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Notice of Entitlement

We, GREAT LAKES CHEMICAL CORPORATION, of Highway 52 N.W., P.O. Box 2200, West Lafayette, Indiana 47906, United States of America, being the Applicant and Nominated Person in respect of Application No. 19016/92, state the following:

The actual inventor of the invention of Application No. 19016/92 are Ahmad Dadgar, Nicolai A. Favstritsky, Julie A. McKeown, Brent M. Sanders, Jonathan N. Howarth, Jane L. Likens and Dennis M. Borden.

The basic application listed on the PCT Request form, namely, United States Serial No. 684,658, was filed in the names of the said actual inventors.

The said basic application listed in the declaration under Article 8 of the PCT is the first application made in a Convention country in respect of the invention.

We have entitlement from the actual inventors, as well as from the applicants of the basic application, by assignment.

Our address for service is care of E. F. WELLINGTON & CO., Patent and Trade Mark Attorneys, 312 St. Kilda Road, Melbourne, Victoria, 3004.

DATED this 4th day of October, 1993

For and on behalf of
GREAT LAKES CHEMICAL
CORPORATION,
By:

. . . .
BRUCE S. WELLINGTON
Patent Attorney for
Applicant/Nominated Person

To: The Commissioner of Patents,
Commonwealth of Australia

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INORGANIC PERBROMIDE COMPOSITIONS AND METHODS OF USE THEREOF

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(56) Prior Art Documents
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US 4190489

(57) Claim

1. A composition the formulation of which comprises water, at least 25% by weight bromine, between 4% and 30% by weight hydrobromic acid, and between 4% and 15% by weight of a metal bromide selected from the group consisting of lithium bromide, sodium bromide, potassium bromide and calcium bromide, said formulation comprising a molar excess of bromide ion over bromine of at least 30%, said composition having a pH of not greater than 1.0.

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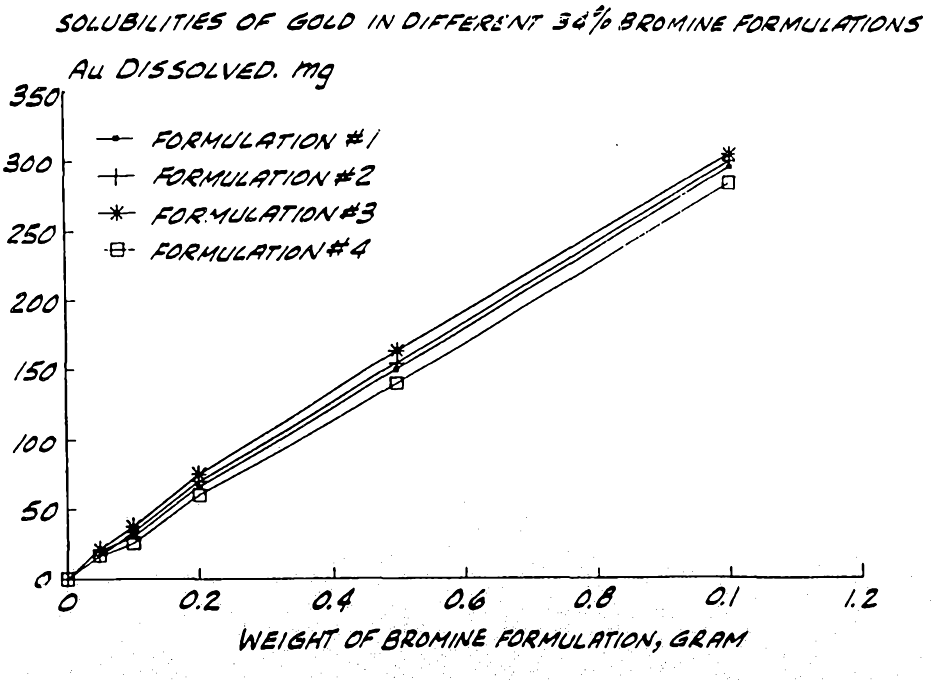

(57) Abstract

This invention relates to compositions for the hydrometallurgical recovery of precious metals, and the use of certain of such compositions in other applications. The composition comprises: water, at least about 25 % by weight bromine, between about 4 % and about 30 % by weight hydrobromic acid, and between about 4 % and about 15 % by weight of a metal bromine. The composition comprising a molar excess of bromide ion over bromine of at least about 30 %. The composition has a pH of not greater than about 1.0.

INORGANIC PERBROMIDE COMPOSITIONS AND METHODS OF USE THEREOF

Background of the Invention

This invention relates to compositions containing inorganic perbromides, the use of such compositions for the hydrometallurgical recovery of precious metals, and the use of certain of such compositions in other applications.

Conventionally, precious metals such as gold and silver have been recovered from ores by leaching with alkaline cyanide solution. Leaching with cyanide dissolves gold, for example, by producing a gold cyanide complex $Au(CN)_2^-$. Gold may be recovered from the leaching solution by various techniques, including precipitation with zinc, carbon adsorption, ion exchange or the like.

While widely practiced on a commercial scale, cyanide leaching suffers from well known disadvantages. Leaching rates are slow, contact times in the range of 24-72 hours being common in the case of gold ores. Because of the toxicity of cyanide, care must be exercised to maintain cyanide solutions on the alkaline side in order to prevent the release of hydrogen cyanide gas. Severe environmental restrictions must be observed, requiring careful monitoring and control of all process purge streams. Spent cyanide leaching solutions must be subjected to waste treatment operations before discharge to the environment.

Gold has also been leached commercially with aqua regia, in which case the gold may also be recovered by reduction with zinc metal, or by raising the pH of the leaching solution. However, this method is highly unattractive because aqua regia is expensive, highly corrosive and emits toxic fumes. Moreover, it readily dissolves base metals and dissolves gold only relatively slowly in aqueous solution.

Thiourea has also been used as a lixiviant for the dissolution of gold from ores. Though generally effective for this purpose, thiourea is subject to oxidative degradation and is, thus, prone to high consumption levels in extracting gold from its ore.

Other processes have been developed for the use of halogens, halides or other halide-bearing compounds for the recovery of precious metals from ores. For example, Shaeffer U.S. patent 267,723 describes a process in which ore is roasted in a vat, water added to the roasted ore, and liquid bromine added to produce a mixture which is agitated, thereby dissolving the gold in the water in the form of a bromide. After filtration to separate the solids, gold is precipitated from the solution by oxalic acid or ferrous ion.

EPO published specification 0 233 918 describes an alkaline concentrate for use in recovering gold from sources thereof. This concentrate contains between about 1% and about 6% by weight bromate ion, between about 55% and about 10% by weight equivalent perbromide ion, has a molar ratio of bromate ion to the sum of perbromide ion and molecular bromine of between about 0.05 and about 0.8, has a bromide ion concentration in excess of $[Br_2]$ +

[Br_3^-] of between 3% and 19% by weight, and exhibits a pH of between about 6.5 and about 7.5. Example 1 describes an alkaline concentrate that contains 31.82% by weight sodium perbromide, 2.14% by weight molecular bromine, 14.80% by weight sodium bromide, 3.94% by weight sodium bromate, and 47.30% by weight water. Example 3 of this specification describes the acidification of this concentrate by mixing 1.4 g of the concentrate with 0.8 g 48% hydrobromic acid. The application further describes the dilution of the acidified concentrate to produce a leaching solution for the recovery of gold from ore.

Fink et al. U.S. Patent 2,283,198 note that chloride and bromide ions accelerate the dissolution of gold in aqueous bromine solution. This disclosure states that chlorine or hypochlorite may be used as intermediate oxidizing agents, as indicated by the reactions:

$$2Br^- + Cl_2 \text{-------}> 2\ Cl^- + Br_2$$

or

$$2Br^- + ClO^- + 2H^+ \text{------}> Cl^- + Br_2 + H_2O$$

They, therefore, proposed a process of extracting gold from its ores by leaching with a solvent prepared by adding free chlorine to a solution containing a bromide and a large excess of chloride salt. Alternatively, a leaching agent is prepared by adding hypochlorite and a mineral acid to a solution containing a bromide and a large excess of chloride salt. Fink et al. describe precipitation of gold from the solution by any of the well known methods, such as addition of zinc or ferrous sulfate.

Harrison U.S. patent 2,304,823 describes the recovery of gold from ores by dissolution in a treatment solution containing iodine, potassium iodide, water and nitric acid. Mercury or zinc may then be added to recover the precious metal from solution. The method is said to be applicable to treatment of refractory material such as refractory sulfide, telluride or the like.

Jacobs U.S. patent 3,625,674 describes oxidizing gold with an alcoholic solution of molecular iodine, pro- ducing AuI which may be decomposed by heating to produce metallic gold and iodine vapors, the iodine being recovered and recycled for treatment of additional ore. AuI obtained from the process is also suitable for forming other gold compounds for use in the industrial arts, such as gold sodium thiomalate.

Wilson U.S. patent 3,709,681 describes a process in which a finely divided source of noble metal is treated with a solution containing a ketone solvent, dissolved iodine, bromine or chlorine, a halide salt, and preferably glacial acetic acid. The noble metal content of the treatment solution is recovered by displacement onto a non-noble metal surface such as aluminum foil.

Homick et al. U.S. patent 3,957,505 describe a process in which gold bearing material is treated in an aqueous solution consisting of iodine and a water soluble iodide salt to produce a solution containing dissolved gold iodide salts. Gold metal is precipitated from the solution by mixing of the solution with a reducing agent such as hydroxylamine, hydrazine, sodium thiosulfite and the like. Iodine from the spent aqueous solution is recovered by acidification of the solution and addition of an oxidizing agent such as hydrogen peroxide, potassium permanganate, sodium chromate, chlorine or bromine to precipitate elemental iodine.

McGrew et al. U.S. patent 4,557,759 describe a process for the hydrometallurgical recovery of gold from materials containing gold by leaching the materials with a lixiviant containing iodine. The lixiviant is prepared by saturating an aqueous solution of iodide with iodine. When a sulfide is added to this reagent, iodine reacts with the sulfide and is converted to iodide. Additional elemental iodine is then added to this iodide bearing solution until the desired concentration of total iodine and ratio of iodine to iodide are achieved for maximum leaching efficiency. The lixiviant is then circulated through the ore zone until all the gold is dissolved. Gold is subsequently recovered on activated charcoal. The excess iodide formed during the process is reoxidized to iodine electrochemically in a special diaphragm cell to regenerate the lixiviant. The desired concentration of iodine in the lixiviant is between 1 and about 20 grams per liter.

