, gold contaminated with silver may be refined by subjecting an anode of such material to electrolysis in a bath comprising solvated N-halosulfamate and halogenated silver complex anions. Silver is deposited at the cathode and as the anode disintegrates a mud rich in gold is collected by conventional means, for example, in a filter bag surrounding the anode. The mud is washed and the gold contained therein is melted down, formed into another anode, and subjected to further electrofining, this time in a bath comprising solvated N-halosulfamate and halogenated gold complex anions, with metallic gold being deposited at the cathode.

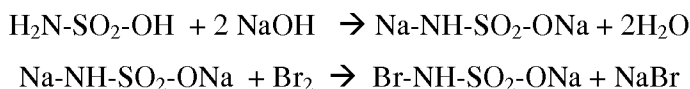
[0082] In electroplating, a part to be plated is immersed in a bath comprising a solvated N-halosulfamate and halogen complex anions of the metal to be deposited. The anode may be either inert or comprise the plating metal. In electrofining and electroplating, as in electrowinning, the temperatures, current densities, voltages, electrode spacings, etc., are those conventionally used in the art.

[0083] The following Examples are provided for the purpose of illustration. They are not intended to limit the invention to only the details presented therein.

EXAMPLE 1

Preparation of Solvated Sodium N-Bromosulfamate “Stabilized Bromine”

[0084] A 5-L reactor fitted with a condenser, an addition funnel, a mechanical stirrer and a thermometer was charged with 1650 g of deionized water and agitated at 150 rpm. Sulfamic acid (440 g; 4.54 moles) was added in small portions and dissolved in water. A solution of 50% NaOH (947g; 11.84 moles) was taken in the addition funnel and added dropwise, keeping the temperature of the mixture below 50°C. After the addition, the mixture was allowed to cool to room temperature. The addition funnel was replaced with a Teflon feeding tube connected to a peristaltic pump. The agitation of the mixture was increased to 200 rpm. Using the peristaltic pump, bromine (529 g; 3.31 moles) was fed to the reactor at a rate of 2mL/minute. Temperature of the mixture was 25-30oC during the addition. The mixture was stirred for an additional 30 minutes after the addition and the clear yellow product solution (3625 g) was then transferred to amber plastic bottles for storage. Analysis of the solution showed a pH of 12.2 and “active” bromine concentration of 14.7 wt%. The chemical reactions involved in Example 1 are as follows:



EXAMPLE 2**Dissolution of Gold in Dilute "Stabilized Bromine"**

[0085] "Stabilized Bromine" solution (10 mL) prepared in Example 1 was diluted with 90 mL of water and pH of the solution was decreased to 5 by adding 2 drops of hydrobromic acid. A piece of gold wire (8.1 mg) was dropped into this solution and stirred magnetically for 40 hours. Analysis of the resulting solution by ICP showed 77.9 ppm of Au -Recovery of gold = 96%.

EXAMPLE 3**Dissolution of Gold in Diluted Stabrom 909**

[0086] Commercial Stabrom[®] 909, 10 mL (Albemarle Corporation) was diluted with 90 mL of water and pH of the solution was brought down with hydrobromic acid to a value of 5. A piece of gold wire (5.9 mg) was dropped into the solution and magnetically stirred for 40 hours. The gold wire dissolved completely in the solution. ICP analysis of the solution showed 55.4 ppm of gold in the solution indicating 94% recovery of gold.

EXAMPLE 4**Leaching of Gold Ore with Stabrom 909**

[0087] A 5 g sample of the gold ore (DS-1 from Natural Resources Canada, containing 32.6 ppm of Au and 2.85 wt% S) was suspended in 20 g of water and magnetically stirred at room temperature. The probes for measuring pH and ORP (oxidation reduction potential) were immersed in the mixture. Stabrom 909 and sulfuric acid were continually added over a period of 6 hours while maintaining the pH of the mixture below 7 and ORP above 800mV. The mixture which has consumed 21.5 g of Stabrom 909 and about 8.5 g of sulfuric acid was then stirred overnight at room temperature. It was then filtered and the filtrate was analyzed by ICP. The analysis showed it had 3.0 ppm of Au indicating about 92% recovery of gold from the ore.

EXAMPLE 5**Regeneration of Used Leaching Solution**

[0088] A leaching solution (lixiviant solution) was used in a leaching operation for recovery of gold pursuant to this invention. The leaching agent used in that operation was produced as in Example 1. The resultant used leaching agent solution was colorless with

an ORP of 520 mV. To a 10g sample of that used solution was added about 100 mg of a 5% solution of sodium hypochlorite (bleach) and the resultant mixture was stirred. The solution immediately turned yellow and the ORP of the solution was found to have been increased to 840 mV.

EXAMPLE 6

Regeneration of Used Leaching Solution

[0089] A leaching solution (lixiviant solution) was used in a leaching operation for recovery of gold pursuant to this invention. The leaching agent used in that operation was produced as in Example 1. The resultant used leaching agent solution was colorless with an ORP of 520 mV. To a 10g sample of that used solution was added about 100 mg of trichloroisocyanuric acid (Trichlor) and the resultant mixture was stirred. The solution immediately turned yellow and the ORP of the solution was found to have been increased to 840 mV.

EXAMPLE 7

Regeneration of Used Leaching Solution

[0090] A leaching solution (lixiviant solution) was used in a leaching operation for recovery of gold pursuant to this invention. The leaching agent used in that operation was produced as in Example 1. The resultant used leaching agent solution was colorless with an ORP of 520 mV. To a 10g sample of that used solution was added about 100 mg of potassium peroxymonosulfate (Oxone) and the resultant mixture was stirred. The solution immediately turned yellow and the ORP of the solution was found to have been increased to 840 mV.

[0091] Example 8 below illustrates the effect of preferred mildly acidic to mildly basic pH levels on the performance of an aqueous leaching solution containing at least solvated N-bromosulfamate and solvated N-chlorosulfamate together with solvated alkali metal halide(s) in dissolving, leaching or extracting gold from a source material on contact between such solution and the gold in such source material pursuant to this invention. As noted above, concentrated forms of such solutions, available commercially as Stabrom[®] 909 biocide, Stabrom[®] Plus biocide, and Maxxis[®] biocide, have pH levels in the range of 12.4-14.0.

EXAMPLE 8**Dissolution of Gold in Diluted Stabrom 909**

[0092] A piece of gold wire (0.25 mm diameter; 6.2 mg weight) was dropped into a solution containing 50 ml of Stabrom 909 solution diluted with 50 ml of deionized water. The alkaline solution with the gold wire was stirred magnetically for 50 hours at room temperature. The gold wire did not dissolve. A sample of the solution was taken out for ICP analysis. The solution was then acidified by dropwise addition of 48% hydrobromic acid to a pH of 5 and stirred with the gold wire for 15 hours. The gold wire completely dissolved in the solution. A sample of the solution was analyzed by ICP. The ICP analysis of the sample before acidification indicated that <0.6 ppm of Au had dissolved. However, the ICP analysis after acidification showed that 50.4 ppm of Au had dissolved and thus a >98% recovery had been achieved. Thus in utilizing such solutions the pH is adjusted, preferably within a reasonably short period before use to a level of about 8 or below and preferably about 4 to about 8 and more preferably in the range of 4 to 7 and still more preferably in the range of 4 to 6.

[0093] Example 9 below demonstrates the efficacy of this invention in recovery of palladium in very high yields under suitable conditions. In fact, in this experimental work a 100% recovery was achieved.

EXAMPLE 9**Dissolution of Palladium in Dilute “Stabilized Bromine”**

[0094] “Stabilized Bromine” solution (10 mL) prepared in Example 1 was mixed with 1 gram of NaBr and diluted with 90 mL of water and pH of the solution was adjusted to 4 by adding a few drops of 48% hydrobromic acid. A piece of palladium wire (0.5 mm diameter; 99.9% purity) weighing 14 mg was dropped into this solution and magnetically stirred at room temperature. After stirring for 24 hours, a sample of the solution was analyzed by ICP. The analysis showed the solution had 93.5 ppm (67% recovery) of palladium. Stirring of the mixture was continued to 60 hours. A sample of the solution after 60 hours of stirring showed 141 ppm (100% recovery) of palladium.

EXAMPLE 10**Dissolution of Silver and Rhodium in “Stabilized Bromine”**

[0095] “Stabilized Bromine” solution (25 grams) prepared in Example 1 was mixed with 1 gram of NaBr and diluted with 25 mL of water and pH of the solution was adjusted to 4 by adding 48% hydrobromic acid. A piece of silver foil (0.025 mm thickness; 99.9% purity) weighing 17 mg, a piece of palladium wire (0.5 mm diameter; 99.9% purity) weighing 16 mg and 10 mg of rhodium black powder (99.9% purity) were dropped in to the stabilized bromine mixture and stirred for 60 hours at room temperature. A sample of the mixture was filtered through a syringe filter and the clear filtrate solution was analyzed by ICP. The analysis showed 66 ppm of silver (19% recovery), 326 ppm of palladium (100% recovery) and 3 ppm of rhodium (1.5% recovery).

[0096] The mixture was acidified to a pH of <1 by adding 10 grams of 48% hydrobromic acid and stirred for additional 40 hours. A sample of the mixture was filtered through syringe filter and the clear filtrate was analyzed for metals by ICP. The solution was found to contain 272 ppm of silver (96% recovery), 253 ppm of palladium (95% recovery) and 33 ppm of rhodium (20% recovery).

[0097] The above Examples illustrate further embodiments or features of this invention which comprise processes and compositions involving solutions containing precious metals including gold, palladium, silver, rhodium, or the like. Thus, one such embodiment is a process for forming a water-soluble form of such metals, the process comprising:

- A) forming or obtaining a composition comprising (i) an aqueous medium containing in the range of about 1 to about 100 grams/liter (preferably in the range of about 1 to about 10 grams/liter for gold and/or palladium and in the range of about 50 to about 75 grams/liter for silver and/or rhodium) of at least one solvated N-bromosulfamate compound and (ii) in the range of about 1 to about 100 grams/liter (preferably in the range of about 1 to about 20 grams/liter) of solvated sodium bromide and in the range of about 5 to about 400 grams/liter (preferably in the range of about 10 to about 200 grams/liter) of solvated sodium hydroxide;
- B) acidifying said composition with a mineral acid to form a lixiviant solution having a pH in the range of about 7.5 ± 0.5 or less (preferably a pH in the range of about 4 to about 6 for gold and/or palladium, and preferably a pH in the range of about 1 or less for silver and/or rhodium), and optionally diluting said lixiviant solution with water to provide a diluted solution having a reduced active bromine content

sufficient to leach gold, palladium, silver, and/or rhodium from a leachable source; and

- C) contacting said leachable source with said lixiviant solution whereby a leachate is formed containing gold, palladium, silver, and/or rhodium in solution, and optionally recovering leachate from the so-processed composition.

[0098] Another such embodiment is a composition comprising gold, palladium, silver, and/or rhodium in the form of a solute in an aqueous medium comprising (A) water, (B) at least one solvated N-bromosulfamate source, and (C1) solvated sodium bromide or (C2) solvated ammonium bromide or (C3) solvated alkaline earth metal bromide, or (C4) a combination of any two or all three of (C1), (C2), (C3), the solution having a pH in the range of about 7.5 ± 0.5 or less.

[0099] An experimental program was conducted by SGS Minerals, Canada for Albemarle Corporation. This experimental program was conducted using a rotating disk fabricated using a pure gold plate mounted in epoxy and attached to a Teflon rod, which was screwed into a rotating shaft. The surface of the gold was polished with grid 2000 sand paper, washed with acetone and rinsed with deionized water. The rotating disk was then inserted in the central port of a 500 mL glass reactor with 4 ports on the top. The other three peripheral ports were used for ORP and pH probes and for pumping pH mediator into the reactor or for sample removal for analysis. The rotation speed of disk was fixed at 500 RPM. The average leaching rates were determined by removing small volumes of solution at specified time intervals and measuring the dissolved metal content.

[0100] Leaching studies on sulphide minerals were conducted using pure minerals purchased from Ward's Natural Science collection and gold bearing mineral samples obtained from SGS Minerals. Mineral samples of pyrite (Peru, Huanzala), arsenopyrite (Huanggang Mine, Ulanhad League, Inner Mongolia, China) and chalcopyrite (Durango, Mexico), received from Ward's Natural Science collection, were ground and washed with deoxygenated water prior to testing. The pyrite sample was subjected to additional treatment in order to remove surface oxides. The treatment included washing with dilute hydrochloric acid followed by deoxygenated water and finally acetone.