Copending and co-assigned application Ser. No. 577,677 describes a process for generating bromine in aqueous solution. An aqueous solution containing 0.5 to 8.8 moles per liter bromide ion and having a pH of 0 to 6 is passed continuously through an electrolytic cell for generation of bromine at the anode. Both divided and undivided cells are disclosed. Conversions per pass through the cell system are in the range of 4% to 50%. The application describes further process steps in which the bromine solution produced by electrolysis is used as a leaching solution for recovery of gold from ore. Example 6 describes a leaching solution containing 0.68% by weight equivalent molecular bromine, about 0.43% by weight bromide ion, and about 0.43% by weight sodium ion. Where a divided cell is used, the cathode side may be used for recovery of gold from the leachate, which preferably contains 1.2×10^{-5} to 1.2×10^{-3} moles per liter $AuBr_4^-$, 0.4 to 3.0 moles per liter bromide ion, and 0.4 to 3.0 moles per liter sodium ion. The pH is preferably 0 to 3.

Dadgar et al., J. Phys. Chem., 68, 106 (1964) and Dadgar et al., J. Inorganic Nucl. Chem., 33, 4155 (1971) report that the equilibrium constant for the ion pair formation increases with the reciprocal of dielectric constant of the medium (organic solvent-water mixtures).

Dubois and Garnier, Bull. Soc. chim. Fr., 1715 (1965) determined the formation constant of ($Br_2 + Br^- = Br_3$) in methanol-water mixtures. These authors derived a semi-empirical equation relating the formation constant of the complexion to the dielectric constant of the medium. Also, Nakagawa et al., J. Phys. Chem., 61, 1007 (1957) investigating the formation of tribormide in acetic acid-water mixtures, have shown that the formation constant increases with increasing concentration of acetic acid just as in the case of methanol-water mixtures.

In addition to ores, there is a substantial number of additional sources of gold and silver which offer the opportunity for economical recovery. In fact, many of these secondary sources are substantially richer than ores with respect of the content of the metal to be recovered. Gold is available from numerous scrap sources, including industrial wastes, gold plated electronic circuit boards, and as an alloy with copper, zinc, silver or tin in the karat gold used in jewelry. Silver is available from photographic and x-ray film emulsions, from scrap sterling, and from numerous industrial sources.

Bazilevsky U.S. patent 3,495,976 describes a process for recovering gold from a plated substrate by dissolving the gold in an aqueous solution of potassium iodide and free iodine. Gold is recovered from the solution by addition of concentrated sulfuric acid and heating of the resultant mixture near the boiling point, which distills off molecular iodine and effects precipitation of the gold.

Bahl et al. U.S. patent 4,190,489 describe a composition and method for etching gold, particularly gold layers on ceramic substrates. The composition is prepared, for example, by mixing potassium bromide (75g), elemental bromine (25g), and water (100 ml.). This solution is effective for recovery of gold from ceramic substrates at essentially room temperature.

Bahl et al. 4,375,984 describe a process in which an alkaline metal bromide/bromine solution is used to etch gold from a substrate. In this disclosure, the etching solution may be prepared, for example, by mixing potassium bromide (2g), bromine (one gram), and water (25 ml.) Gold dissolved in the etching solution is recovered as metallic gold, either by precipitation using an alkali metal hydroxide or by decomposition in which the etching solution is driven off. The alkali metal bromide/bromine etchant solution may be regenerated by the addition of an acid thereto.

Kalocsai B1 4,684,404, based on re-examination of U.S. patent 4,684,404, describes dissolution of metallic gold in a reagent comprising a protic solvent such as water or alcohol, a nonreducing cation source such as sodium, potassium, ferrous or ammonium, and a source of free bromine such as molecular bromine, bromine water, or an inorganic or organic bromine containing compound from which bromine can be liberated in the reagent. Optionally, the solution further contains a strong oxidizing agent such as hydrogen peroxide, sodium peroxide, potassium peroxide, sodium permanganate, potassium permanganate, potassium chromate or ferric sulfate. Among the exemplary reagents disclosed by

Kalocsai is a composition (Example 28) containing 1.0% v/v Br_2, 1% w/v NaBr, and 0.6% w/v NaOH, and having a pH of 7.35.

Sergent et al. U.S. patent 4,637,865 describe a process for extracting a precious metal from a source material by contacting the source material with an aqueous leaching solution containing a leaching agent comprised of an N-halohydantoin compound. Leaching solutions are described containing 1,3-dibromo-5,5-dimethylhydantoin, 1-bromo-3-chloro-5,5-dimethylhydantoin and 1,3-dichloro-5,5-dimethylhydantoin. Precious metal may be removed from the leaching solution by precipitation of the less noble metal, ion exchange, treatment with activated carbon, solvent extraction or electrowinning.

Simpson U.S. patent 4,439,235 describes a process for removing precious metal values from comminuted carbonaceous ores in which the comminuted ore is contacted with an aqueous solution of hypochlorite, iron ion, and acid.

Falanga et al. U.S. patent 4,319,923 teaches a process in which gold and palladium are etched with a potassium iodide/iodine etching solution and the metal is recovered from the solution by addition of alkaline compound, preferably KOH, to increase the pH to at least 12.5 and precipitate metallic gold from the solution. A borohydride is used to precipitate palladium. A similar process is described in MacDonald U.S. patent 4,319,922.

Jolles, "Bromine and its Compounds", Academic Press, New York, 1966, page 173, states that a mixture of sodium bromate and sodium bromide has been used under the name of "mining salts" in the extraction of gold ore. Jolles states that the proportion of the respective components vary but are usually 43% sodium bromate and

57% sodium bromide, i.e., two moles sodium bromide to one mole sodium bromate.

Belohlav et al. U.S. patent 3,222,276 describe a process for producing an aqueous bromine solution from an aqueous solution of bromide/bromate salts and mineral acid. In accordance with the process, a concentrated aqueous solution of bromide and bromate salts at a 5:1 molar ratio is pumped to a mixing zone where it is mixed with a mineral acid to convert the bromide/bromate solution into a concentrated aqueous bromine solution. This concentrated aqueous bromine mixture is pumped to a second mixing zone where it is diluted with a larger volume of water to produce a diluted stream of aqueous bromine, and the latter stream is further diluted with a large body of water to produce a highly dilute aqueous bromine solution in substantially quantitative yield from the mineral acid and the bromide/bromate salt solution. The process as described is useful in the bromination of swimming pool water. The reference contains no mention of the use of bromine or bromides in the recovery of precious metals from sources thereof.

Although prior art processes which use molecular bromine have been effective for recovery of gold from source materials, pure bromine is a corrosive, fuming liquid which generates a suffocating vapor and must be subjected to special handling. Bromine may be dissolved to a certain extent in water, or incorporated in an alkali metal perbromide solution, but these aqueous materials exhibit a substantial bromine vapor pressure, so that their use also commonly entails special handling. Alternatively, molecular bromine can be generated from the acidification of alkali metal bromates, but by themselves bromates provide only a limited source of molecular bromine. Additionally, bromate salts have a high crystallization temperature which makes them inconvenient to use as leaching agents for precious metals. Mixtures of bromides and bromates, such as the "mining salts" described by Jolles, have found their place in the technology of precious metal recovery, but have not provided a sufficient source of molecular bromine to be as effective as those known solutions whose bromine vapor pressure is relatively high.

In addition to their use in the recovery of precious metals from ores, inorganic bromine compositions have been used as disinfectants. As noted above with regard to Belohlav U.S. patent 3,222,276, among the particular applications of inorganic bromine compositions has been in the disinfection of swimming pools. The noxious character of bromine fumes and the relatively high bromine vapor pressure of conventional aqueous bromine concentrates creates inconvenience and nuisance in the treatment of pool water or other water circuits with these concentrates. Organic bromine compounds have also been widely used for such applications, but are generally more expensive than inorganic compositions.

In shipping and handling aqueous bromine compositions for various uses, especially for use in recovery of gold 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. Many mining sites are in locations where climate is harsh. Moreover, many known compositions have rather high freezing points, so that freezing is a problem even at relatively moderate environmental temperatures.

Summary of the Invention

Among the several objects of the present invention, therefore, may be noted the provision of an improved process for the hydrometallurgical recovery of gold and silver from ores or other sources thereof; in particular, the provision of such a process which provides a substantial source of bromine for dissolution of a metal without requiring the handling of liquid bromine or solutions having a substantial bromine vapor pressure; the provision of such a process which avoids the use of cyanide; the provision of such a process which may be used for recovery of gold from various types of ores, including refractory ores; and the provision of a such a process which produces a leachate from which gold or silver metal may be readily recovered.

Further objects of the invention include the provision of compositions useful and effective for the leaching of gold and silver from source materials; the provision of such compositions which contain a substantial source of molecular bromine; the provision of such compositions which do not exhibit a high bromine vapor pressure; the provision of such compositions which exhibit low thermodynamic crystallization temperatures so they will not freeze during storage or transport even in harsh climates; the provision of such compositions which exhibit a high degree of freeze/thaw stability; the provision of such compositions which can be used directly or with water dilution, and which do not require prior activation with acid.

It is a further object of the present invention to provide compositions that are useful as disinfectants, and in particular for the control of microorganisms in swimming pool water and cooling tower water.

Briefly, therefore, the present invention is directed to a composition the formulation of which comprises water, at least 25% by weight bromine, between about 4% and about 30% by weight hydrobromic acid, and between about 4% and about 15% by weight of a metal bromide. The metal bromide is selected from among LiBr, NaBr, KBr and $CaBr_2$. The composition comprises an excess of bromide ion over bromine of at least about 5% expressed in weight percentage of excess bromide ion, and has a pH of not greater than about 1.0.

The invention is further directed to a composition the formulation of which comprises water at least about 25% by weight bromine, at least about 4% by weight hydrochloric acid, and between about 10% and about 15% by weight sodium bromide, said formulation comprising a molar excess of halide ion over bromine of at least about 30%, said composition having a weight ratio of water to NaBr of not less than about 4.0, and a pH of not greater than about 1.0.

The invention is also directed to a method for recovering a precious metal, such as silver or gold, from a source thereof. The method comprises preparing a leaching solution by dilution with water of a concentrate of the type described above, and contacting said source with the leaching solution, thereby producing a leachate containing the precious metal.

The compositions of the invention may further be used in a method for controlling the micro-organisms in a body or stream of water. Bromine from a concentrate of the type defined above is introduced, either directly or after dilution, into the body or stream of water in amounts sufficient to suppress growth of micro-organisms in said body or stream.

Brief Description of the Drawings

Fig. 1 is a plot of solubility vs. bromine concentration for tests of solubility of gold in the diluted concentrates of Example 5 herein;

Fig. 2 is a plot of amount of gold dissolved vs. time for simulated batch kinetic tests of the dissolution of gold in the concentrates of Example 5 herein;

Fig. 3 is a plot of gold dissolved vs. time for rotating disk kinetic tests of the dissolution of gold in the concentrates of Example 6 herein;

Fig. 4 is a plot of amount of gold dissolved vs. time for simulated batch kinetic tests of the dissolution of gold in the concentrates of Example 6 herein.