[0101] The bench scale leaching set-up consisted of a 1000 mL baffled reactor and an overhead stirrer with a flat-bladed impeller. At the start of each test, 5 g of mineral was added to 250 mL of 10 g/L NaBr solution and placed in the reactor. The stirring speed was maintained at 375 RPM. The rate of addition of stabilized bromine was generally

synchronized with the redox controlled pumping system. The rate of oxidation of sulphide was estimated by analysing the kinetic solution samples for their sulphate content. The unreacted sulphide in the solids at the end of each test was also determined and the amount of sulphide oxidized was compared to the calculated amount based on the increase in sulphate concentration in solution. There was good agreement between the two methods of determining the extent of sulphide oxidation.

[0102] In the gold ore leaching experiments, predetermined amounts of solid feed and deionized water were added to the reactor and the pH was adjusted with dilute sulphuric acid. The solution potential was then controlled during leaching by the addition of bromine reagent, and samples were taken at intervals for analysis.

[0103] The gold analyses were performed using the fire assay method and the bromide content was quantitatively determined by Ion Chromatography. The copper, iron and arsenic concentrations were determined X-ray Fluorescence analysis. The sulphides were determined by Leco analysis. The concentration of bromine was estimated by titrating against thiosulphate in the presence of starch indicator.

[0104] The leaching agent used in this program was a concentrated aqueous solution containing 11-15 wt% active bromine and comprising solvated N-bromosulfamate, solvated sodium bromide, and solvated sodium hydroxide. The concentrated solution has a pH in the range of about 11 to about 13, and was diluted in water to the desired active bromine concentrations used in the testing operations. For convenience, the leaching agent is often referred to as stabilized bromine or as a “bromine/bromide lixiviant”.

[0105] Preferably the leaching solutions of this invention have an oxidation potential of >600 mV, more preferably >750 mV; and/or preferably an “active” halogen concentration of 0.5 g/L to 75 g/L, more preferably, 1 g/L to 10 g/L; and/or preferably a halide to “active” halogen ratio of 100/1 to 1/5, more preferably 10/1 to 1/1.

[0106] Methods for the determination for the concentration of active bromine are well known. A well-established method in the art for determining the amount of active bromine in a solution is starch-iodine titration, which determines all of the active bromine in a sample, regardless of what species may constitute the active bromine. A typical starch-iodine titration to determine active bromine is carried out as follows: A magnetic stirrer and 50 milliliters of glacial acetic acid are placed in an iodine flask. The sample (usually about 0.2-0.5 g) for which the active bromine is to be determined is weighed and added to the flask containing the acetic acid. Water (50 milliliters) and aqueous potassium iodide (15%

(wt/wt); 25 milliliters) are then added to the flask. The flask is stoppered using a water seal. The solution is then stirred for fifteen minutes, after which the flask is unstoppered and the stopper and seal area are rinsed into the flask with water. An automatic buret (Metrohm Limited) is filled with 0.1 normal sodium thiosulfate. The solution in the iodine flask is titrated with the 0.1 normal sodium thiosulfate; when a faint yellow color is observed, one milliliter of a 1 wt % starch solution in water is added, changing the color of the solution in the flask from faint yellow to blue. Titration with sodium thiosulfate continues until the blue color disappears. The amount of active bromine is calculated using the weight of the sample and the volume of sodium thiosulfate solution titrated. Thus, the amount of active bromine in a composition of this invention, regardless of actual chemical form, can be quantitatively determined. Such a method is described for example in Chapter XIV of Willard-Furman, *Elementary Quantitative Analysis*, Third Edition, D. Van Nostrand Company, Inc., New York, Copyright 1933, 1935, 1940.

[0107] Another method of determining active bromine especially at relatively low concentrations is the so-called DPD Method which uses N,N'-diethyl-p-phenylenediamine as the indicator in this titration method in which KI and a buffer are also used. This method is described in *Hach Water Analysis Handbook*, 3rd edition, copyright 1997. Although the method refers primarily to determination of "free chlorine" and "total chlorine" values i.e., "active chlorine" values, it can also be used for determination for active bromine values. To convert "free chlorine" and "total chlorine" values into "free bromine" and "total bromine" i.e., "active bromine" values, the respective value for "free chlorine" or "total chlorine" is multiplied by 2.25.

Rate of Gold Dissolution

[0108] The rate of gold dissolution was estimated at various Stabilized Bromine dosages and active bromine concentrations between 0.65 g/L and 38.4 g/L. The sodium bromide was added at a concentration of 9 to 10 g/L except for one test, where the addition of large volumes of acid, necessary to reach the target pH 4, diluted the sodium bromide concentration to ~5 g/L. The test conditions and experimental results are summarized in Table 1 and the rate of gold dissolution is plotted in Figure 1.

Table 1 - Varying Bromine Concentrations in Rotating Disk Gold Leaching Tests

Reagents	Test Conditions					Initial Rate	Final
	Au	Br ₂	NaBr	pH	E _H	Au	Br ⁻
	cm ²	g/L	g/L		V	mg cm ⁻² h ⁻¹	g/L
Neat Br ₂	0.60	0.75	10.0	4.2	1.11	6.53	8.3
Stab. Br ₂	0.41	0.65	9.83	4.6	1.06	1.39	8.8
Stab. Br ₂	0.62	1.47	9.82	4.2	1.07	1.59	9.3
Stab. Br ₂	0.62	6.93	9.25	4.1	1.07	2.48	13
Stab. Br ₂	0.62	12.9	8.60	4.1	1.04	3.45	18
Stab. Br ₂	0.62	38.4	5.12	4.0	1.04	9.22	35

[0109] The trend to a higher gold leaching rate with increasing Stabilized Bromine is evident. It is also evident that pure bromine achieved higher gold dissolution rates at lower reagent concentrations than Stabilized Bromine, presumably because the active bromine concentration was higher. The experimental technique developed in this project was validated by the observed gold dissolution rate of 6.5 mg/cm²/h with 0.75 g/L of pure bromine, which is close to published rates of 5.07 and 7.6 mg/cm²/h for bromine concentrations of 0.62 g/L and 0.93 g/L, respectively (Pesic and Sergent, 1991).

[0110] It is well known that the activity of bromine increases with the acidity of solution. Table 2 summarizes the results of tests run under similar conditions, but at different pH. In addition, a single test was run with cyanide under the same experimental conditions and at a similar reagent concentration, so that rates of gold leaching with bromine could be compared with the conventional gold leaching process. The kinetic plots are presented in Figure 2 and Figure 3.

Table 2 - Varying pH of Bromine Solution in Rotating Disk Gold Leaching Tests

Reagents	Test Conditions						Initial Rate	Final
	Au	Br ₂	NaBr	NaCN	pH	E _H	Au	Br ⁻
	cm ²	g/L	g/L	g/L		V	mg cm ⁻² h ⁻¹	g/L
Stab. Br ₂	0.62	6.93	9.25	-	4.1	1.07	2.48	13
Stab. Br ₂	0.62	12.9	8.60	-	4.1	1.04	3.45	18
Stab. Br ₂	0.62	12.8	8.45	-	6.0	1.02	0.06	17
Stab. Br ₂	0.60	14.1	9.40	-	3.3	1.14	17.1	-
NaCN	0.62	-	-	5.0	11	0.17	3.03	-

[0111] In order to show all three rates in a single graph (Figure 2), the gold dissolution values corresponding to pH 6 and pH 4 for illustration purposes were multiplied by 40 and 4, respectively. The test conducted at pH 6 produced very little gold dissolution, and a leach rate of only about 0.06 mg/cm²/h. The rates of gold dissolution increased to 3.45 mg/cm²/h when the leach solution was acidified to pH 4. The highest rate of gold dissolution (17.1 mg/cm²/h) was achieved with Stabilized Bromine at pH 3.

[0112] Rates of gold dissolution in cyanide and stabilized bromine are compared in Figure 3. The dissolution rate in cyanide was 3.03 mg/cm²/h which is in the same range as rate of gold dissolution achieved with Stabilized Bromine. However, whereas gold dissolution rates with cyanide are limited by the low solubility of oxygen in aqueous solution, the rate of gold leaching with bromine can be increased by increasing the concentration of active bromine in solution, as illustrated in Figure 3 (concentration of 12.9 g/L Stabilized Bromine). This study has determined a gold dissolution rate in cyanide of 3.03 mg/cm²/h, which is close to a rate of 3.25 mg/cm²/h under ideal conditions reported by Fleming (2012) and 2.88 mg/cm²/h reported by Marsden and House (2006).

[0113] In bromine/bromide medium, the gold is oxidized by bromine and stabilized by bromide as the gold bromide complex, in an electrochemical reaction represented by the half cell reactions below:



[0114] The thermodynamics of this system dictate that the stability region for gold bromide extends from acid to neutral pH at potentials between ~0.9-1.5 V vs. SHE, as depicted in Figure 4. This E_H-pH diagram was constructed for gold and bromide concentrations of 10⁻⁴ M and 10⁻¹ M, respectively. At lower gold concentrations, the stability region of gold bromide shifts towards more acidic region (not shown here).

[0115] According to the half cell reactions, the product of bromine reduction is the bromide ion. The data in Table 1 and Table 2 show the final bromide concentration is higher than the concentration of bromide added as the sodium salt at the start of the tests. If the difference is plotted against the amount of bromine consumed in the test, the production of bromide from added bromine may be correlated. This relationship has been plotted in Figure 5. Based on this approach, it appears that about 1.7 mol of bromide was produced from every mol of

bromine added as Stabilized Bromine, which is slightly less than the theoretical ratio of 2. The balance presumably represents bromine that was lost as unreacted vapour.

[0116] The plot of gold dissolution rates versus final bromide concentrations is shown in Figure 6. The data points lie closely to a single straight line with the slope of ~1.3, which is therefore the reaction order with respect to bromide concentration. By comparison, a reaction order of 1.4 for gold dissolution was estimated using a different type of bromine/bromide carrier, Geobrom 3400, in acidified solution (Pesic and Sergent, 1991).

[0117] In order to evaluate the effect of minerals on gold dissolution, tests were designed in such a way that both pure gold and the relevant mineral were rotating on separate shafts in a single reactor. Three minerals were independently mounted in epoxy disks of the same dimensions as the disks containing the pure gold sample. The test results are summarized in Table 3. The calculation of initial dissolution rates was based on the concentration of gold in the leach solution after 0.5 hour.

Table 3 - Rates of Gold Dissolution in the Presence of Sulphide and Oxide Minerals

Au & Minerals	Test Conditions					Initial Rate	Final Solution Composition			
	Au cm ²	Br ₂ g/L	NaBr g/L	pH	E _H V	Au mg cm ⁻² h ⁻¹	Au mg L ⁻¹	Fe mg L ⁻¹	Cu mg L ⁻¹	As mg L ⁻¹
Pure Gold	0.62	12.9	8.6	4.1	1.0	3.66	30.8			
Pyrite	0.62	14.2	9.4	3.9	1.0	5.37	13.5	2.32	-	-
Chalcopyrite	0.62	14.2	9.5	3.3	1.1	1.47	6.57	131	319	-
Copper Oxide	0.62	14.2	9.5	4.3	1.1	2.67	15.2	-	12.5	-
Arsenopyrite	0.62	13.8	9.2	4.2	1.1	2.97	18.2	0.13	-	<1

[0118] All minerals tested slowed the rate of gold dissolution after the first hour or so of leaching. The initial gold dissolution rate was actually enhanced in the presence of pyrite, but the rate then quickly levelled off, indicating some kind of passivation. A similar increase of the initial gold dissolution rate in the presence of pyrite was detected by Meersbergen et al (1993) while conducting electrochemical studies with both gold and pyrite rotating in the same reactor. Chalcopyrite was the most reactive mineral in acidified bromine, and slowed the gold leaching rate the most in all the tests, probably by consuming active bromine and leaving too little for effective gold leaching. The solution assays confirmed the highest copper and iron concentrations when chalcopyrite was used. In addition, some precipitate was detected in this solution.

Leaching of Pure Minerals

[0119] Pyrite oxidation was carried out at a constant potential. The pH was not controlled, but it was recorded periodically. It was observed that the oxidation reaction consumed bromine and produced acid. The consumption of bromine was higher at higher operating potential. The rate of sulphide oxidation was calculated from the rate of sulphate build up in the leach liquor, and is shown versus the rate of bromine consumption in Figure 8. Table 4 presents the test conditions and shows the amount of iron and sulphide reacted as a function of the amount of bromine consumed.

TABLE 4 - Pyrite Oxidation Tests

Conditions		mmol of species reacted			% reacted	
Br ₂ mmol	pH	E _H , V	Fe	S ⁻²	Fe	S ⁻²
119	2.5	1.00	14.5	29.9	33.7	39.6
196	2.0	1.10	26.7	48.5	62.0	64.2

[0120] According to the reaction below, the theoretical ratio for the mol of bromine consumed per mol of sulphide oxidized is 3.75.