Fig. 5 is a plot of total residual oxidant (TRO) content of cooling tower water vs. time during the course of the cooling tower water treatment tests of Example 8; and

Fig. 6 is a plot of bacterial density in the cooling tower water vs. time during the tests of Example 8. This plot is superimposed on the plot of Fig. 5.

Description of the Preferred Embodiments

In accordance with the invention, inorganic perbromide concentrates have been discovered which may be used advantageously in a variety of applications. In certain methods of use, such as the recovery of gold from ores, these concentrates may be diluted with water to provide aqueous working solutions that are used in practicing the method. In other applications, such as the treatment of swimming pool or cooling tower water, the concentrates may be metered into a circulating stream of the body of water to be treated. Although the concentrates generally contain a substantial percentage of equivalent molecular bromine and are acidic, having a pH of zero or below, they exhibit remarkably low vapor pressures. This facilitates handling of the concentrates and avoids the hazards that are incurred where molecular bromine is used in comparable applications.

A number of the compositions of the invention are advantageously adapted for shipping, storage and/or use in harsh climates. Various of these concentrates exhibit favorable freeze/thaw stability, and certain of them exhibit exceptionally low thermodynamic crystallization temperatures.

Generally, the compositions of the invention are formulated from a metal bromide, a hydrogen halide acid, molecular bromine, and a protic solvent. The protic solvent may be water, alcohol or an organic acid, or a mixture thereof. Compositions of the invention may contain 10-40% by weight equivalent molecular bromine, defined in molar terms as the sum of the actual molar concentration of molecular bromine, the molar concentration of perbromide ion, the molar concentration of hypobromous acid, and the molar concentration of hypobromite ion. In accordance with the invention, it has been found that concentrates containing 25% or more equivalent molecular bromine exhibit remarkably low bromine vapor pressures, excellent freeze/thaw stability, and exceptionally low thermodyamic crystallization temperatures. Advantageously, the molecular bromine concentration is between about 30% and about 35% by weight.

Each of the compositions is prepared by mixing a source of halide ion with molecular bromine in such proportions that the bromide ion is in excess. Halide sources generally include both a metal halide salt and a hydrogen halide. Preferably, the halide ion is bromide and the molar ratio of bromide ion to molecular bromine in the formulation is between about 1.2:1 and about 2.0:1, most preferably between about 1.4:1 and about 1.8:1. In solution, the molecular bromine combines with bromide ion to form perbromide or a mixed perhalide ion in accordance with the equations:

$$Br^- + Br_2 = Br_3^- \qquad (1)$$

or

$$Cl^- + Br_2 = ClBr_2^- \qquad (2)$$

By control of the ranges of proportions of bromide ion (and other halide ion), complementary countercation, and molecular bromine used in formulating the composition, it has been found that a solution of low vapor pressure can be produced at both high concentrations of equivalent Br_2 and very low pH, i.e., zero or below.

Among the metal bromides which can be incorporated in the composition of the invention are alkali metal salts such as sodium bromide, potassium bromide, and lithium bromide, and alkaline earth metal salts such as calcium bromide. Hydrogen halides used in preparing the composition include HCl, HI and HBr, preferably the latter.

Optionally, the concentrates of the invention further contain an alcohol or a low molecular weight organic acid. Alcohols and organic acids have a lower dielectric constant than water. Because the equilibrium constant for the above reactions increases with the reciprocal of the dielectric constant, the inclusion of an organic solvent in the composition also conduces to maintaining a low bromine vapor pressure at a high molecular bromine concentration. Useful organic acids include acetic, propionic, succinic, adipic and the like. Useful alcohols include methanol, butanol, and the like.

It is known that compositions containing alcohol and bromine can be unstable, under certain circumstances explosive, due to reaction of alcohol with bromine. Thus, it is generally preferred that organic solvents other than alcohols be used. However, as explained by Bowman, et al. "A Potential Hazard in Preparing Bromine-Methanol Solutions," J. Electrochem. Soc., Vol. 137, No. 4 (April 1990) 1309-11, Br_2/alcohol compositions can be stable, and use safely, if the alcohol content is sufficiently low. Bowman, et al. report that methanol/Br_2 compositions are essentially nonreactive, provided that the alcohol content is less than 10% by volume on an alcohol + Br_2 basis.

Compositions of the invention which contain hydrobromic acid and an organic protic solvent are generally formulated from:

Br_2	10-40% by wt.
Metal bromide	4-30% by wt.
HBr	5-24% by wt.
organic solvent	10-40% by wt.

Water is optionally present as a co-solvent. Preferred compositions are formulated from:

Br_2	20-35% by wt.
Metal bromide	8-16% by wt.
HBr	10-20% by wt.
Organic solvent	15-30% by wt.

These compositions exhibit a bromine partial vapor pressure not greater than about 40 mm Hg at 25% bromine and 20°C, and a bromine vapor pressure not greater than about 50 mm Hg at 34% bromine and 20°C. Thermodynamic crystallization temperatures are in the range of between about -30°C to about -50°C at 34% Br_2 for compositions in which water is the solvent, and between about -55°C and about -68°C for compositions in which the solvent comprises an organic solvent. pH is less than 1.0 and generally less than 0.20. Preferred compositions have a pH <0.

Regardless of whether the solvent comprises water, an organic acid, or a mixture thereof, it is especially preferred that the Br_2 concentration be greater than 25%. Such compositions are formulated from:

Br_2	$\geq$ 25% by wt.
HBr	4-20% by wt.
metal bromide	4-15% by wt.
$[Br^-]/[Br_2]$	1.2:2.0 (molar ratio)
protic solvent	bal.

The pH is <0. More preferably, such compositions are formulated from:

Br_2	25-35% by wt.
HBr	10-20% by wt.
metal bromide	10-15% by wt.
$[Br^-]/[Br_2]$	1.4:1.8 (molar ratio)
protic solvent	bal.

Again, the pH is < 1.0. Advantageously, such formulations may contain $\geq$ 30%, optimally 32-36% Br_2, and a molar excess of bromide over Br_2 of $\geq$ 30%.

Similar compositions in which HCl is substituted for HCl are preferably formulated from:

Br_2	$\geq$25% by wt.
HCl	$\geq$4% by wt.
Metal bromide	10-15% by wt.
$[H_2O]/[NaBr]$	$\geq$4.0 (wt. ratio)

and have a pH <0.

In the $NaBr_3$ compositions, it is particularly preferred that the sodium ion content of the formulation be in the range of between about 1% and about 3% by weight, and that the molar ratio of Na+ to equivalent Br_2 be no greater than about 0.8. It has been found that such relatively low proportions of Na^+ conduce to a relatively low thermodynamic crystallization temperature, and to excellent freeze/thaw stability of the concentrate. A preferred formulation for a freeze/thaw stable $NaBr_3$ concentrate is:

NaBr	5-15%
HBr	15-30%
Br_2	25-35%
H_2O	bal.

An especially preferred low Na+ composition comprises:

NaBr	5-10%
HBr	17-27%
Br_2	30-35%
H_2O	bal.

Calcium bromide compositions exhibit exceptionally low vapor pressure at high equivalent molecular bromine concentrations. This is believed to be attributable to the greater ionic strength of calcium bromide as compared to alkali metal bromides. Greater ionic strength tends to increase the equilibrium constant for the reactions:

$$Br^- + Br_2 = Br_3^- \qquad (1)$$

or

$$Cl^- + Br_2 = ClBr_2^- \qquad (2)$$

At an equivalent molecular bromine concentration of 25%, the $Ca(Br_3)_2$ concentrates have a bromine partial vapor pressure of less than about 40 mm Hg at 20°C, while at 34% equivalent molecular bromine, they have a bromine partial vapor pressure of less than about 50 mm Hg at such temperature. Additionally, calcium perbromide compositions provide an especially low thermodynamic crystallization temperatures (TCTs), e.g., in the range of between about -50°C and about -60°C where water only is the solvent, and below -60°C where the solvent comprises an organic solvent. Such TCTs are also believed to be attributable to the greater ionic strength of these formulations as compared to alkali metal perbromides. Calcium perbromide compositions preferably are formulated from:

Br_2	$\geq$25% by wt.
$CaBr_2$	$\geq$5% by wt.
HBr	$\geq$10% by wt.
$[Br^-]/[Br_2]$	1.4:1.8 (molar ratio)

and have a pH <1.0

The concentrates described above are preferably prepared by adding the bromide or other halide salt and hydrogen halide to protic solvent, and then adding liquid bromine to the acidic bromide salt solution. This sequence insures the presence of an excess of bromide ion for reaction with the liquid bromine to form perbromide or XBr_2^- ion (where X is halide) during bromine addition. Advantageously, saturated or nearly saturated premix solutions are prepared for both the bromide salt and hydrogen halide, and these premix solutions are added to water to produce a precursor solution to which the liquid bromine is added. Thus, for example, a solution containing an organic protic solvent may be prepared by mixing:

10 to 40 wt.%	organic solvent
8 to 45 wt.%	46% by weight NaBr solution;
10 to 50 wt.%	48% by weight HBr solution
10 to 40 wt.%	liquid bromine;

or

10 to 40 wt.%	organic solvent
8 to 40 wt.%	52% by weight $CaBr_2$ solution;
10 to 50 wt.%	48% by weight HBr solution
10 to 40 wt.%	liquid bromine;

or

10 to 40 wt.%	organic solvent
10 to 50 wt.%	38% by weight KBr solution;
10 to 50 wt.%	48% by weight HBr solution
10 to 40 wt.%	liquid bromine;

or

10 to 40 wt.%	organic solvent
7 to 35 wt.%	54% by weight LiBr solution;
10 to 50 wt.%	48% by weight HBr solution
10 to 40 wt.%	liquid bromine;

Where water alone is the solvent, an $NaBr_3$ concentrate is preferably prepared by mixing:

6 to 40 wt.%	water
9 to 35 wt.%	46% by weight NaBr solution
10 to 50 wt.%	48% by weight HBr solution
$\geq$25% by wt.	liquid bromine;

Although the concentrates are preferably prepared as described above, they may also be provided by acidification of a alkaline solution of bromate salt and bromide salt. Such an alkaline concentrate can be prepared, for example, in the manner generally described in U.S. Ser. No. 401,036 (attorneys' docket no. GLC 4007A). Acidification converts the bromate to bromine in accordance with the reaction:

$$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O \qquad (3)$$

Acidification to a pH approaching zero drives the above equation quantitatively to the right. Reaction of the Br_2 with Br^- per equation (1) further drives the conversion of bromate.

Further included in the compositions of the invention are hydrogen perbromide concentrates formulated from:

Br_2	$\geq$ 15% by wt.
HBr	15-40% by wt.
organic solvent	40-60% by wt.

Where water alone is the solvent, the composition preferably contains:

Br_2	$\geq$ 25% by wt.
HBr	30-40% by wt.

At a bromine concentration of 25% and a temperature of 20°C, these HBr_3 compositions exhibit a bromine partial vapor pressure of less than about 40mm-Hg.