[0121] The actual relationship between sulphide oxidized and bromine consumed is depicted in Figure 9. The linear relationship indicates the bromine consumption was close to the stoichiometric value of 3.75 in the first test (1.0 V). In the second test (1.1 V), slow purging of oxygen in the leach solution was applied to support the oxidation reaction, which might account for less bromine consumption and lower slope of sulphide oxidation shown in Figure 9.

[0122] Figure 10 maps the molar ratio of aqueous iron produced in solution versus bromine consumption, which should be 7.5 based on the equation above. All points lie above the theoretical line. This suggests that some of the leached iron oxidized to ferric, hydrolyzed and re-precipitated during the test. This is supported by the observation that the data points furthest from the theoretical line belong to the test (1.0 V) that was run at pH 2.5-2.2. The data points for the second test (1.10 V), which was conducted at pH 1.9-2.1 were situated closer to the line.

[0123] Two tests were run with the pure arsenopyrite sample using the same conditions as for the pyrite tests. However, the reactivity of arsenopyrite was low, and it was necessary to

add acid to about pH 4 before the potential reached the level needed for sulphide oxidation. The pH changed only slightly (0.5 unit) over the following four hours and the solution potential remained high, indicating that bromine was not reacting with the arsenopyrite. Very little acid was apparently produced in this test, and there was no increase in the concentration of sulphate in solution. It is possible that sulphide was oxidized only as far as elemental sulphur under the chosen experimental conditions.

[0124] In second test, the Stabilized Bromine solution was left at its natural pH of ~ 12, and although the solution potential was lower than in the previous test (~ 650 mV vs. SHE) it was evident that the arsenopyrite was significantly more reactive under these conditions. The test results are summarized in Table 5.

Table 5 - Arsenopyrite Oxidation Tests

Conditions		mmol of species reacted				% reacted		
Br ₂ mmol	pH	E _H , V	Fe	S ⁻²	As	Fe	S ⁻²	As
45	3.6	1.11	-	4.0	2.1	-	13.5	7.1
120	12	0.65	1.3	17.0	16.3	4.6	57.4	56

[0125] A brief study was made of the effect of stabilized bromine when evaluated with mixtures of arsenopyrite and pyrite. These results are summarized in Table 5A

TABLE 5A – Arsenopyrite + Pyrite Oxidation Tests

Conditions	mmol of species reacted		% reacted	
Br ₂ , mmol	S ⁻²	As	S ⁻²	As
144	20.6	2.6	47.0	44.7
151	20.2	3.0	46.5	20.7

[0126] The profile of arsenic dissolution as a function of bromine addition is depicted in Figure 11, which show that the solubility of arsenic increases with bromine concentration under alkaline conditions. It is difficult to make the same deduction for the test run a pH 3.6 since the addition of bromine in this test was curtailed due to the apparent inertness of arsenopyrite under acidic conditions.

[0127] Chalcopyrite reacted with bromine only after the addition of sulphuric acid lowered the pH to 2-3. The test summary is shown in Table 6. The amount of copper dissolved as a

function of bromine addition is depicted in Figure 12, showing a linear relationship. It is unclear, based on these results alone, whether sulphuric acid affects the reaction of copper with bromine or only initiates the solubilisation of copper as copper sulphate. A single point at pH 12 corresponding to an intermediate sample taken before the addition of acid, indicated that the copper from chalcopyrite does not dissolve in alkaline bromine.

TABLE 6 - Chalcopyrite Oxidation Tests

Conditions		mmol of species reacted				% reacted		
Br ₂ mmol	pH	E _H , V	Fe	S ⁻²	Cu	Fe	S ⁻²	Cu
119	2.2	1.00	8.3	22.7	17.8	31.4	45.0	67.8
141	2.7	1.01	0.5	38.0	20.5	1.8	75.2	78.1

Gold Leaching from Oxide and Sulphide Feeds

[0128] Several tests were conducted with an oxidized gold concentrate to investigate the effect of different variables. The tests were run with high and low bromine additions, at a fixed pH of 4. A further test was then run at a controlled pH of 6, controlling both the potential and pH by the addition of bromine reagent as required. In the final two tests, the sulphide concentration (of the oxidized sample) was increased to 1.56% and then to 3.15% by adding pure powdered pyrite to the feed concentrate. The test results are presented in Table 7 and gold leaching profiles are presented in Figure 13 and Figure 14.

Table 7 - Summary of Leaching Tests using the Oxidized Ore

Feed		Conditions				Consumption	Extraction	Residue	Oxidation
Au	S ⁻²	Br ₂	NaBr	pH	E _H	Br ₂	Au	Au	S ⁻²
g/t	%	kg/t	kg/t		mV	kg/t	%	g/t	%
50.0	0.6	192	50	3.7	1.03	66	92.4	3.82	-
50.0	0.6	13.1	50	6.0	1.06	4.0	86.8	7.19	-
50.0	0.6	11.0	50	3.2	1.02	6.9	88.3	5.90	-
49.0	1.6	149	50	2.3	1.09	148	85.7	6.11	73.0
47.3	3.2	643	50	2.3	1.10	455	91.3	4.00	77.8

[0129] Leaching the oxidized ore with an acidic bromine/bromide solution revealed that gold extraction was fairly insensitive to the amount of bromine added, increasing by only 4% when bromine addition was increased from 11 kg/t to 192 kg/t, as shown in Table 7. At low pH, the initial amount of gold dissolved was less sensitive to the duration of the

reaction than to bromine availability. Figure 13 depicts the rate of gold leaching under weakly acidic (pH 4) and near neutral (pH 6) conditions. The kinetics at neutral pH were slower, although the final gold extraction was almost the same. Adding pure pyrite did not change the gold leaching kinetics significantly (Figure 14), but bromine consumption was very high in these tests (Table 7). These results indicated that gold leaches and sulphide oxidizes simultaneously as long as sufficient bromine is added to the leach reactor to maintain the redox potential.

[0130] Several tests were conducted using a different oxidized material, which contained ~ 29 g/t Au. Cyanide leaching extracted 95.8% of the contained gold and bromine extracted 95.6% of the gold when the leach solution was acidified to pH 3.4. The consumption of bromine in this test was ~21 kg/t, which was very high in comparison to the consumption of 0.43 kg/t sodium cyanide. The consumption of bromine was reduced to 1.45 kg/t by running the test at pH 6. Gold extraction was still reasonable in this test, and peaked at 92.3% after 4 hours. However, the gold in solution decreased slowly after the first 4 hours, and extraction efficiency had dropped to 89.1% after 24 hours. The instability of the gold bromide complex in solution was probably caused by a lack of free bromine in solution after the first few hours of this test. The leaching kinetics are depicted in Figure 15 while the test conditions and results are summarized in Table 8.

Table 8 - Summary of Leaching Tests on Oxidized Ore

Conditions				Reagent addition					Reagent Consumption			Au		
Solids	pH	E _H	Res.Time	Br ₂	NaBr	H ₂ SO ₄	NaCN	CaO	Br ₂	NaCN	CaO	Extraction	Residue	Head
%		V	h	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	%	g/t	g/t
29	3.4	1.11	6	48.5	26.5	18.6	-	-	21.0	-	-	95.6	1.29	29.2
29	6.1	1.05	24	3.8	13.4	0.0	-	-	1.45	-	-	89.1	3.25	29.7
29	11	-	24	-	-	-	1.40	3.79	-	0.43	3.74	95.8	1.28	31.0

[0131] The sample that yielded the biggest difference in gold recovery between bromine and cyanide was a refractory gold ore in which most of the gold was locked in a sulphide mineral matrix. Cyanide leaching yielded only ~23% gold extraction, whereas ~ 70% of the gold was leached with bromine. In this case, the higher gold extraction with bromine resulted from the simultaneous oxidation of sulphide, which liberated some of the locked gold. Unfortunately, very high bromine consumption in this test (>500 kg/t) renders this option for processing this type of refractory gold ores very unattractive. The data are presented in Table 9 and leaching kinetics in Figure 16.

Table 9 - Summary of Leaching Tests on Refractory Ore

Conditions			Reagent addition					Reagent Consumption				Au	
Solids	pH	EH	Br ₂	NaBr	H ₂ SO ₄	NaCN	CaO	Br ₂	NaCN	CaO	Extraction	Residue	Head
%		V	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	kg/t	%	g/t	g/t
17.0	3.7	1.12	869	54	618	-	-	530	-	-	70.8	1.30	4.46
17.0	11.0	-	-	-	-	11.3	1.8	-	2.97	1.61	23.8	3.32	4.18

[0132] One possible application of stabilized bromine leaching would be in the treatment of oxidized copper/gold ores. The copper in oxidized copper/gold ores reacts readily with cyanide and consumes about 4 mole of cyanide for every mole of copper leached (~3 kg NaCN per kg Cu). This can render the processing of such ores with cyanide uneconomic. By contrast, the copper in oxidized copper/gold ores is fairly inert in a bromine/bromide leaching medium, and there is a possibility that this process will enjoy lower reagent consumption than cyanide. To test this, an ore was prepared by mixing a copper oxide ore and an oxidized gold ore, and samples of the blended feed were treated with both bromine/bromide and cyanide. The leaching of both copper and gold were monitored, as well as reagent consumptions, and the data are presented in Table 10.

Table 10 - Summary of Leaching Tests on Copper Oxide Ore

		Sample 1	Sample 2
Conditions	Solids	17%	17
	pH	5.6	11
	ORP	0.98	--
Reagent Addition	Br ₂	36.9 kg/t	--
	NaBr	50.0 kg/t	--
	NaCN	--	34.0 kg/t
	CaO	--	4.3 kg/t
Reagent Consumption	Br ₂	20.3 kg/t	--
	NaCN	--	23.9 kg/t
	CaO	--	23.9 kg/t
Au	Extraction	85.4%	85.3%
	Residue	2.31 g/t	1.93 g/t
	Head	15.7 g/t	14.6 g/t
Cu	Extraction	20.4%	76.6%
	Residue	0.86 %	0.21 %
	Head	1.06 %	0.97 %

[0133] The above results are favorable in that only ~20% of the copper leached in the bromine/bromide lixiviant, whereas ~77% of the copper leached in cyanide, with a very

high cyanide consumption of 24 kg NaCN/t. Gold extraction was similar in both tests (~85%).

[0134] In accordance with this invention, it was found in additional test work that the stabilized bromine lixiviant of this invention is especially effective when applied to extraction of gold from cyanide-robbing ores, such as copper containing ores. Additional tests involving use of oxidized copper-containing gold ore further demonstrated such highly desirable performance. These gold extraction tests and the results therefrom are summarized in Table 11 and are presented in Figs. 17 and 18.

Table 11
Extraction of Copper-Containing Gold Ore With Stabilized Bromine Lixiviant

pH	Au Concentration	Cu Content	Br ₂ Consumption	Au Extracted	Cu Extracted
5.7	7 g/t	0.8%	21.4 kg/t	91.1%	1.7%
4.1	7 g/t	0.8%	21.6 kg/t	85.1%	56.4%
5.2	7 g/t	0.4%	14.8 kg/t	87.6%	8.2%

[0135] A direct comparison of the superior performance of stabilized bromine as compared to cyanide in extracting gold from high copper ores is demonstrated by the results shown in Table 11A.

TABLE 11A – Direct Comparison of Stabilized Lixiviant versus Cyanide

pH	Au Concentration	Cu Content	Reagent Consumption	Au Extracted	Cu Extracted
5.6	15 g/t	1.01%	20.3 kg/t Br ₂	85.4%	20.4%
11	15 g/t	1.01%	23.9 kg/t NaCN	85.3%	76.6%

[0136] As noted above there are various ways of recovering the precious metal from the pregnant solution. Experimental work in accordance with this invention examined the efficacy of several such recovery methods. One method examined was use of adsorption material to adsorb the precious metal so that it could be readily isolated from the pregnant solution. The results of such tests are summarized in Table 12.

Table 12 – Gold Adsorption From a Pregnant Solution

Adsorbent	Adsorbent Type	Assays		Distribution	
		Adsorbent g/t	Solution mg/L	Adsorbent %	Solution %
	Fresh Adsorbents				
A 500	Strong base resin	18829	1.99	91.2	8.8
Aurix 100	Weak base resin	18754	4.53	79.2	20.8
	Spent Adsorbents				
A 500	Strong base resin	18289	1.75	92.1	7.9
Aurix 100	Weak base resin	17557	4.60	79.7	20.3
XAD-4	non-anionic resin	12733	9.52	53.4	46.6
Act. Carbon	Activated carbon	10683	3.51	80.1	19.9
Reillex 425	Weak base resin	24970	3.93	83.7	16.3
Smopex 105	Weak base resin(fiber)	18375	0.18	99.3	0.7

[0137] Laboratory experiments have shown that effective adsorption of gold from the pregnant solutions formed from use of stabilized bromine leaching can be effectively achieved by the different adsorbents. Among the adsorbents tested, it was found that A-500 gave exceptionally high rates of adsorption as shown in Adsorption Isotherm Tables 13, 14, and 15 and as set forth in Figure 19.