It should be noted that the compositions of the concentrates of the invention, as outlined above are formulations, i.e., summaries of the components from which the concentrates are formed in the relative proportions used in forming the concentrates. As indicated, these formulations equilibrate to convert Br_2 and Br^- to Br_3^-. Additionally, some of the Br_2 reacts with water to produce hypobromous acid, which in turn dissociates to a limited degree:

$$Br_2 + H_2O \rightleftharpoons H^+ + HOBr + Br^- \qquad (4)$$

$$HOBr \rightleftharpoons H^+ + OBr^- \qquad (5)$$

Based on known equilibrium constants, the exact equilibrium composition of each of the formulations can be computed. Applicants invention encompasses to such equilibrated compositions, however produced. However, for purposes of clarity and simplicity, the concentrates are defined in terms of their formulation from water, bromide salt, hydrogen halide and liquid bromine in the manner described above.

For recovery of precious metals, the concentrates of the invention are diluted to produce a leaching solution that is used essentially in the manner described in copending and coassigned application Ser. No. 401,036 (attorneys' docket number GLC 4007A). Thus, a concentrate of the type described above is diluted to provide a leaching solution containing between about 0.01% and about 1% by weight, preferably about 0.02% to about 0.5% by weight, equivalent molecular bromine, between about 0.005% and about 10%, preferably about 0.01% to about 1%, by weight bromide ion, and between about 0.005% and about 15%, preferably about 0.01% to about 1.5%, by weight total halide ion. However, in certain applications such as, for example, recovery of metallic gold from an electronic circuit board or jewelry scrap, a more concentrated leaching solution may be used. Such may be prepared from the above described concentrates by modest dilution with water. In some instances, the concentrate may even be used directly for dissolution of metallic gold or silver.

Gold and silver are recovered from a source thereof, such as comminuted gold ore, by contacting the source material with the aqueous bromine leaching solution. In the case of gold, oxidation and complexing of the gold is believed to proceed in accordance with the equations:

$$2Au + 3Br_2 + 2Br^- \text{------>} \quad 2AuBr_4^- \qquad (6)$$

or

$$2Au + 3HOBr + 5Br^- \xrightarrow{H^+} 2AuBr_4^- + 3H_2O \qquad (7)$$

Depending on the nature of the ore, the relative proportions of ore (or other source material) and leaching agent may be such that the leaching slurry contains between about 1 and about 100 lbs. active agent per ton of source. Active agent in this instance is defined as the sum of the amounts of bromide, perbromide, metal hypobromite, hypobromous acid, and molecular bromine in the leaching solution.

If the source material is a refractory ore, it may be necessary to pretreat it for removal of sulfide and carbonaceous material. Such may be accomplished by methods known to the art such as roasting or pressure oxidation. Roasting may be sufficient pretreatment if carried out at a temperature of 500-750°C. The leaching composition and method of the invention also may be used advantageously for recovery of gold from high grade non-refractory ores, low grade refractory and oxide ores, electronic component scraps, jewelry scrap and similar low grade refractory and oxide ores. The composition and method may be used for recovery of silver from various sources, including photographic film.

The slurry of ore in leaching solution is preferably agitated to promote transfer of precious metal from the ore particles to the aqueous phase. A leachate is thus produced containing gold or silver complexed with bromide ions. Leaching may be carried out at ambient temperature. Preferably, contact is maintained for a period of 2 to 6 hours to achieve the maximum transfer of gold or silver from the ore.

After treatment of the precious metal source with the leaching solution is completed, the leachate is separated from the leached ore, as by filtration. The filtrate (leachate) is washed with an aqueous washing medium, the spent wash solution is combined with the filtrate, and the combined filtrate and wash solution is treated for recovery of the precious metal therefrom.

Advantageously, particularly in the case of silver, the filter cake is washed with a 2-4 molar HCl. Washing the filter cake in such fashion may be effective to remove further quantities of silver in the form of $AgCl_2^-$ from the cake. A solution of 4M HCl is especially preferred.

Gold may be recovered from the combined filtrate and wash solution by conventional means such as zinc or aluminum precipitation, ion exchange, carbon adsorption, or electrowinning. In similar fashion, the leaching solution of the invention may be used for recovery of silver.

In disinfecting bodies of water, such as swimming pools and cooling tower basins, the concentrate may be added to the body of water in various different ways. Advantageously, the concentrate is metered into a circulating stream of the water. For example, in the case of a cooling tower, the concentrate may be metered into the stream of water circulated between the cooling tower and heat exchanger(s) for which it provides cooling. In the case of a swimming pool and stream of water may be continuously or intermittently withdrawn from the pool and circulated through a brominator to which the concentrate is added. If desired, the concentrate may be diluted with water before addition to the body of water to be treated.

In the case of swimming pool treatment, the concentrate should be added in a proportion sufficient to kill bacteria in the circulating water. This may also be done in the case of cooling tower water. Advantageously, however, cooling tower water is treated with only enough of the bromine concentrate to contain the growth of the microorganisms, but not enough to kill them. This method provides savings in the consumption of bromine, and minimizes corrosion to cooling tower components, piping and heat exchangers which utilize the cooling tower water. Preferably, the concentrate is metered into the cooling tower basin using a positive displacement pump, e.g., a diaphragm pump. A peristaltic pump is most preferred because it is self priming and not subject to back siphoning. By feeding at a rate sufficient to maintain a total residual oxidant (TRO) level of between about 0.2 and about 2 ppm, preferably between about 0.2 and about 0.7 ppm (measured as Cl_2), microfouling can be prevented while minimizing corrosion of pipes, pumps and other cooling tower system components.

The following examples illustrate the invention.

EXAMPLE 1

Precursor compositions were prepared by adding a 48% HBr solution and a 46% NaBr solution to water. Liquid bromine was added to the precursor solution to produce acidic concentrates containing 34% by weight equivalent molecular bromine. Satisfactory solutions were prepared from the proportions of water, HBr solution, NaBr solution and liquid bromine set forth in Table 1.

Table 1

Composition	H_2O(g)	48% HBr(g)	46% NaBr(g)	Br_2(g)	pH
25	26	10	30	34	<0
26	16	20	30	34	<0
27	6	30	30	34	<0
28	36	10	20	34	<0
29	24	20	20	34	<0
30	14	30	20	34	<0
32	36	20	10	34	<0
33	26	30	10	34	<0

These solutions were clear and stable. No phase separation occurred on standing.

EXAMPLE 2

Using the method generally described in Example 1, acidic concentratres containing 34% by weight equivalent molecular bromine were prepared from water, a 46% by weight NaBr solution, and a 37% by weight HCl solution. Satisfactory compositions were prepared from the proportions set forth in Table 2.

Table 2

Composition	H_2O(g)	37% HCl(g)	46% NaBr(g)	Br_2(g)
1	26	10	30	34
13	26	10	30	34
14	16	20	30	34
15	6	30	20	34
17	24	20	20	34
18	14	30	20	34

EXAMPLE 3

Using the method generally described in Example 1, acidic concentrates containing 34% by weight equivalent molecular bromine were prepared from water, a 48% by weight HBr solution, a 52% by weight $CaBr_2$ solution, and liquid bromine. Satisfactory compositions were prepared from the proportions set forth in Table 3.

Table 3

Composition	H_2O(g)	48% HBr(g)	52% $CaBr_2$(g)	Br_2(g)	pH
37	26	10	30	34	<0
38	16	20	30	34	<0
39	6	30	30	34	<0
40	36	10	20	34	0.6
41	24	20	20	34	0.2
42	14	30	20	34	<0
44	36	20	10	34	0.7
45	26	30	10	34	0.4

Additional compositions were prepared from $CaBr_2$, Br_2, methanol, either HBr or HCl and, optionally, water. Satisfactory compositions were prepared from the proportions set forth in Table 4.

Table 4

Comp. #	H_2O(g)	48% HBr(g)	37% HCl(g)	52% $CaBr_2$(g)	Br_2(g)	MeOH(g)
1	--	30	--	20	34	16
2	10	--	--	41	34	15
3	--	33	--	33	34	--
4	--	--	16	30	34	20
5	--	--	--	40	34	20

EXAMPLE 4

Acidic concentrates were prepared from water or organic solvent, 46% by weight NaBr solution, 48% HBr solution, and liquid bromine. NaBr and HBr solution were added to the water or organic solvent, and liquid bromine was added at a modest rate to the precursor mixture. The mixture was stirred constantly but not too vigorously during the addition of Br_2. Four separate concentrates were prepared, each of which was a stable, clear liquid. The partial vapor pressures were measured 24 hours after the concentrates were formulated. The compositions of these concentrates, their bromine partial vapor pressures and the thermodynamic crystallization temperatures are set forth in Table 5.

Table 5

Physical and Chemical Characteristics of formulations of Example 4

Parameters	Comp. #1	Comp. #2	Comp. #3	Comp. #4
Wt.% H_2O	--	--	6	10
Wt.% Methanol	15	26	--	--
Wt.% 46% NaBr, or 52% $CaBr_2$, or 38% KBr or 54% LiBr	25	42	30	20
Wt. % 48% HBr	25	--	30	36
Wt.% Br_2	34	34	34	34
% Available Br_2 by Titration	33.6	34.6	35.1	34.5
Density (g/mL)	1.67	1.56	1.92	1.72
Partial Vapor Pressure (mm Hg at 20°C)	22.5	39.5	48.5	39.5
Crystallization Temp. (°C)	$-55<X<-68$	$X<-68$	-50	-30
pH	$X<0$	0.11	$X<0$	$X<0$

Tests were conducted on the solubility of gold in these concentrates. Solubilities at five different equivalent molecular bromine concentrations were tested for each of the concentrates by dilution of the concentrate with water prior to testing its solubility. These concentrations were 2.00 g/L, 1.00 g/L, 0.40 g/L, 0.20 g/L and 0.10 g/L of different 34% bromine concentrates. The amount of gold added to the concentrate was varied with the bromine content. After each gold specimen had been agitated in the diluted concentrate for 24 hours, the solutions were filtered using a 0.45 micron membrane. Gold analysis was conducted by ICP using a Thermo Jarrell Ash Atomscan 25. The gold solubility is set forth in Fig. 1.

Simulated batch kinetic tests were also conducted to determine the activity of each of the concentrates of this example for the dissolution of gold. The experiments were performed using Corning stir plates and sealed glass bottles. In each test run, a specimen of minus 325 mesh powdered gold (99.99% purity) was introduced at a concentration of 0.6 g/L into a specimen of the concentrated which had been diluted to a concentration of 2 g/L equivalent molecular bromine. The total volume of the kinetic test batch was brought to 500 mL by addition of deionized water. The resulting mixture was agitated at room temperature. Samples of 20mL each were withdrawn at time intervals of 0.25, 0.5, 1, 2, 4, and 24 hours. The volume of the batch was held constant during the test period by additions of deionized water equivalent in volume to the sample withdrawn. The results of the kinetic tests are set forth in Fig. 2.