TABLE 13

Carbon – pH 2.4, ORP 714 Mv, Br₂ 1.26 g/L		
Solution/carbon	Au, mg/L	Cu, mg/L
	15.6	950
34	0.01	736
135	0.02	886
676	0.36	935
1327	2.12	933
1970	4.45	947

TABLE 14

A-500 resin –pH 1.8, ORP 796 mV, Br₂ 1.23 g/L		
Solution/A-500 resin	Au, mg/L	Cu, mg/L
	16.8	870
33	0.01	858
134	0.03	984
671	0.31	940
1360	1.12	933
2058	2.17	925

TABLE 15

Aurix 100 resin –pH 1.9, ORP 780 mV, Br₂ 1.23 g/L		
Solution/Aurix 100 resin	Au, mg/L	Cu, mg/L
	16.8	870
33	0.03	849
132	0.10	889
652	0.89	920
1309	3.80	906
1926	6.93	933

[0138] Additional experimental studies established that gold from use of stabilized bromine leachants can be effectively recovered from various solid adsorbents followed by use of appropriate eluent solutions. This data is shown in Tables 16-18 and in Figure 20. It will be noted that of the adsorbents tested, the combination of thiourea with A-500 gave the highest recovery.

TABLE 16

0.1M Thiourea, 1M H₂SO₄, 2BV/h, 22°C			
Adsorbent	% Au eluted	Au	
		Initial, g/t	Residual, g/t
A-500 Strong base resin	97.5	8970	225

TABLE 17

0.1M NaCN, 2M NaOH, 2BV/h, 60°C			
Adsorbent	% Au eluted	Au	
		Initial, g/t	Residual, g/t
Aurix 100 Weak base resin	85.5	7951	1126

TABLE 18

0.2M NaCN, 1M NaOH, 4BV/h, 90°C			
Adsorbent	% Au eluted	Au	
		Initial, g/t	Residual, g/t
Activated Carbon	77.1	8071	1783

[0139] Preliminary experiments have indicated that regeneration of bromine by electrolytic oxidation of bromide ions offers promise as an effective way of regenerating used stabilized bromine lixiviant. This is illustrated by the data shown in Table 19.

TABLE 19 – REGENERATION OF BROMINE BY ELECTROLYSIS

Current 10 A, 25°C							
Conditions			Solution Composition				Current
Time min	pH	ORP mV	Br- mg/L	BrO ₃ mg/L	Br ₂ titration (1) as is	Br ₂ titration (2) acidified	Efficiency %
0	5.4	601	24000				
30	-	-	-	206	467		
60	10.3	987	15578	2130	438	12390	49.1
0	5.4	539	35000				
30			-	311	425		
60	10.4	983	-	2070	449	12420	48.8

[0140] In accordance with this invention, the use of one or more solvated N-halosulfamate sources and at least one solvated alkali metal halide, at least one solvated ammonium halide or at least one solvated alkaline earth metal halide, or a combination of any two or all three of these as the lixiviant, preferably involves utilization of additional operations in an overall integrated process for the recovery of gold. A preferred overall integrated process of this

invention is depicted in Figure 21. As shown, there are four operations labeled as “Leaching Process”, “Gold Recovery”, “Conversion by Electrolysis”, and “Leachant Makeup”. The “Leaching Process” represents the processes and resultant compositions formed in the leaching processes. The “Gold Recovery” represents adsorption and elution operations referred to and described herein such as carbon in pulp (CIP), or carbon in leach (CIL), or resin in pulp (RIP), or resin in leach (RIL). The “Conversion by Electrolysis” represents the electrolytic regeneration of the bromine lixiviant for reuse. The “Leachant Makeup” represents the reuse of bromine lixiviant as well as use of additional makeup lixiviant. Accordingly, the integrated process as a whole is as set forth in the foregoing specification, appended claims and Figures.

[0141] Thus, pursuant to another embodiment of this invention there is provided an integrated process for the recovery of the precious metal, especially gold, from a precious metal source (especially a gold source), which process comprises:

- A) extracting the precious metal (especially gold) in at least one dissolved form from at least one source material containing at least water-contactable precious metal (especially containing water-contactable gold), which process comprises contacting said source material with an aqueous leaching solution comprising (i) water, (ii) at least one solvated N-bromosulfamate source, and optionally at least one solvated N-chlorosulfamate source, (iii) solvated sodium bromide and optionally sodium chloride thereby producing a pregnant product solution containing gold in solvated form and a residual source material in the forms of solids;
- B) separating said solids and said pregnant product solution from each other;
- C) passing said pregnant product solution through at least one solid adsorbent to remove the precious metal (especially gold) complex from the solution resulting in a barren leaching solution (*i.e.*, a leaching solution from which the precious metal (especially gold) has been removed), the barren leaching solution containing halide ions; and
- D1) recovering the precious metal (especially gold) from said at least one solid adsorbent by contacting said adsorbent with an elution solvent to obtain a concentrated precious metal (especially gold) solution; and
- D2) electrolyzing the barren leaching solution to oxidize the halide ions and regenerate the aqueous leaching solution (active lixiviant solution) for re-use.

[0142] If desired, the aqueous leaching solutions of this invention may be used in combination with other known precious metal lixiviants such as, for example, 1,3-dibromo-

5,5-dialkylhydantoins (*e.g.*, 1,3-dibromo-5,5-dimethylhydantoin) and/or N,N'-bromochloro-5,5-dialkylhydantoins (*e.g.*, N,N'-bromochloro-5,5-dimethylhydantoin).

[0143] As used herein, the term "about" modifying the quantity of an ingredient in the compositions of the invention or employed in the methods of the invention refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use solutions in the real world; through inadvertent error in these procedures; through differences in the manufacture, source, or purity of the ingredients employed to make the compositions or carry out the methods; and the like. The term "about" also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term "about", the claims include equivalents to the quantities.

[0144] The invention may comprise, consist, or consist essentially of the materials and/or procedures recited herein.

[0145] Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, the description or a claim to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

[0146] This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove.

CLAIMS:

1. A process for extracting at least one precious metal in at least one dissolved form from at least one source material containing at least one precious metal, which process comprises contacting said source material with an aqueous leaching solution comprising (A) water, (B) at least one solvated N-halosulfamate source, and (C1) at least one solvated alkali metal halide or (C2) at least one solvated ammonium halide or (C3) at least one solvated alkaline earth metal halide, or (C4) a combination of any two or all three of (C1), (C2), (C3).

2. A process as in Claim 1 wherein (B) comprises at least one solvated N-bromosulfamate source, and wherein (C) is (i) at least one solvated alkali metal bromide, or (ii) at least one solvated ammonium bromide, or (iii) at least one solvated alkaline earth metal bromide; or (iv) a combination of any two or all three of (i), (ii), (iii), said aqueous leaching solution being a bromine-containing solution that is chlorine-free, iodine-free, and fluorine-free, and also chloride-free, iodide-free, and fluoride-free.

3. A process as in Claim 1 wherein (B) comprises at least one solvated N-bromosulfamate source and at least one solvated N-chlorosulfamate source, and wherein (C) comprises:

- (i) at least one solvated alkali metal bromide, or
- (ii) at least one solvated ammonium bromide, or
- (iii) at least one solvated alkaline earth metal bromide, or
- (iv) a combination of any two or all three of (i), (ii), (iii) and
- (v) at least one solvated alkali metal chloride, or
- (vi) at least one solvated ammonium chloride, or
- (vii) at least one solvated alkaline earth metal chloride, or
- (viii) a combination of any two or all three of (v), (vi), (vii)

said aqueous leaching solution being a bromine- and chlorine-containing solution that is fluorine-free and iodine-free and also fluoride-free and iodide-free.

4. A process as in Claim 1 wherein (B) comprises solvated sodium bromosulfamate and (C) comprises solvated sodium bromide.

5. A process as in Claim 1 wherein (B) comprises solvated sodium bromosulfamate and solvated sodium chlorosulfamate and (C) comprises solvated sodium bromide and solvated sodium chloride.

6. A process as in Claim 5 wherein said aqueous leaching solution further comprises solvated sodium sulfamate.
7. A process as in Claim 1 wherein (B) comprises solvated sodium bromosulfamate, solvated sodium chlorosulfamate, solvated potassium bromosulfamate, and solvated potassium chlorosulfamate.
8. A process as in Claim 7 wherein said aqueous leaching solution further comprises solvated sodium sulfamate and solvated potassium sulfamate.
9. A process which comprises regenerating the aqueous leaching solution chemically or electrolytically from a used aqueous leaching solution formed by the process of any of Claims 1-8 and employed in extracting at least one of said precious metals from a source thereof.
10. A process as in Claim 9 where the regenerating is effected by contacting the used aqueous leaching solution with a chemical oxidant selected from the group consisting of potassium peroxymonosulfate, sodium hypochlorite, chlorine, and trichloroisocyanuric acid.
11. A process as in any of Claims 1-8 wherein said aqueous leaching solution has a pH in the range of about 7.5 ± 0.5 or less.
12. A process as in Claim 11 wherein said precious metal comprises gold, palladium, silver, or rhodium or any mixture of any two or more of these metals.
13. A process as in Claim 12 wherein said precious metal comprises gold or palladium or a mixture thereof, and wherein said pH is in the range of about 4 to about 6.
14. A process as in Claim 12 wherein said precious metal comprises silver or rhodium or a mixture thereof and wherein said pH is in the range of 1 or less.
15. A process as in Claim 11 wherein the precious metal is gold or palladium or both, wherein the aqueous leaching solution has dissolved therein as a solution a precious metal selected from gold or palladium or both, and at least one dissolved metal other than gold or palladium, wherein (B) comprises at least one solvated N-bromosulfamate source, wherein (C) comprise solvated sodium bromide or solvated ammonium bromide or solvated alkaline earth metal bromide or a combination of any two or all three of these, and wherein the solution has a pH in the range of about 4 to about 6.
16. A composition comprising at least one precious metal in the form of a solute in an aqueous medium comprising (A) water, (B) at least one solvated N-halosulfamate source, and (C) at least one solvated alkali metal halide or at least one solvated ammonium halide or

at least one solvated alkaline earth metal halide, or a combination of any two or all three of these.

17. A composition as in Claim 16 wherein (B) comprises at least one solvated N-bromosulfamate source, and wherein (C) is (i) at least one solvated alkali metal bromide, or (ii) at least one solvated ammonium bromide, or (iii) at least one solvated alkaline earth metal bromide; or (iv) a combination of any two or all three of (i), (ii), (iii), said aqueous medium being a bromine-containing solution that is chlorine-free, iodine-free, and fluorine-free, and also chloride-free, iodide-free, and fluoride-free.

18. A composition as in Claim 16 wherein (B) comprises at least one solvated N-bromosulfamate source and at least one solvated N-chlorosulfamate source, and wherein (C) comprises:

- (i) at least one solvated alkali metal bromide, or
- (ii) at least one solvated ammonium bromide, or
- (iii) at least one solvated alkaline earth metal bromide, or
- (iv) a combination of any two or all three of (i), (ii), (iii) and
- (v) at least one solvated alkali metal chloride, or
- (vi) at least one solvated ammonium chloride, or
- (vii) at least one solvated alkaline earth metal chloride, or
- (viii) a combination of any two or all three of (v), (vi), (vii)

said composition being a bromine- and chlorine-containing solution that is fluorine-free and iodine-free and also fluoride-free and iodide-free.

19. A composition as in Claim 16 wherein (B) comprises at least one solvated N-bromosulfamate source, wherein (C) comprises solvated sodium bromide, and wherein said composition optionally comprises (D) solvated sodium sulfamate.

20. A composition as in Claim 19 wherein (B) comprises both said at least one solvated N-bromosulfamate source and at least one solvated N-chlorosulfamate source, and wherein (C) comprises both said solvated sodium bromide and solvated sodium chloride.

21. A composition as in Claim 16 wherein (B) comprises solvated sodium bromosulfamate and (C) comprises solvated sodium bromide.

22. A composition as in Claim 16 wherein (B) comprises solvated sodium bromosulfamate and solvated sodium chlorosulfamate and (C) comprises solvated sodium bromide and solvated sodium chloride.

23. A composition as in Claim 22 wherein said composition further comprises solvated sodium sulfamate.
24. A composition as in Claim 22 wherein said composition further comprises solvated sodium sulfamate and solvated potassium sulfamate.
25. A composition as in Claim 16 wherein (B) comprises solvated sodium bromosulfamate, solvated sodium chlorosulfamate, solvated potassium bromosulfamate, and solvated potassium chlorosulfamate.
26. A composition as in any of Claims 16-25 wherein said aqueous medium has a pH in the range of about 7.5 ± 0.5 or less.
27. A composition as in Claim 26 wherein said precious metal comprises gold, palladium, silver, or rhodium or any mixture of any two or more of these metals.
28. A composition as in Claim 27 wherein said precious metal comprises gold or palladium or a mixture thereof and wherein said pH is in the range of about 4 to about 6.
29. A composition as in Claim 27 wherein said precious metal comprises silver or rhodium or a mixture thereof and wherein said pH is in the range of 1 or less.
30. A composition as in Claim 26 wherein the precious metal is gold or palladium or both of them, wherein said composition contains at least one solvated metal other than gold or palladium, wherein (B) comprises at least one solvated N-bromosulfamate source, wherein (C) comprises solvated sodium bromide or solvated ammonium bromide or solvated alkaline earth metal bromide, or a combination of any two or all three of these, and wherein said pH is in the range of about 4 to about 6.
31. A composition as in Claim 16 wherein the precious metal is palladium, wherein (B) comprises at least one solvated N-bromosulfamate source, wherein (C) comprises solvated sodium bromide or solvated ammonium bromide or solvated alkaline earth metal bromide, or a combination of any two or all three of these, and wherein the composition has a pH in the range of about 7.5 ± 0.5 or less.
32. A process for forming a water-soluble form of at least one precious metal, the process comprising:
- A) forming or obtaining a composition comprising an aqueous medium containing (i) at least one solvated N-halosulfamate compound and (ii) at least one solvated alkali metal halide, and/or at least one solvated ammonium halide and/or at least one solvated alkaline earth metal halide;

- B) acidifying said composition with a mineral acid to form a lixiviant solution having a pH in the range of about 7.5 ± 0.5 or less, and optionally diluting said lixiviant solution with water to provide a diluted lixiviant solution having a reduced active bromine content sufficient to leach the precious metal from its source; and
 - C) contacting a precious metal-containing source material with said lixiviant solution or diluted lixiviant solution whereby a leachate is formed containing in solution said at least one precious metal, and optionally recovering leachate from the solution.
33. A process as in Claim 32 wherein (i) comprises at least one solvated N-bromosulfamate compound and at least one solvated N-chlorosulfamate compound.
34. A process as in Claim 33 wherein (ii) comprises at least one solvated sodium halide.
35. A process as in Claim 32 wherein at least one solvated N-bromosulfamate compound comprises (i), and wherein (ii) comprises at least one solvated sodium halide and/or solvated potassium halide (preferably solvated sodium bromide and/or solvated potassium bromide and/or solvated ammonium bromide, or a mixture of any two or all three of these).
36. A process as in Claim 35 wherein (ii) comprises at least one solvated sodium halide and at least one solvated potassium halide.
37. A process as in Claim 35 wherein (ii) comprises solvated sodium bromide or solvated potassium bromide, or solvated sodium bromide and solvated potassium bromide.
38. A process as in Claim 35 wherein the precious metal is gold, wherein (i) is an aqueous medium containing about 11 to about 15 wt% active bromine comprising solvated N-bromosulfamate, solvated sodium bromide, and solvated sodium hydroxide, to provide a composition having a pH in the range of about 10 to about 14.
39. A process as in Claim 35 wherein (i) contains in the range of about 1 to about 100 grams/liter of at least one solvated N-bromosulfamate compound, (ii) contains in the range of about 1 to about 100 grams/liter of solvated sodium bromide, and in the range of about 5 to about 400 grams/liter of solvated sodium hydroxide.
40. A process as in Claim 39 wherein the precious metal is gold, palladium, silver, rhodium or any mixture of any two or more of these metals.
41. A process for extracting at least one precious metal or a base metal from a source material containing said metal, which process comprises contacting said source material with an aqueous leaching solution containing a leaching agent comprising at least one

solvated alkali metal halosulfamate, thereby producing an aqueous leachate-containing said metal in dissolved form.

42. A process as in Claim 41 wherein said alkali metal halosulfamate is selected from the group consisting of sodium bromosulfamate, potassium bromosulfamate, lithium bromosulfamate, sodium chlorosulfamate, potassium chlorosulfamate, lithium chlorosulfamate, sodium iodosulfamate, potassium iodosulfamate, lithium iodosulfamate, sodium fluorosulfamate, potassium fluorosulfamate, and lithium fluorosulfamate.

43. A process as in Claim 42 wherein any two or more of said alkali metal halosulfamates is used in the process.

44. A process as in Claim 42 wherein said alkali metal halosulfamate is sodium bromosulfamate.

45. A process for extracting at least one precious metal from a material containing or composed of at least one of said precious metals in leachable form and optionally at least one base metal in leachable form, the process comprising:

- A) forming or obtaining a composition comprising an aqueous medium containing (i) at least one solvated N-halosulfamate compound and (ii) at least one solvated alkali metal halide, and/or at least one solvated ammonium halide and/or at least one solvated alkaline earth metal halide;
- B) acidifying said composition with a mineral acid to form a lixiviant solution having a pH in the range of about 7.5 ± 0.5 or less, and optionally diluting said lixiviant solution with water to provide a diluted lixiviant solution having a reduced active bromine content sufficient to leach said precious metal from its source;
- C) contacting said material or source material with said lixiviant solution or diluted lixiviant solution at a pH resulting in formation of a leachate containing said at least one precious metal and optionally at least one base metal; and
- D) recovering leachate from the solution.

46. An integrated process for recovery of gold from a gold source, which process comprises:

- A) extracting gold in at least one dissolved form from at least one source material containing at least water-contactable gold, which process comprises contacting said source material with an aqueous leaching solution comprising (i) water, (ii) at least one solvated N-bromosulfamate source, and optionally at least one solvated N-chlorosulfamate source, (iii) solvated sodium bromide and optionally sodium

chloride thereby producing a pregnant product solution containing gold in solvated form and a residual source material in the forms of solids;

- B) passing said pregnant product solution through at least one solid adsorbent to remove the gold from the solution, and also producing a barren leaching solution containing halide ions;
- C) recovering gold from said solid adsorbent either by contacting the adsorbent with an eluting solution or by incinerating the adsorbent, and
- D) oxidizing the halide ions in the barren leaching solution by electrolysis to regenerate the aqueous leaching solution for re-use.

47. A process which comprises preforming or generating *in situ* at least one N-halosulfamate by chemically or by electrolytically oxidizing at least one halide source in presence of at least one sulfamate source selected from sulfamic acid or a water soluble salt of sulfamic acid.

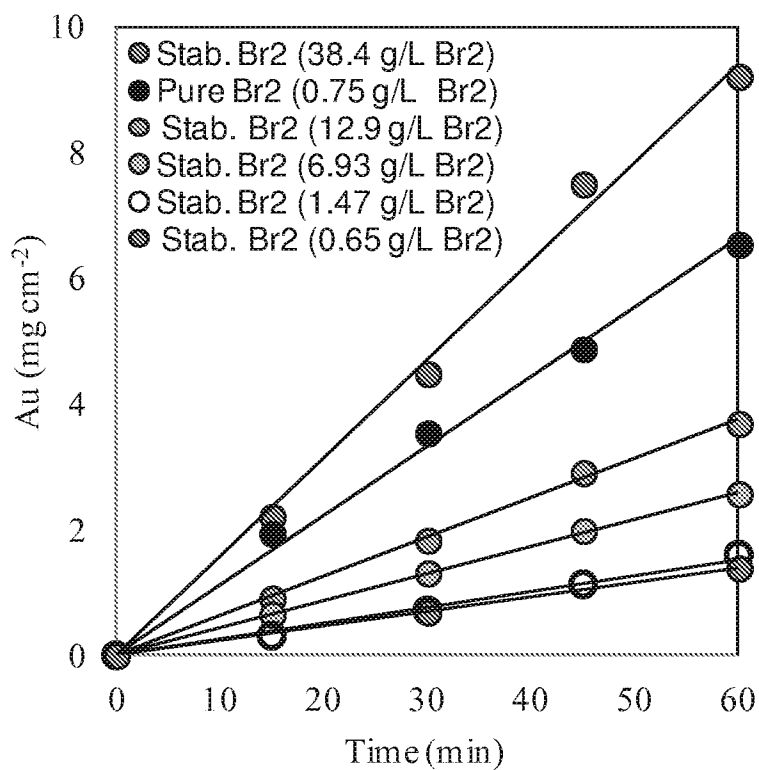


Figure 1 – Rates of Gold Dissolution at Various Bromine Concentrations

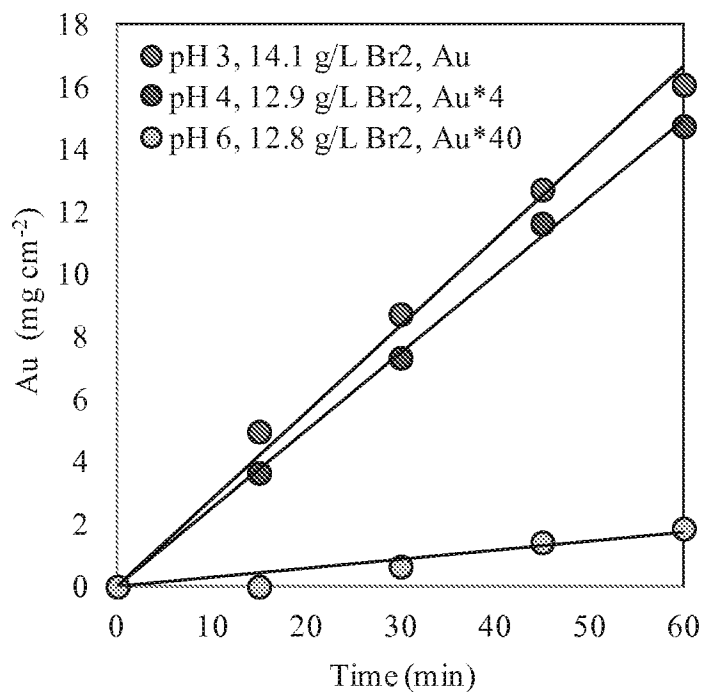


Figure 2 – The effect of pH on the Dissolution of Gold in a Bromine/Bromide Lixiviant