EXAMPLE 5

The four concentrates of Example 4 were tested as reagents for recovery of gold from a refractory gold concentrate sample. The conditions and results of these tests are set forth in Tables 6-9.

Table 6

Leaching of Refractory Concentrate

Sample Size:	50.00 g Calcine
Fire Assay (Calcine):	17.3 oz/t Au
Feed Preparation:	-100 mesh; roasted at 700°C
Conditions:	22°C; pH = 5; 20.0% solids; 4 hours mixing; ORP = 930 mv
Lixiviant:	1.0 g Formula # 1

Metallurgical Balance

Calcine to leach 50.00 g	17.3 oz/t Au (29.64 mg)
Filtrate 65.0 mL	43.17 mg/L Au (28.06 mg)
Residue 47.9 g	1.11 oz/t Au (1.82 mg)
Au Solubilized	93.91%

Table 7

Leaching of Refractory Concentrate

Sample Size:	50.00 g Calcine
Fire assay (Calcine):	17.3 oz/t Au
Feed Preparation:	-100 mesh; roasted at 700°C
Conditions:	22°C; pH = 5; 20.0% solids; 4 hours mixing; ORP = 930
Lixiviant:	1.0 g Formula # 2

Metallurgical Balance

Calcine to Leach 50.00 g	17.3 oz/t Au (29.64 mg)
Filtrate 650 mL	44.62 mg/L Au (29.00 mg)
Residue 44.4 g	1.19 oz/t Au (1.96 mg)
Au Solubilized	93.67%

Table 8

Leaching of Refractory Concentrate

Sample Size:	50.00 g Calcine
Fire Assay (Calcine):	17.3 oz/t Au
Feed Preparation:	-100 mesh; roasted at 700°C
Conditions:	22°C; pH = 5; 20.0% solids; 4 hours mixing; ORP = 930 mv
Lixiviant:	1.0 g Formula # 3

Metallurgical Balance

Calcine to leach 50.00 g	17.3 oz/t Au (29.64 mg)
Filtrate 650 mL	46.04 mg/L Au (29.93 mg)
Residue 47.95 g	1.00 oz/t Au (1.64 mg)
Au Solubilized	94.81%

Table 9

Leaching of Refractory Concentrate

Sample Size:	50.00 g Calcine
Fire assay (Calcine):	17.3 oz/t Au
Feed Preparation:	-100 mesh; roasted at 700°C
Conditions:	22°C; pH = 5; 20.0% solids; 4 hours mixing; ORP = 930 mv
Lixiviant:	1.0 g Formula # 4

Metallurgical Balance

Calcine to Leach 50.00 g	17.3 oz/t Au (29.64 mg)
Filtrate 492.65 mL	63.14 mg/L Au (31.11 mg)
Residue 44.4 g	0.695 oz/t Au (1.06 mg)
Au Solubilized	96.7%

EXAMPLE 6

Using the method generally described in Example 1, a concentrate was prepared having the formulation of Composition #4 of Table 4 (Example 4). The effectiveness of this composition for recovery of gold from ore was tested using a rotating disk technique, and also using the simulated batch technique as generally described in Example 4.

The rotating disk test was conducted using a Pine Instrument model AFASR Rotator having a gold disk electrode. The parameters of the experiment were:

temperature:	25°C
rotation rate:	500 rpm
volume of sample:	200 mL
electrode area:	0.203 cm^2
perbromide concentration:	5 g/L
pH:	3.2

The rotating disk experiment was initiated by the introduction of the gold disk electrode, while rotating, into the solution. Samples of the solution were withdrawn at 5 minute intervals for gold analysis, pH and temperature being recorded.

In the simulated batch kinetic experiments, samples were withdrawn at intervals of 0.16, 0.33, 0.5, 1, 2, 4, 8 and 24 hours.

In both experiments, the volume was maintained constant by additions of deionized water to compensate for sample withdrawal. All gold analyses were done by ICP (Inductively Coupled Plasma Spectrophotometer) using a Thermol Jarrell Ash Atomscan 25.

The results of the simulated batch kinetic studies are illustrated in Fig. 3, while the results of the rotating disk studies are shown in Fig. 4.

EXAMPLE 7

Compositions were prepared having the formulations indicated in Table 10. The bromine partial vapor pressure and initial crystallization temperature were determined for each of these compositions. These data are also recorded in Table 10.

Table 10

Composition	NaBr wt.%	HBr wt.%	Br_2 wt.%	H_2O wt.%	F_C[1]	p.Vp[2]
A.*	28.1	0	43.7	28.1	-	79.5
C.	9.55	9.69	21.1	59.7	-15	42.0
D.*	-	24.6	48.7	26.7	-	74.5
E.	15.8	16.0	35.0	33.2	+13	-
F.	8.3	26.8	24.1	40.8	-35	28.0
G.	7.2	23.1	34.7	35.1	-2	42.0
H.	7.4	23.9	32.5	36.3	-2	40.0
K.	10.3	19.2	28.2	42.4	-6	37.0
L.	13.6	13.4	30.1	42.9	-5	47.5
M.	4.88	29.1	23.8	42.2	-	24.0
N.	3.75	22.4	41.4	32.4	-	53.0
O.	4.3	25.7	32.8	37.2	-	29.0

1 Temperature at which first crystal appears in °C

2 Partial vapor pressure of bromine in mm of Hg

* A = $NaBr_3$ and D = HBr_3

Set forth in Table 11 are the NaBr/HBr ratio, Br_2 content and bromine partial vapor pressure of formulations F, G, H, M, N, and O of Table 10.

Table 11

	NaBr/HBr		Br^-/Br_2	Br_2		
Composition	wt. ratio	mol. ratio	wt. ratio	wt.%	mol.%	Vp.*
F.	0.31	0.24	1.4	24.1	5.3	28
G.	0.31	0.25	0.8	34.7	8.6	42
H.	0.31	0.25	0.9	32.5	7.9	40
M.	0.17	0.13	1.4	23.8	5.1	24
N.	0.17	0.13	0.6	41.4	10.9	53
O.	0.17	0.13	0.9	32.8	7.8	29

*Partial vapor pressure of Br_2 in mm Hg.

Formulations G and H were prepared by adding bromine to formulation F. Each of formulations F through H have an NaBr/HBr weight ratio of 0.31 but vary in bromine content. It will be noted that the bromine partial vapor pressure is 40 mm Hg at a bromine content of 32.1% and a Br^-/Br_2 weight ratio of 0.9. By comparison, compositions M, N and O, which have an NaBr/HBr weight ratio of only 0.17, appear to exhibit lower vapor pressures for comparable combinations of Br^-/Br_2 ratio and Br_2 content. Thus, a preferred range of compositions of the invention have an NaBr/HBr ratio of less than 0.25, preferably, less than about 0.2, with a Br^-/Br_2 weight ratio of at least about 1.0 and a bromine content of at least about 30% by weight.

Each of compositions of Table 10 was tested for recovery of gold from ore concentrates, and each was found to be effective for that purpose.

EXAMPLE 8

Acidic bromine concentrates were prepared having the compositions set forth in Table 12. Measurements were made of Br_2 partial pressure and other parameters. These are also set forth in Table 12. The compositions of this table are effective for precious metal recovery and industrial water treatment.

Table 12

Organic Solvent	-----	Acetic Acid	Propionic Acid
Wt.% H_2O (from 48% HBr)	33.8	19.3	19.3
Wt.% 48% HBr	65.0	37.0	37.0
Wt.% Organic Solvent	-----	28.0	28.0
Wt.% Br_2 (experimental)	36.5	36.8	36.6
pH	<0	<0	<0
Br_2 Partial Pressure (mm Hg at 20°C)	39.0	20.0	17.0
Density (g/mL)	1.87	1.64	1.60
Crystallization Temp (°C)	-45	<-50	-42

EXAMPLE 9

Cooling tower water was treated with a concentrate comparable to that of the first column of

Table 12 (Example 8). Using a diaphragm pump (Liquid Metronics, Model A151-92T) and #15 Viton tubing, the concentrate was delivered into the basin of a cooling tower. Two methods were employed to determine the most efficient delivery of the product. The first method was simply letting the product drip into the water from the end of tubing attached to the discharge side of the pump. The feed rate was calculated by measuring the volume pumped into a graduated cylinder over a 1 minute time interval. The last 1 foot of tubing was placed horizontal to the surface of the water about 1.5 feet high. In the second method, the end of the discharge tubing was below the surface of the water. The feed rate was calculated in the same manner as the first method, but for this method a larger stroke size and frequency in the pump was used to inhibit back siphoning. The only indication of proper pump action was the presence of a brown cloud in the water when the pump was activated.

The total residual oxidant (TRO) sample site was approximately at the turning point for the water before it is routed back to the tower. The TRO was determined by a Hach Cl-17 Chlorine Analyzer. The analyzer employs the DPD colorimetric method, by which the analyzer compares the optical absorbance of the raw water with the optical absorbance of the water with the DPD reagents. The difference is used to calculated the TRO in ppm as Cl_2. The optical frequency used for this method was 510 nm. The Cl-17 had a LED display to two decimal points for recording immediate data, and also a chart recorder for obtaining overnight data. The analyzer was checked for accuracy by a hand-held DPD colorimeter (colorwheel).

Selecticult-TTC (Scott Laboratories, Inc.) dipslides were used to determine the microbial density of the cooling tower water. The sample sites were in the basin of the cooling tower, above the basin, and at the normal site for operator water analysis. The dipslides were submerged in the water for approximately 1 second, then incubated at room temperature for 2-3 days before reading the slides.

Table 13 lists all the cooling tower data generated during the tests. Samples of the cooling from water were analyzed for calcium concentration, chlorine residual, and pH. All readings for the week of the tests showed no significant changes in concentration or level.

Table 13

Plant Data

TEST DAY	CALCIUM	ALKALINITY	CONDUCTIVITY	PHOSPHATE	CHLORINE	pH
1st	50 ppm	20 ppm	240 mV	100 ppm	0.1 ppm	T.T
2nd	60 ppm	40 ppm	240 mV	100 ppm	0.1 ppm	T.5
3rd	--	2 ppm	--	--	--	-
4th	50 ppm	18 ppm	240 mV	50 ppm	0.4 ppm	T.5
5th	50 ppm	18 ppm	240 mV	50 ppm	0.3 ppm	T.5

Table 14 is a listing of the data generated on second day of the tests. The data include time, air temperature, TRO, volumetric feed rate of CN-1767, feed method, pump setting, and microbial density. The initial microbial density was approximately 10^5 organisms/mL. At 9:45 am, started feeding of concentrate was at approximately 2.0 mL/minute by letting the product drip in the water. The pump stroke size was set at the smallest setting and the frequency set at 25 strokes per minute (spm) (approximate). The TRO was recorded every hour, and at 14:45 the TRO stabilized at 0.27 ppm as Cl_2. The feed rate was then increased to approximately 4.0 mL/minute by changing the pump frequency to 35 spm while maintaining the minimum stroke setting. During the next 15 hours, the average TRO was 0.44 ppm as Cl_2.

Table 14

November 6, 1990
Field Trial Data

TIME	AIR TEMPERATURE	TRO as Cl2	FEED RATE ml/min	FEED METHOD	PUMP SETTING stroke/ freq.	CELL COUNT cells/ml
9:45	45 F	-	2.0	drip	min/25	100.E+05
10:45		0.11	2.0	drip	min/25	
11:45		0.22	2.0	drip	min/25	
12:45		0.24	2.0	drip	min/25	
13:45		0.28	2.0	drip	min/25	1.00E+04
14:45	60 F	0.27	2.0	drip	min/25	
14:55	-	4.0	drip	min/35		
15:45		0.33	4.0	drip	min/35	
16:45		0.40	4.0	drip	min/35	
17:45	50 F	0.40	4.0	drip	min/35	
18:45		0.40	4.0	drip	min/35	
19:45		0.43	4.0	drip	min/35	
20:45		0.44	4.0	drip	min/35	
21:45		0.36	4.0	drip	min/35	
22:45		0.36	4.0	drip	min/35	
23:45		0.39	4.0	drip	min/35	
24:45		0.44	4.0	drip	min/35	

- = Not Determined
min = minimum

On the third day at 7:45, the TRO was 0.53 ppm as Cl_2 and the microbial density was $<10^3$ organisms/mL. The feed method was changed to the submerged tubing method. The pump was set at a minimum stroke and the frequency at 25 spm. The TRO decreased to 0.16 ppm as Cl_2 so at 13:50, the pump settings were increased to 17 stroke/30 spm frequency. At 15:45, the TRO was 0.35 ppm, which was higher than anticipated. At 15:50, the settings were then decreased to 18 stroke/25spm frequency, which was 2.0 mL/min. These data are presented in Table 15. Over the next 15 hours, the average TRO was 0.44 ppm as Cl_2.

Table 15

November 7, 1990
Field Trial Data

TIME	AIR TEMPERATURE	TRO as Cl2	FEED RATE ml/min	FEED METHOD	PUMP SETTING stroke/ freq.	CELL COUNT cells/ml
1:45			0.44	4.0	drip	min/35
2:45			0.44	4.0	drip	min/35
3:45			0.42	4.0	drip	min/35
4:45			0.64	4.0	drip	min/35
5:45			0.52	4.0	drip	min/35
6:45			0.51	4.0	drip	min/35
7:45		35 F	0.53	4.0	drip	min/35
8:15		0.53	4.0	drip	min/35	<1.00E+03
8:20		-	2.0	submerged	min/25	
8:45		0.48	2.0	submerged	min/25	
9:45		0.35	2.0	submerged	min/25	
10:45		0.26	2.0	submerged	min/25	
11:45		0.21	2.0	submerged	min/25	
12:45		0.19	2.0	submerged	min/25	
13:45		0.16	2.0	submerged	min/25	
13:50				change feed	to 18/30	
14:45	59 F	0.26	N.A.	submerged	30	
15:45		0.35	N.A.	submerged	18/30	
15:50				change feed	to 18/25	
16:45		0.33	2.0	submerged	18/25	
17:45	50 F	0.34	2.0	submerged	18/25	
18:45		0.32	2.0	submerged	18/25	
19:45		0.36	2.0	submerged	18/25	
20:45		0.37	2.0	submerged	18/25	
21:45		0.44	2.0	submerged	18/25	
22:45		0.48	2.0	submerged	18/25	
23:45		0.52	2.0	submerged	18/25	
24:45		0.53	2.0	submerged	18/25	

N.A. = Not Available
- = Not Determined

On the fourth day at 7:45, the TRO was 0.51 ppm as Cl_2 and the microbial density was $<10^3$ organisms/ml. To obtain a TRO of 0.30 ppm as Cl_2, the pump settings were decreased to 18 stroke/20 spm frequency or 1.0 mL/min. The TRO dropped to 0.08 ppm as Cl_2.

Figure 5 shows the hourly TRO and the daily bacterial density. At the beginning of the trial, the cell density was 10^5 organisms/mL. As the TRO increased to 0.28 and 0.53 ppm as Cl_2, the cell densities decreased to $<10^4$ and $<10^3$ organisms/ml, respectively. As the TRO decreased to 0.10 ppm as Cl_2 through the rest of the trial, the cell density remained $<10^3$ organisms/mL. The dipslide method for determining cell density will not differentiate cell densities less than 10^5 organisms/mL.

Figure 6 compares the TRO with the feed style. The two feed styles used are labeled "DRIP IN" and "SUBMERGED" as described above. The "DRIP IN" style was used first at a feed rate of 2.0 mL/min until the TRO leveled out at 0.28 ppm as Cl_2. The feed rate was increased to 4.0 mL/min, and the TRO leveled out around 0.53 ppm as Cl_2. The feed style was changed to the "SUBMERGED" style and for 2.0 mL/min. The TRO dropped to 0.[illegible] ppm as Cl_2 apparently because the product was siphoning back into the 5 gallon bucket. The pump settings were changed from minimum stroke/25 spm frequency to 18 stroke/30 spm frequency, this limited the back siphoning and the TRO increased to about 0.50 ppm as Cl_2. Using the same feed style, the feed rate was decreased to 1.0 ml/min, and the TRO decreased to about 0.28 ppm as Cl_2 dropped to 0.10 ppm as Cl_2 at the beginning of the work day.

As a material of construction for the delivery tubing, three types of plastic have been tested to date: standard PVC, Polypropylene, and XL-Polyethylene. The PVC surfaces that were in intimate contact with the concentrate showed no signs of incompatibility, however, some distress was noticed where the two coupons were in contact with each other. The Polypropylene and XL-Polyethylene coupons showed similar characteristics.

Both types of plastic absorbed the bromine color into the coupons, yet maintaining the integrity and flexibility of the plastic. The smell of bromine is very noticeable from the XL-Polyethylene coupons, but not from the Polypropylene or PVC coupons. The coupons were immersed in the concentrate for 3-4 months at room temperature.

At the end of the trial, the pump was inspected. The PVC head was scored on the inside, but the Teflon diaphragm was not even stained. The inlet and out-flow valves on the pump were stained, but not rendered functionless. The Viton tubing used with the pump showed excellent compatibility.

In view of the above, it will be seen that the several objects of the invention are achieved and other advantageous results attained.

As various changes could be made in the above products and methods without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

The claims defining the invention are as follows:

1. A composition the formulation of which comprises water, at least 25% by weight bromine, between 4% and 30% by weight hydrobromic acid, and between 4% and 15% by weight of a metal bromide selected from the group consisting of lithium bromide, sodium bromide, potassium bromide and calcium bromide, said formulation comprising a molar excess of bromide ion over bromine of at least 30%, said composition having a pH of not greater than 1.0.

2. A composition as set forth in claim 1 wherein said formulation comprises at least 30% by weight bromine, between 10% and 20% by weight hydrobromic acid, and between 10% and 15% by weight metal bromide.

3. A composition as set forth in claim 1 wherein said metal bromide consists substantially of sodium bromide.

4. A composition as set forth in claim 3 in which the molar ratio of sodium ion to equivalent molecular bromine is not greater than 0.8.

5. A composition as set forth in claim 1 wherein said formulation has a bromide ion to bromine mole ratio of between 1.2 and 2.0.

6. A composition as set forth in claim 1 wherein said formulation comprises water, at least 25% by weight bromine, between 10% and 30% by weight hydrobromic acid, and between 5% and 15% by weight calcium bromide.

7. A composition the formulation of which comprises water, at least 25% by weight bromine, at least 4% by weight hydrochloric acid, and between 10% and 15% by weight sodium bromide, said formulation comprising a molar excess of halide ion over bromine of at least 30%, said composition having a weight ratio of water to NaBr of not less than 4.0, and a pH of not greater than 1.0.

DATED this 19th day of October, 1995

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By:

(B. S. Wellington)