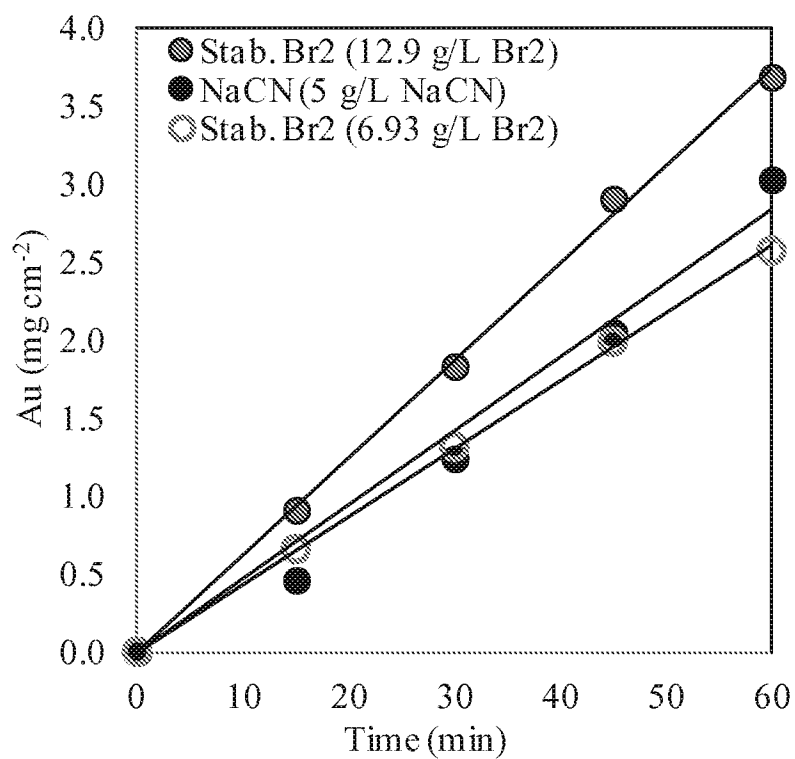


Figure 3 – Rates of Gold Leaching with Bromine/Bromide and Cyanide

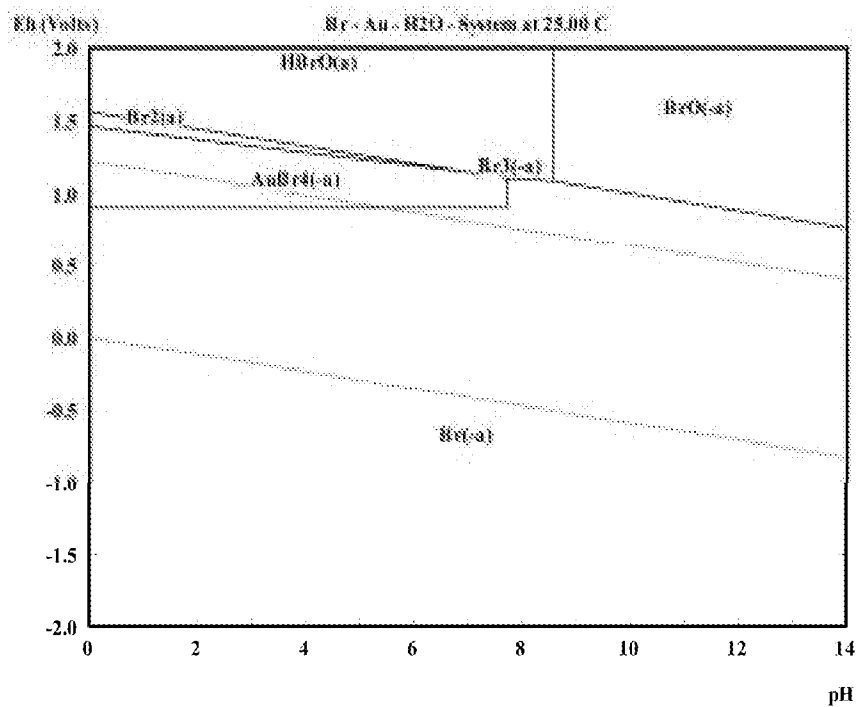


Figure 4- EH-pH Diagram by HSC

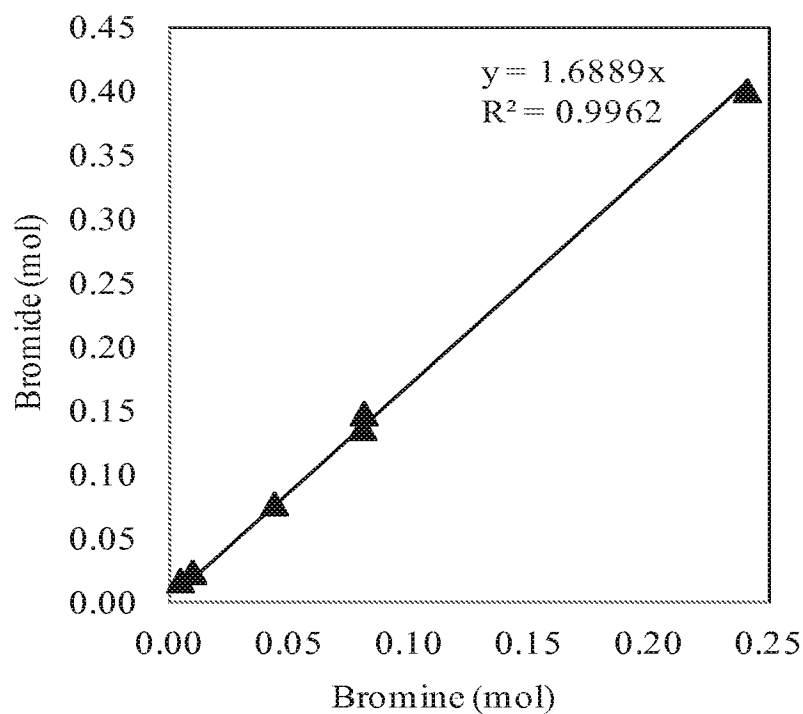


Figure 5 - The Relationship between Bromine addition and Bromide Production

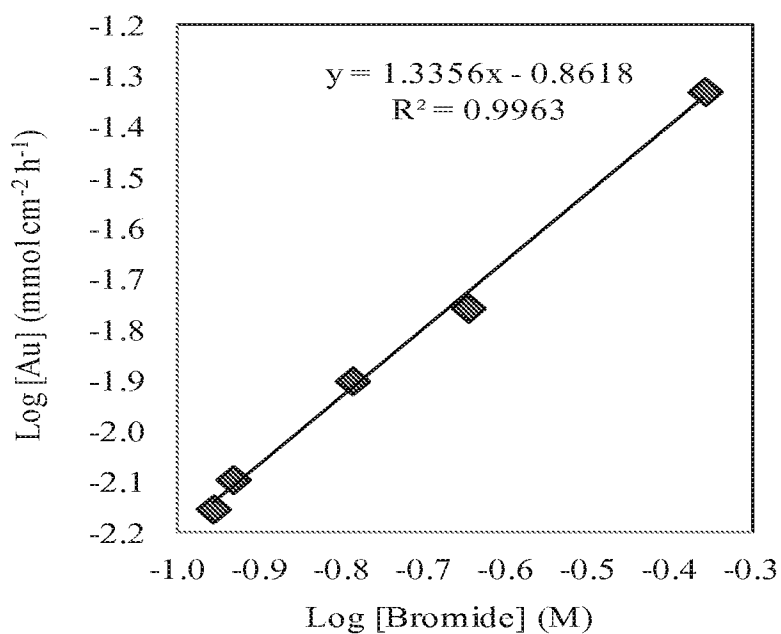


Figure 6 - The Rate of Gold Dissolution as a function of Total Bromide Concentration

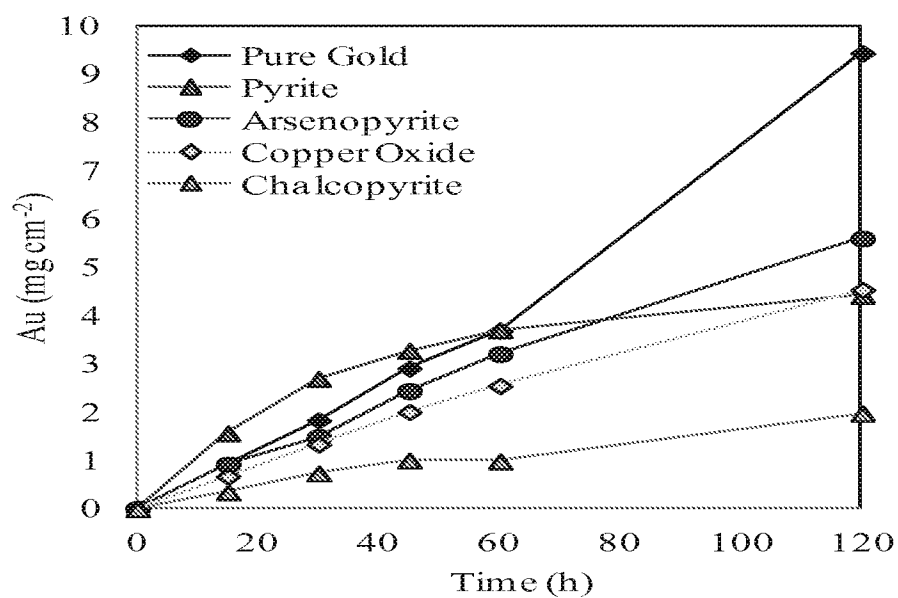


Figure 7- The Effect of Different Minerals on the Rate of Gold Dissolution

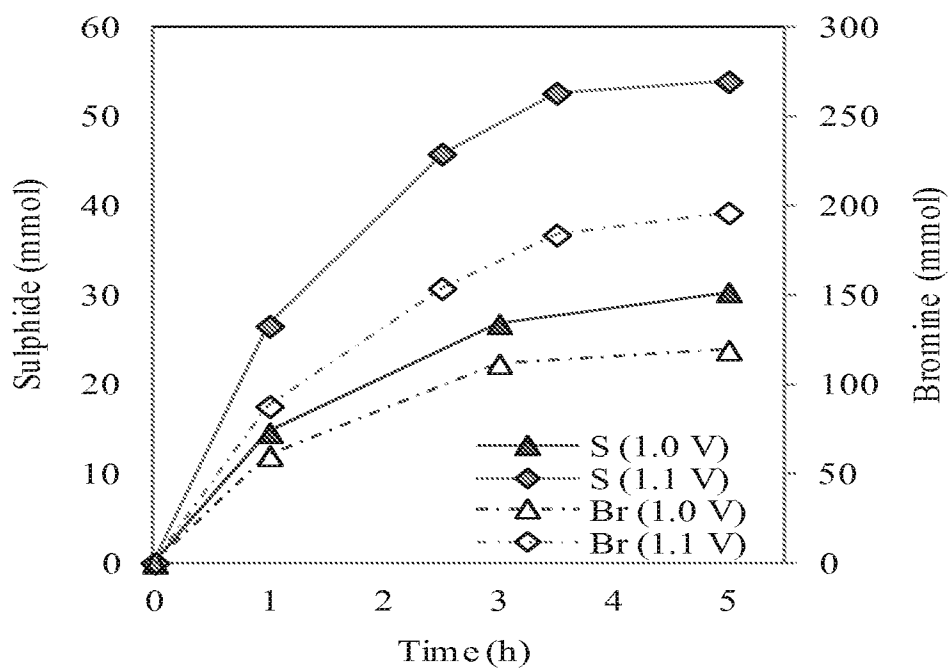


Figure 8 - Rates of Pyrite Oxidation and Bromine Consumption

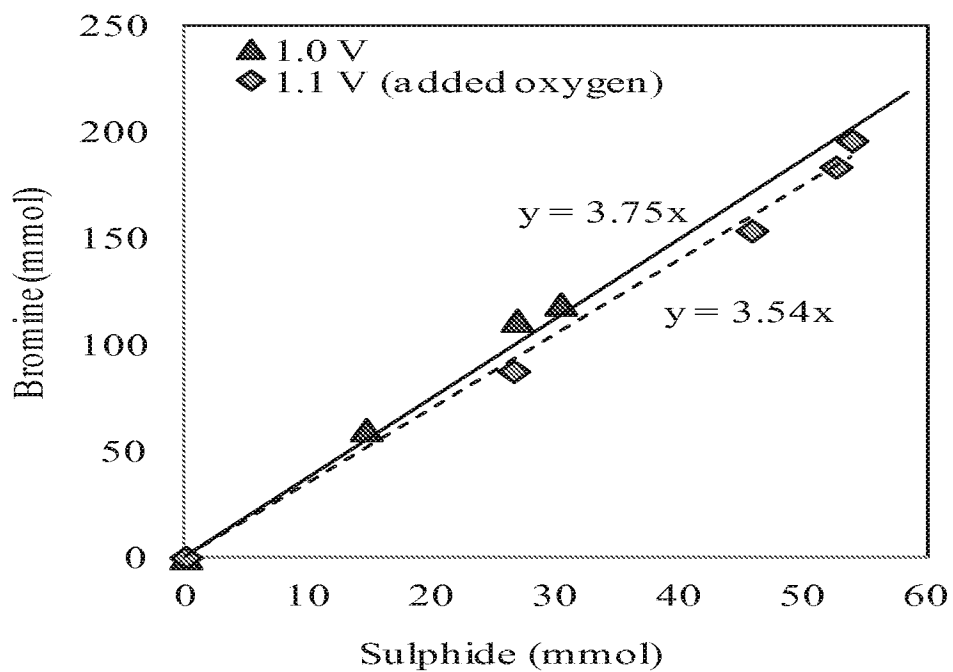


Figure 9 - Molar Ratio of Bromine Consumed and Sulphide Oxidized during Pyrite Oxidation

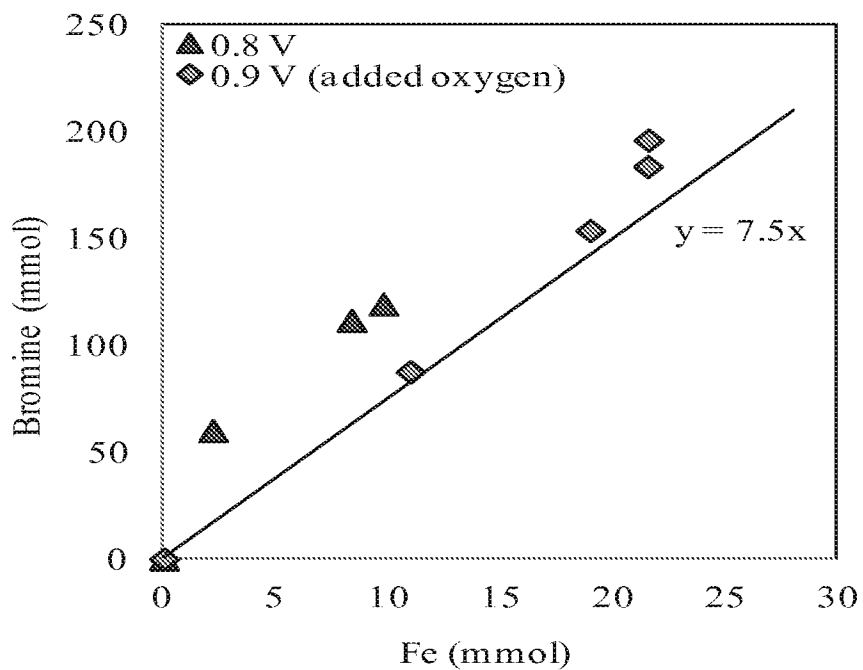


Figure 10 - Molar Ratio of Bromine Consumed and Iron Dissolved during Pyrite Oxidation