A/JD/3823

FIG. 1

SOLUBILITIES OF GOLD IN DIFFERENT 34% BROMINE FORMULATIONS

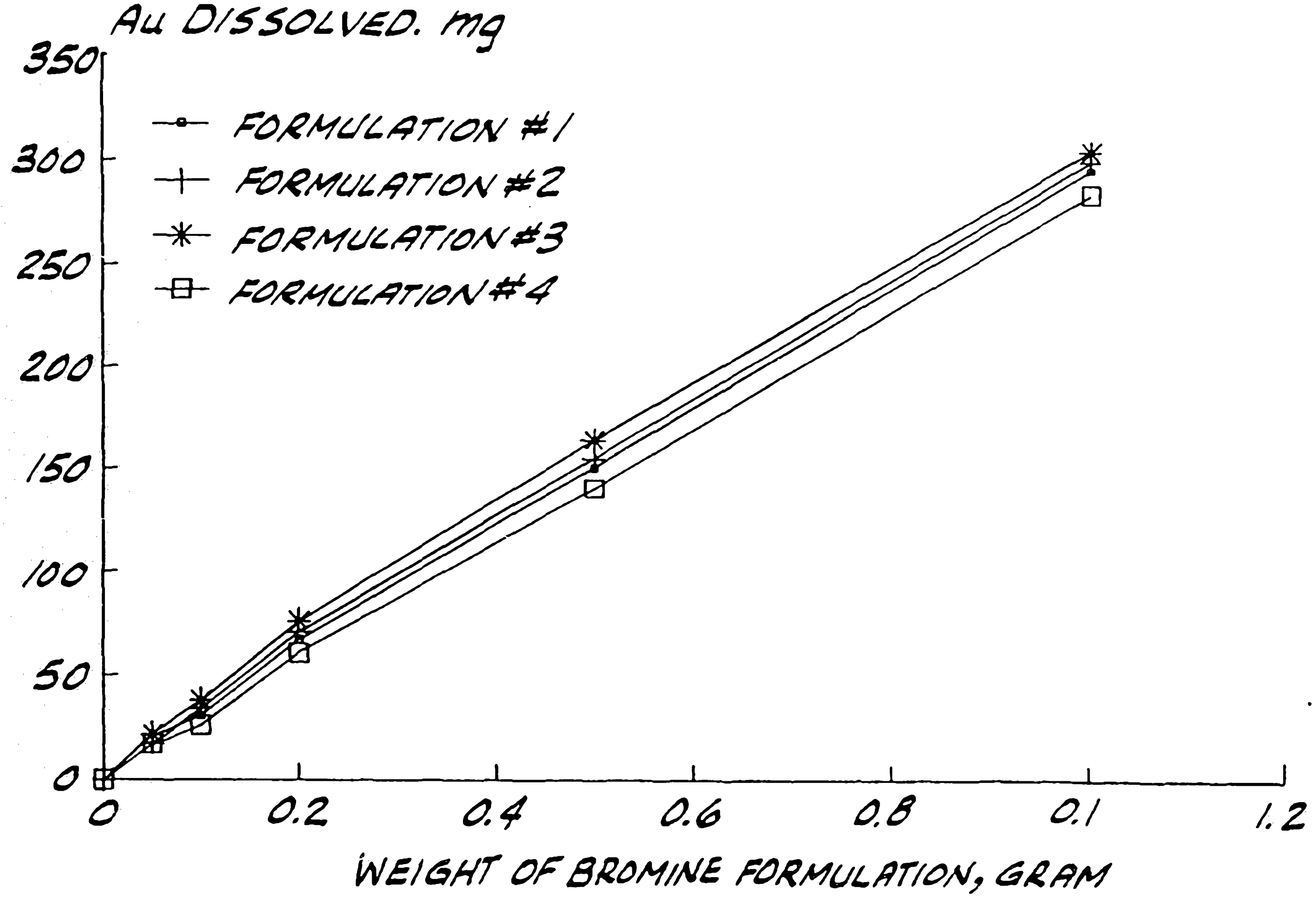


FIG. 2

KINETIC COMPARISON OF THE FOUR BROMINE FORMULATIONS

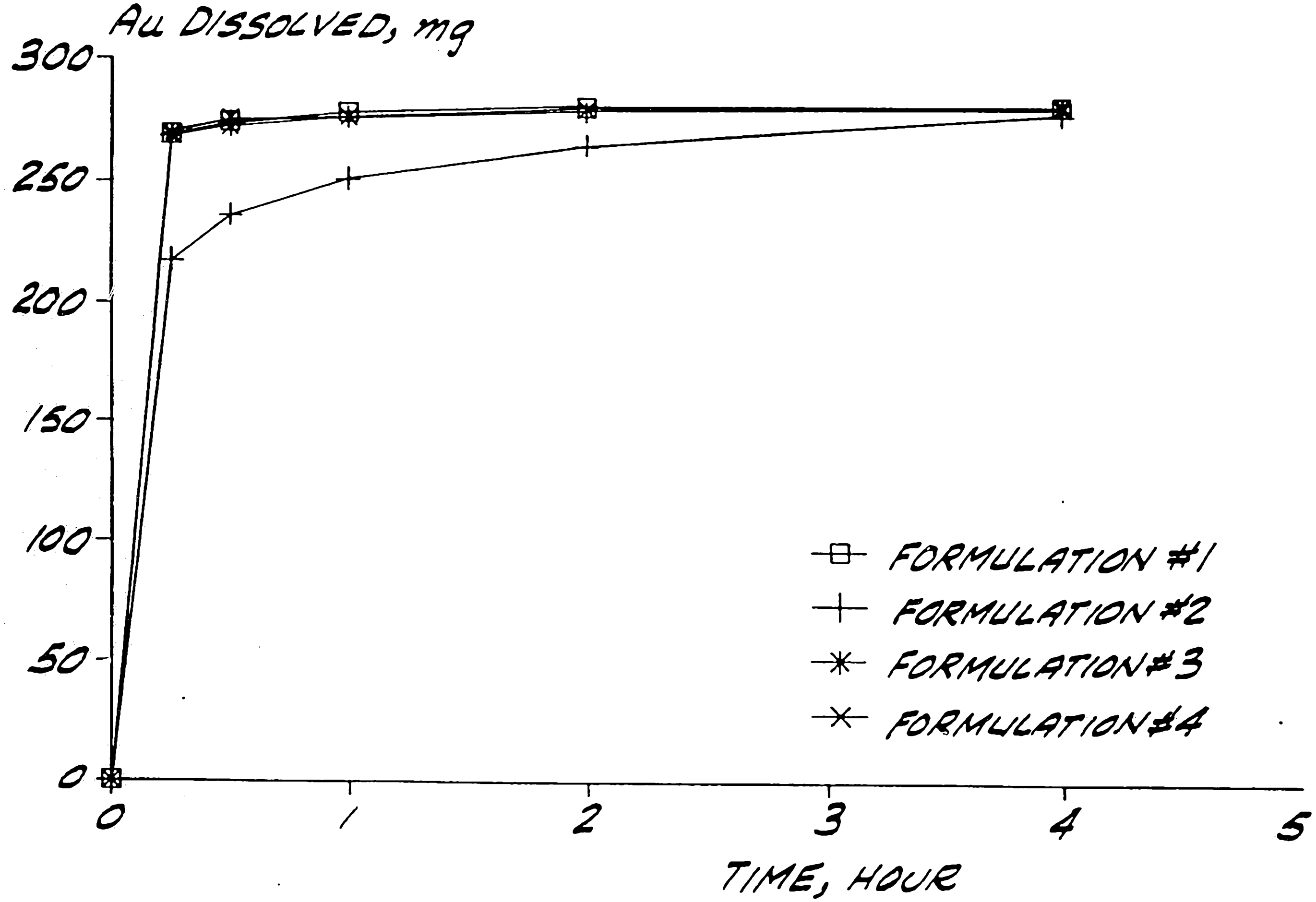
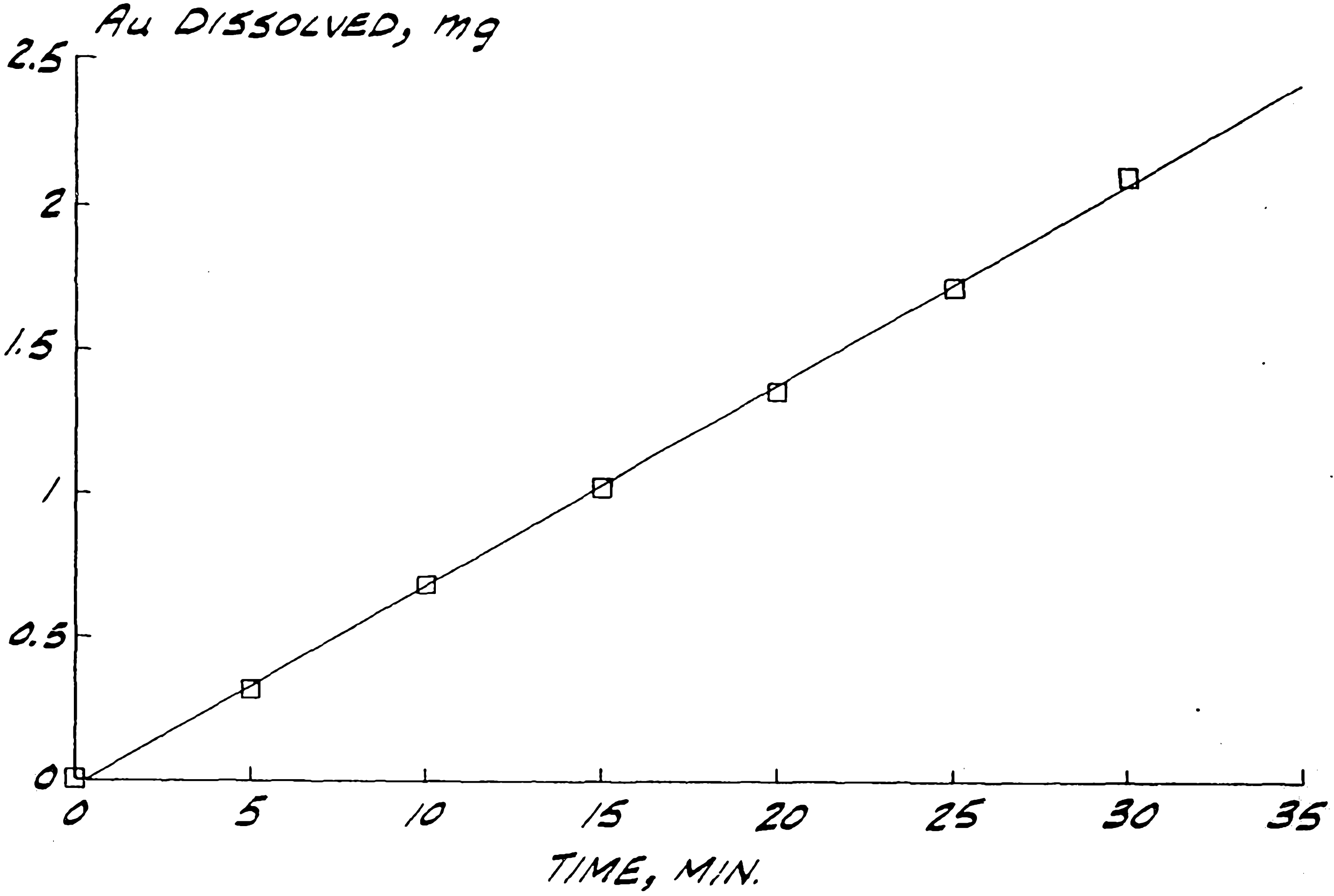