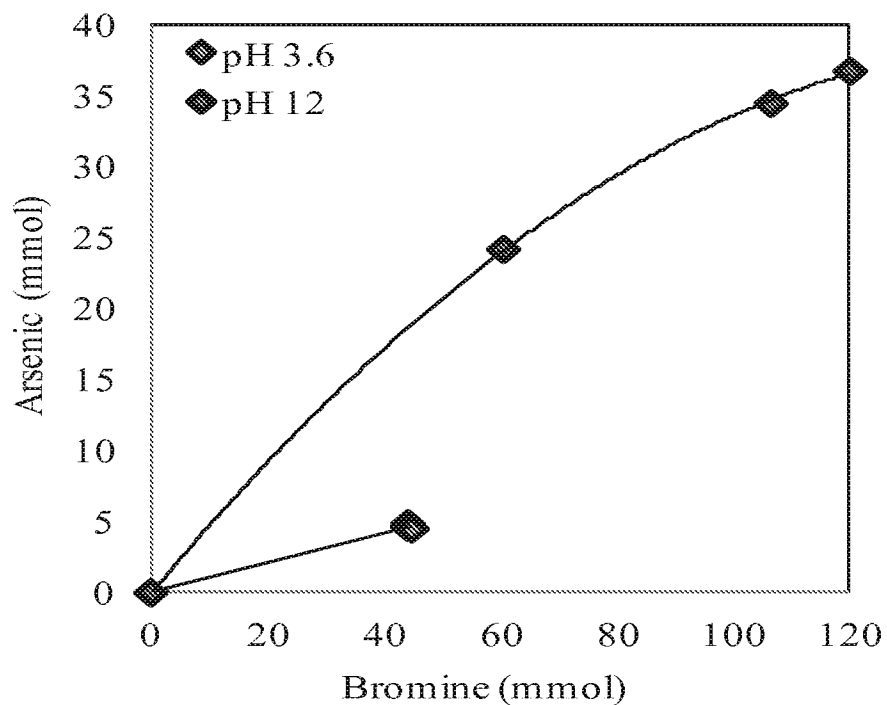


Figure 11 - Arsenic Extraction vs. Added Bromine in Arsenopyrite Oxidation Tests

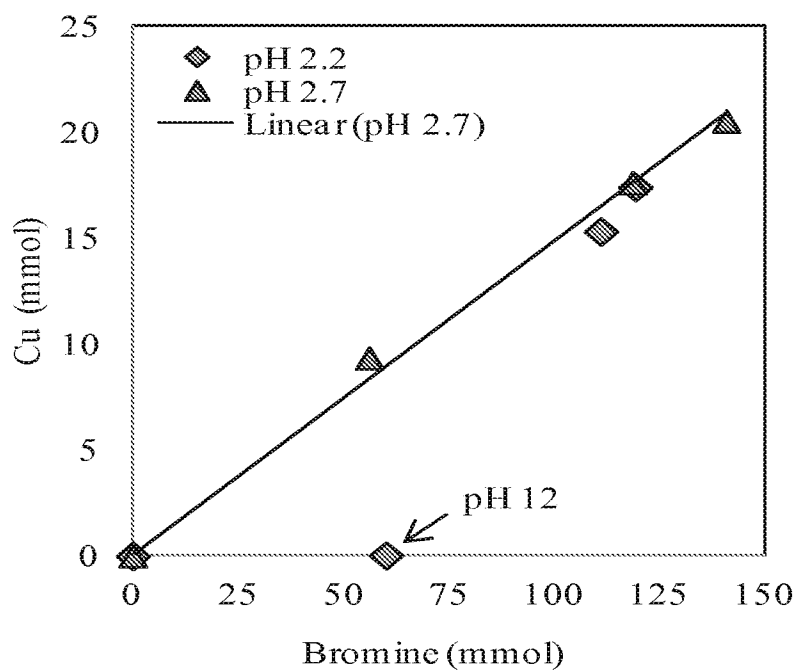


Figure 12- Moles of Copper Dissolved vs. Moles of Added Bromine

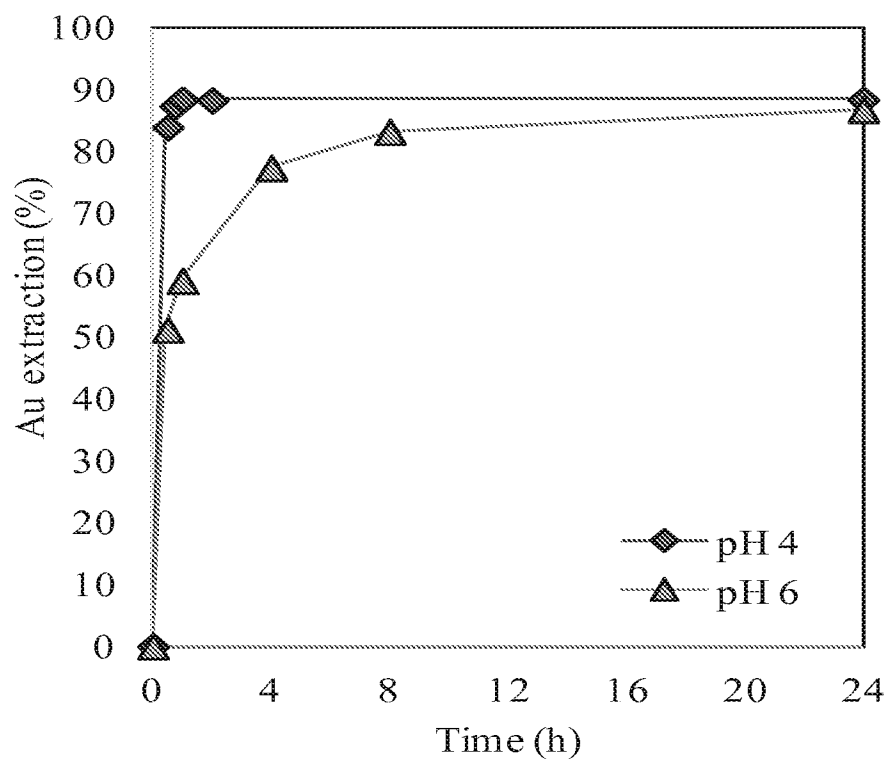


Figure 13 – The Effect of pH on the Rate of Gold Leaching from The Oxidized Concentrate

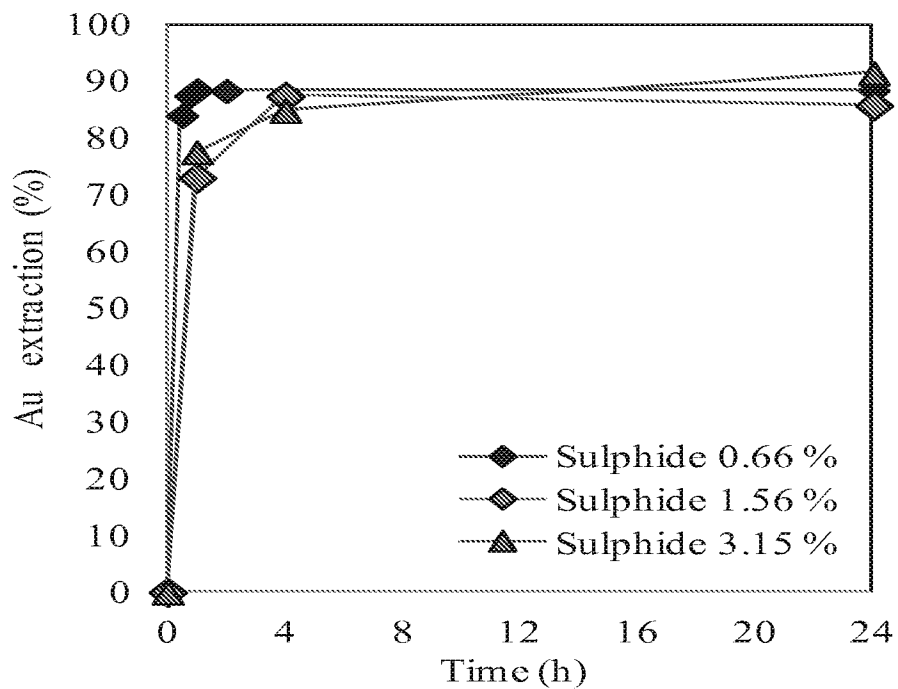


Figure 14– The Effect of Sulphide Concentration on the Rate of Gold Leaching from The Oxidized Concentrate

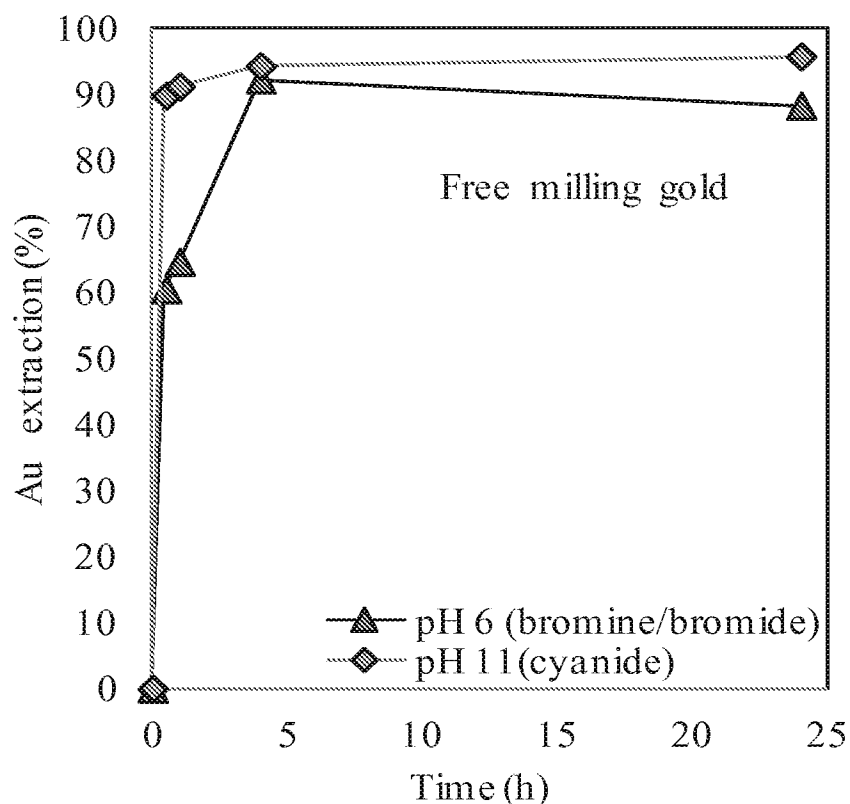


Figure 15 - Gold Extraction by Bromine/Bromide and Cyanide from Oxidised Material