FIG.3



KINETICS OF GOLD DISPOSITION IN A 34% BROMINE SOLUTION USING THE ROTATING DISC TECHNIQUE

FIG. 4

KINETICS OF GOLD DISSOLUTION IN 34% BROMINE FORMULATIONS USING THE SIMULATED BATCH TECHNIQUE

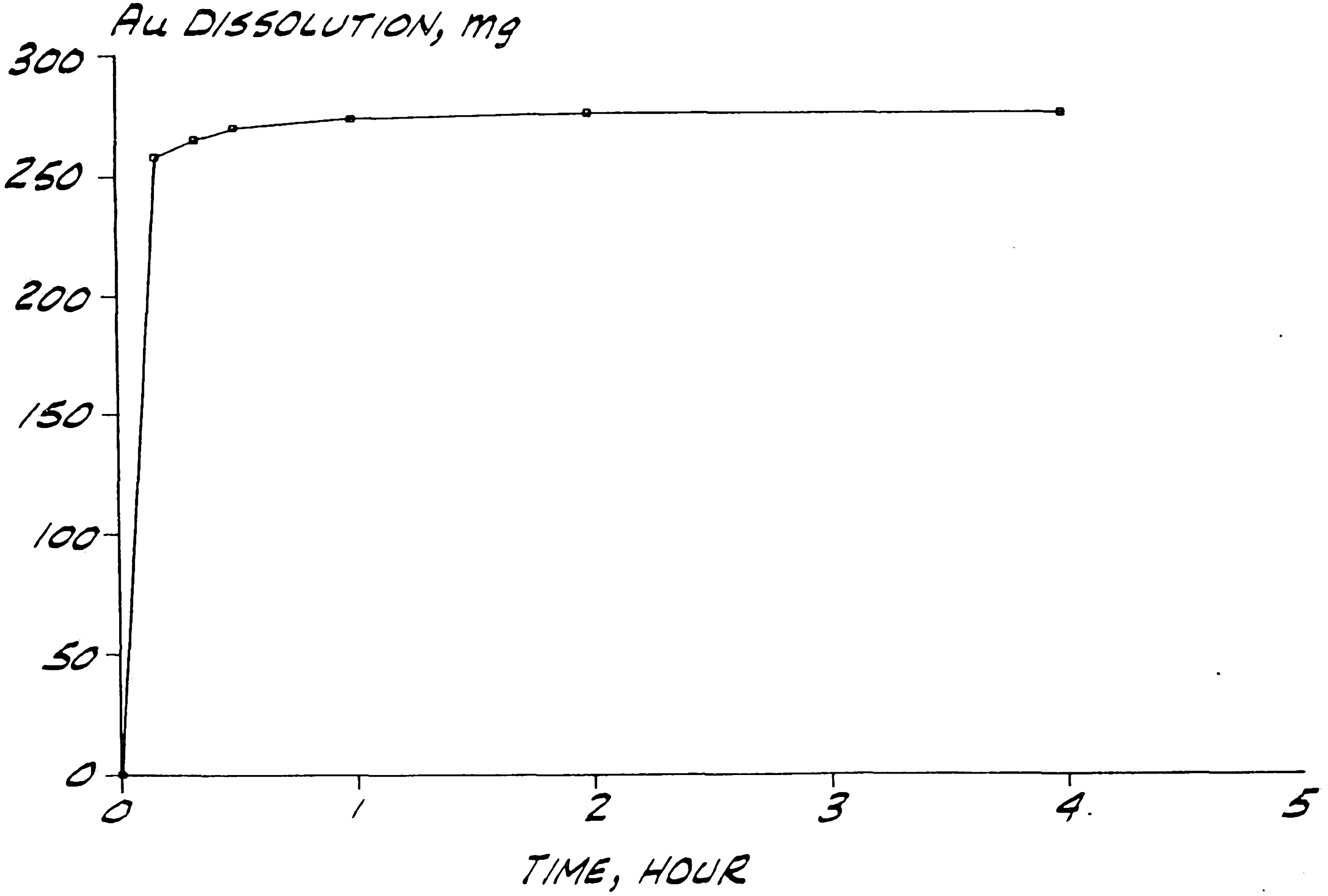


FIG. 5

CN-1767 FIELD TRIAL

TRO AND BACTERIAL DENSITY VS. TIME

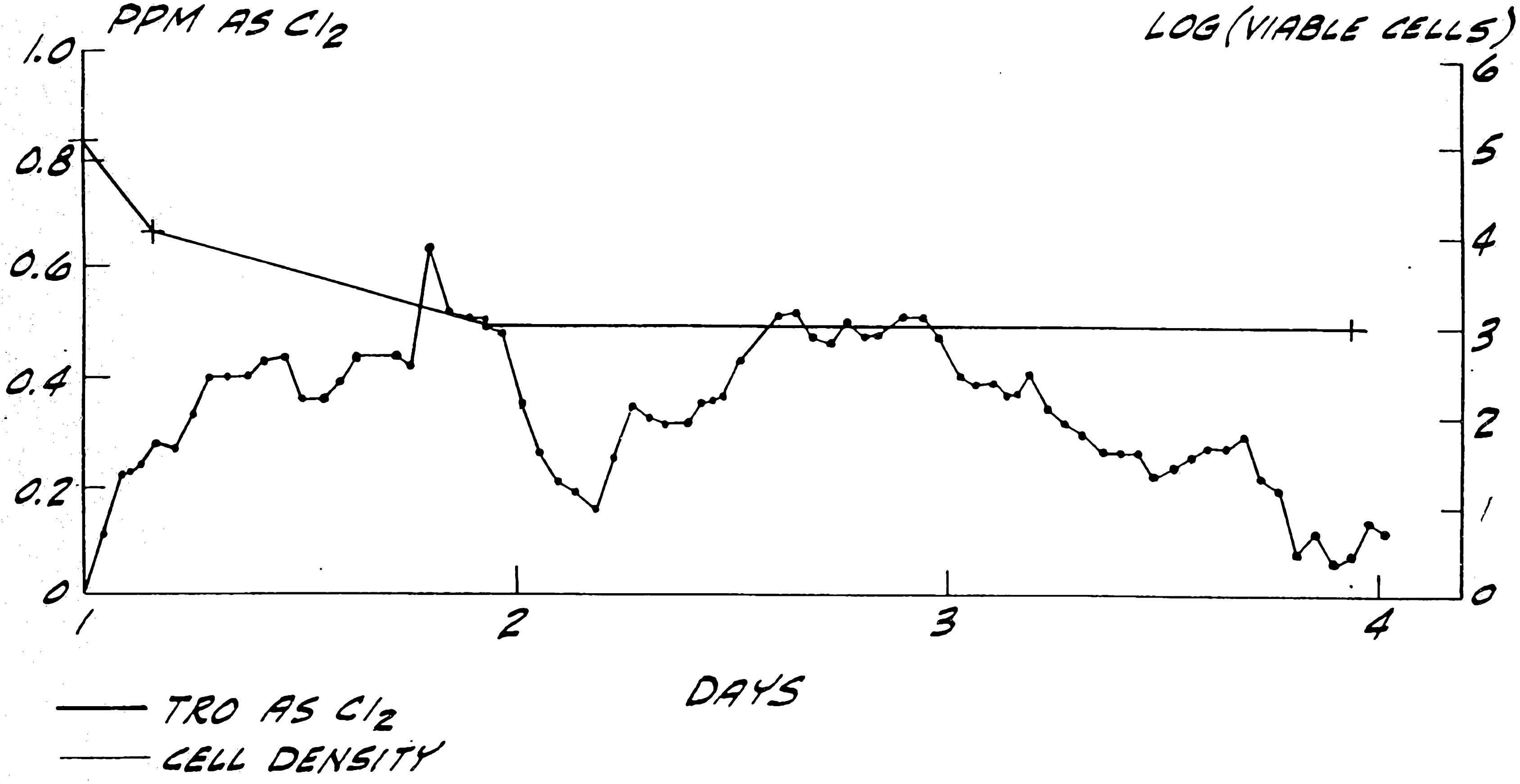
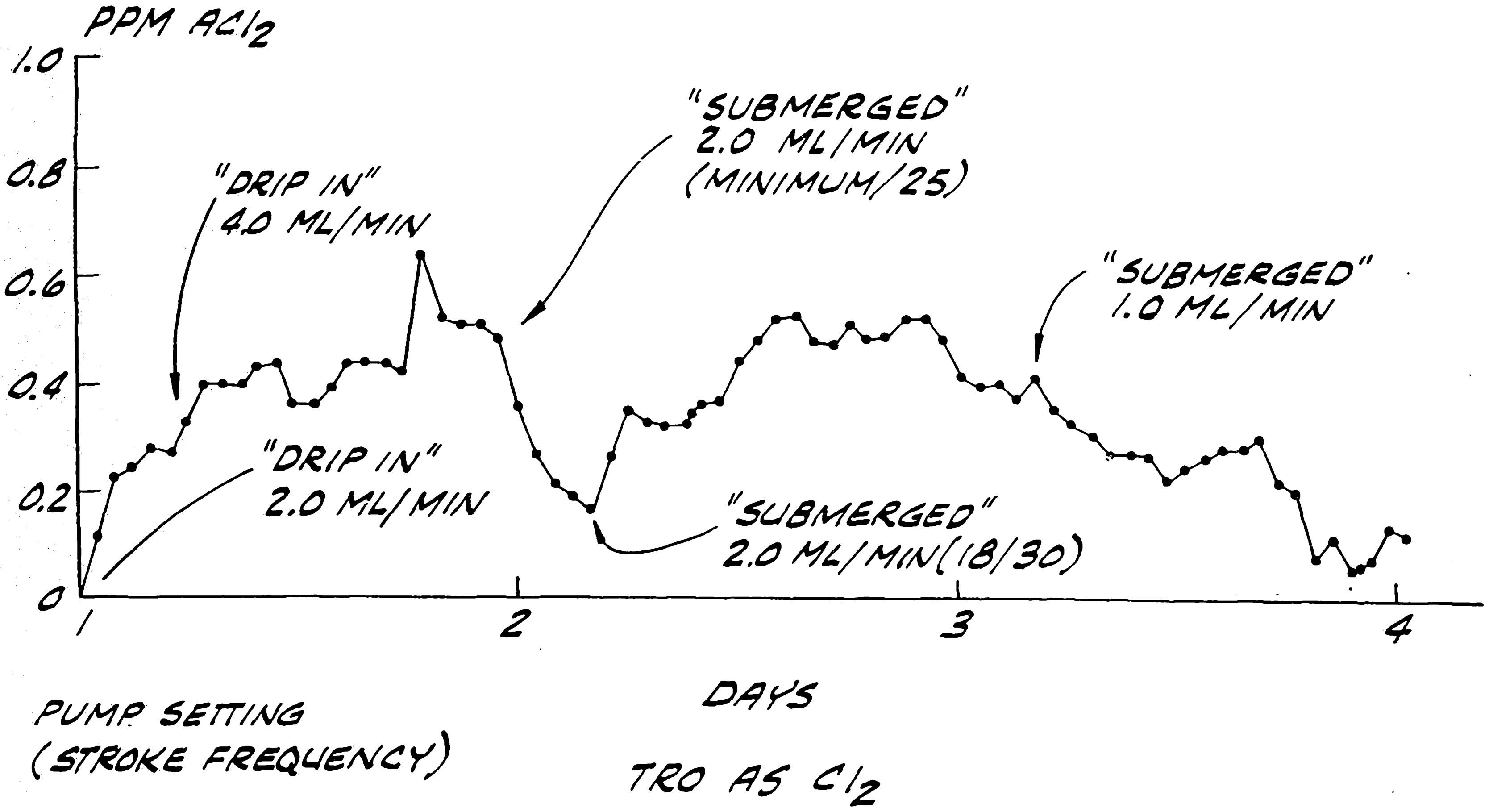


FIG.6

CN-1767 FIELD TRIAL
TRO AND FEED STYLE VS. TIME



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/02128

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :CO1B 7/09; B01D 11/02
US CL :252/187.2; 423/38 252/79.1,79.2; 423/46
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)

U.S. : 75/733,736

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A 4,190,489 (BAHL ET AL) 26 FEBRUARY 1989 (SEE SUMMARY OF INVENTIONS AND CLAIMS)	1-21
Y	US,A 4,936,910 (DADGOR ET AL) 26 JUNE 1990 (SEE ABSTRACT AND COLUMN 3 AND EXAMPLE 1)	1-21
A	US,A 3,936,332 (MATSUMOTO ET AL) 03 FEBRUARY 1976 (SEE ABSTRACT, DESCRIPTION OF THE INVENTION)	1-21
A	US,A 4,684,404 (KALOCSAI) 04 AUGUST 1987 (SEE ABSTRACT)	1-21

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be part of particular relevance
"E"	earlier document published on or after the international filing date
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"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

18 AUGUST 1992

Date of mailing of the international search report

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