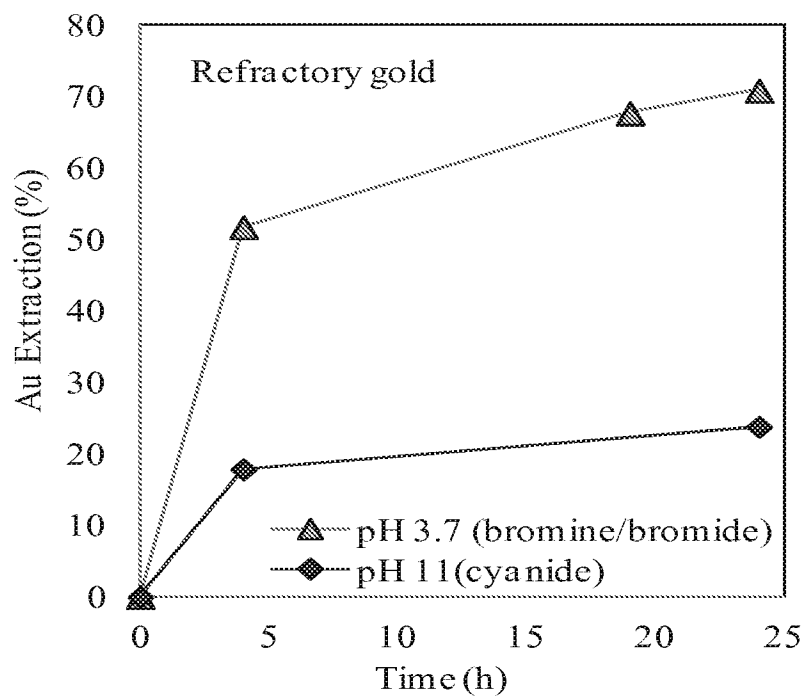
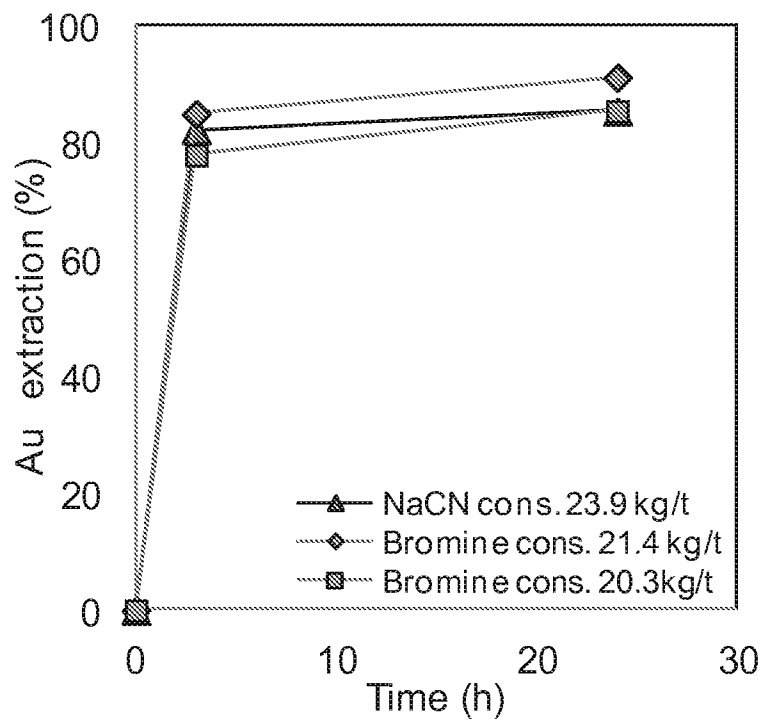
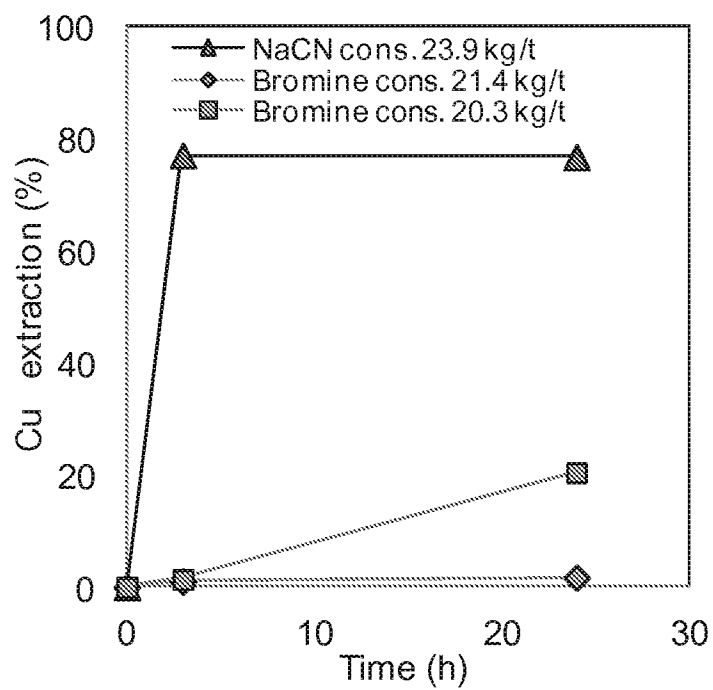


Figure 16 - Gold Extraction by Bromine/Bromide and Cyanide from Refractory Ore

**Fig. 17****Fig. 18**

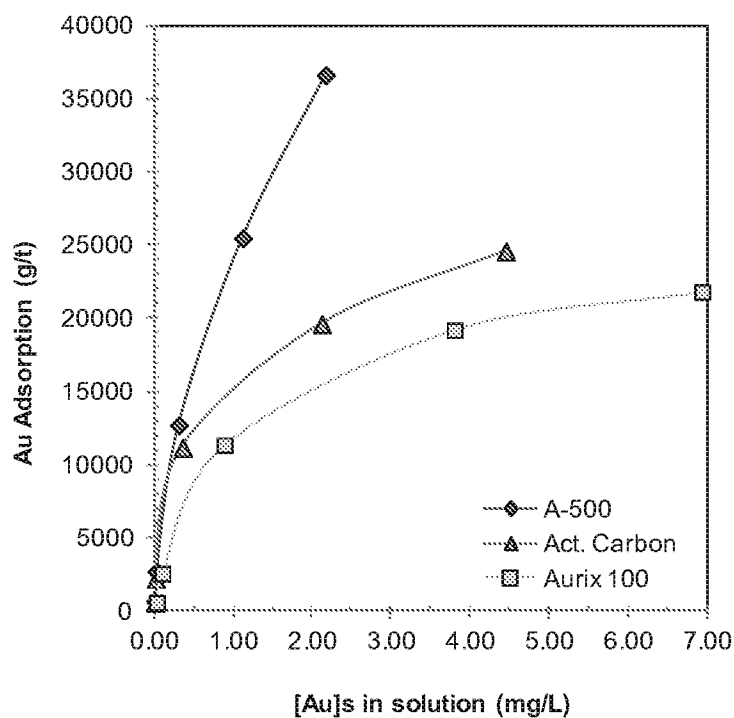


Fig. 19

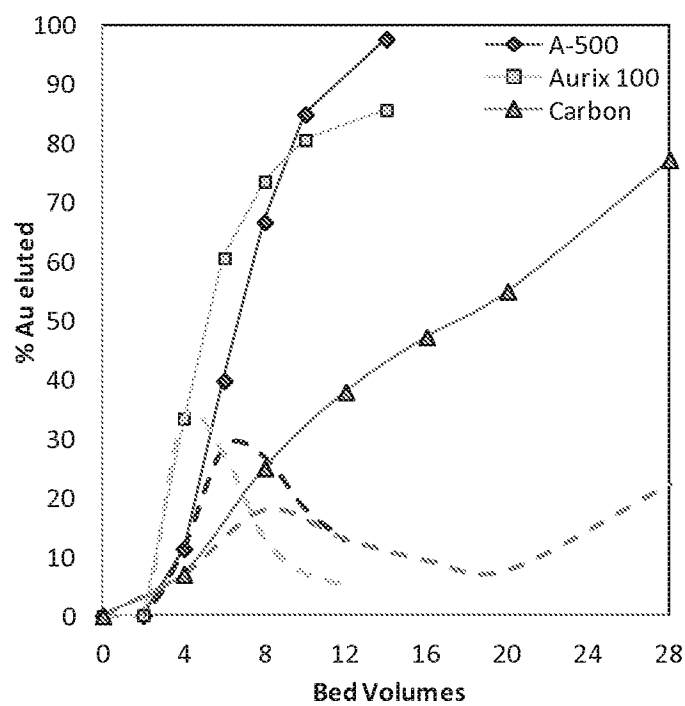


Fig. 20

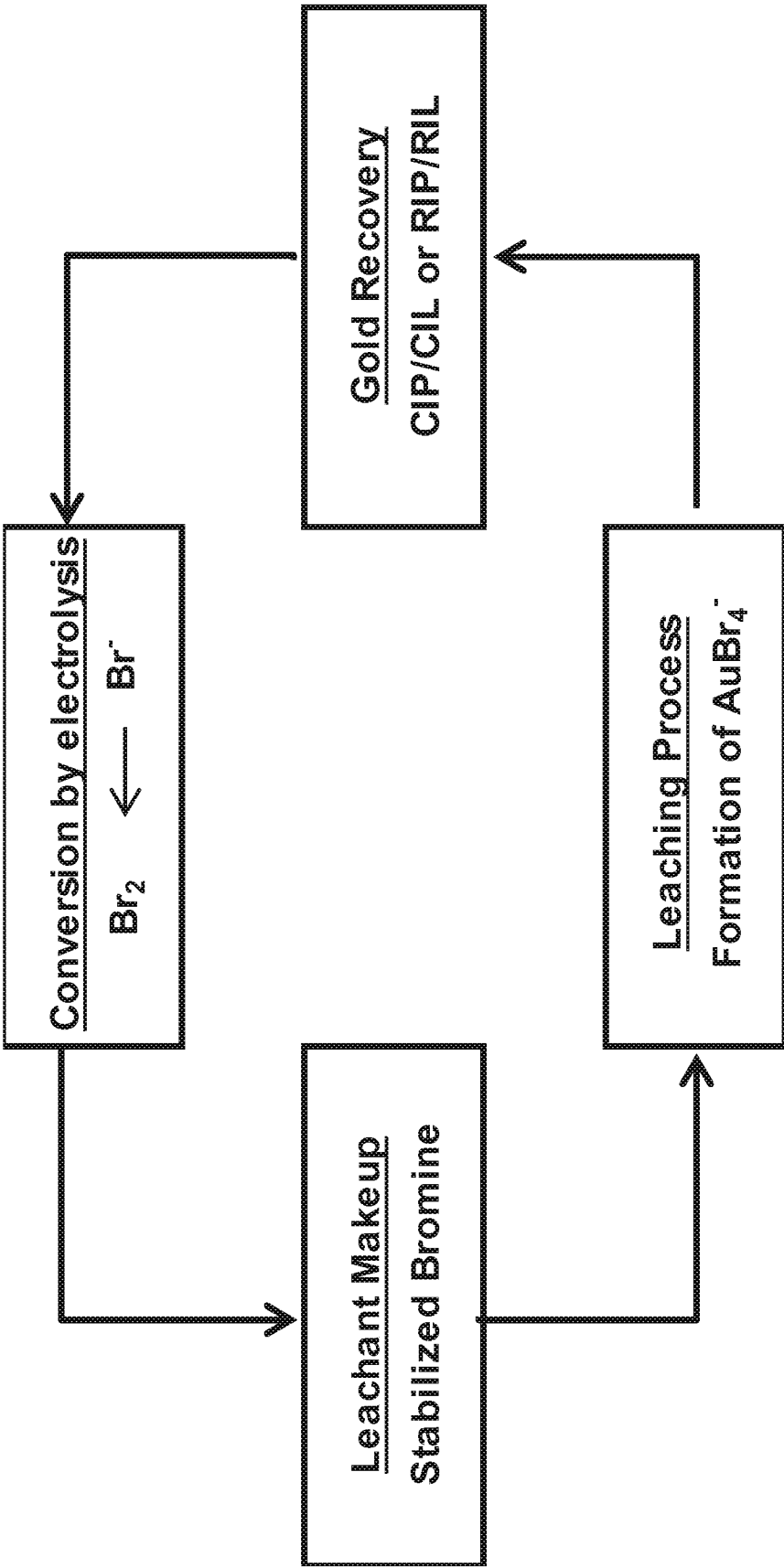


Fig. 21

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/070325

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22B3/00 C22B11/00
ADD.

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)
C22B

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 484 470 A (KRISTJANSDDTTIR SIGRIDUR S [US] ET AL) 16 January 1996 (1996-01-16) the whole document	1-9, 11-45,47
X	US 2004/262239 A1 (HOWARTH JONATHAN N [US] ET AL) 30 December 2004 (2004-12-30) the whole document	47
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Further documents are listed in the continuation of Box C.



See patent family annex.

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"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 March 2015

Date of mailing of the international search report

07/04/2015

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Swiatek, Ryszard

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/070325

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AYLMORE M G ED - ADAMS ET AL: "Alternative lixivants to cyanide for leaching gold ores", 1 January 2005 (2005-01-01), ADVANCES IN GOLD ORE PROCESSING / [ED. BY] MIKE D. ADAMS; [DEVELOPMENTS IN MINERAL PROCESSING , ISSN 0167-4528 ; ZDB-ID: 4301122 ; 15], AMSTERDAM [U.A.] : ELSEVIER, 2005, NL, PAGE(S) 501 - 539, XP008175539, ISBN: 0-444-51730-8 [retrieved on 2007-09-27] the whole document -----	1-47

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/070325

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 2004262239	A1	30-12-2004	AU 2003258962 A1 14-02-2005
			CA 2530802 A1 03-02-2005
			CN 1949965 A 18-04-2007
			EP 1638394 A1 29-03-2006
			US 2004262239 A1 30-12-2004
			WO 2005009127 A1 03-02-2005
