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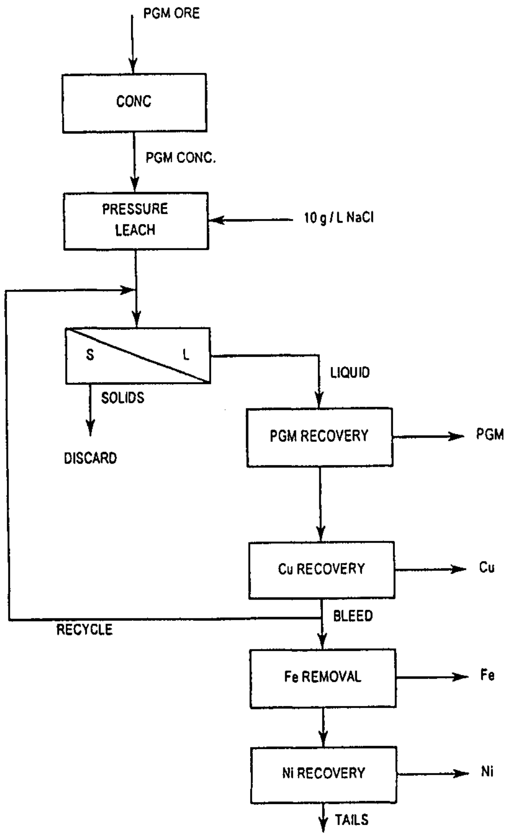
## (54) Title: OXIDATIVE PRESSURE LEACH RECOVERY OF PRECIOUS METALS USING HALIDE IONS

## (57) Abstract

A method for recovering a precious metal from a host material, comprises the steps of subjecting the host material to an oxidative pressure leach process, in the presence of a halide ion constituent, preferably a chloride ion, which is reactive with the precious metal, and at an elevated temperature of at least 170°C to cause at least a portion of the precious metal to be extracted by a leach solution in the form of a precious metal–bearing chloride complex, and recovering the precious metal from the leach solution. When the host material is a smelt malte material including a base metal and a precious metal, said malte is subjected to a first oxidative pressure leach process to recover substantially all of said base metal in the form of at least one sulphate complex into a first leach solution, and then said malte material is subjected to a second oxidative pressure leach process in the presence of a halide ion constituent and at a temperature sufficient to cause at least a portion of said precious metal to be recovered into a second leach solution, from which the precious metal is extracted.



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# OXIDATIVE PRESSURE LEACH RECOVERY OF PRECIOUS METALS USING HALIDE IONS

## BACKGROUND OF THE INVENTION

### 1. FIELD OF THE INVENTION

The present invention relates to methods for the recovery of precious metals from host materials, using pressure oxidation.

### 2. DESCRIPTION OF THE RELATED ART

Traditionally, gold is not included in the group of metals known as the platinum group metals which include platinum and palladium, rhodium, ruthenium, osmium and iridium. For the sake of brevity, the term 'precious metals' as used herein will refer to both gold and the platinum group metals that are present in the host material either as single elements or in any combination thereof . Typically, these precious metals are present in host materials along with other metals such as the base metals copper and nickel, in varying concentrations. These host materials are normally treated by grinding and flotation to produce a concentrate, which is then smelted. The constituent precious and base metals typically report to a matte phase during smelting. The matte phase is then processed by a variety of well established techniques to separate and recover the individual constituents in substantially pure form.

The matte typically undergoes oxidative pressure leaching at temperatures of 130 to 150 degrees Celsius which leaches the base metal component of the matte leaving the platinum group metals in the residue. After separating the solution from the residue, the residue is then typically leached, in atmospheric conditions, with concentrated hydrochloric acid and chlorine gas as the oxidant to dissolve the platinum group metals.

In certain cases, when the concentrations of valuable base metals (such as copper and nickel for example) are low, or when the concentrations of metals that are deleterious to smelting (such as arsenic or bismuth) are high, it is not economical to process the concentrates by smelting. In these instances, it can be advantageous to process the concentrate directly by a pressure leach process to leach the base metals.

Typically, the solid phase leaving the pressure leach step retains the precious metals while the copper and nickel transfer to the leach solution, for further processing by various hydrometallurgical procedures well known to the art. In this case, the precious metal constituent is recovered from the solid phase by relatively complex and expensive procedures, including leaching by chlorination or pressure cyanidation, followed by precious metal recovery by precipitation, solvent extractions or ion exchange techniques well known to the art. Though these processing routes may prove satisfactory in some cases, there are many host materials in which either the leach efficiency or the concentration of precious metals is insufficient for this relatively complex metallurgical flowsheet to be economically viable.

It is an object of the present invention to provide an improved technique for the recovery of precious metals.

## SUMMARY OF THE INVENTION

Briefly stated, the invention provides a method for recovering a precious metal portion and a base metal portion from a host material, comprising the steps of:

- subjecting said host material to an oxidative pressure leach process, in the presence of a chloride ion constituent at a temperature of at least 170 degrees Celsius in order to form a leach solution containing at least one precious metal-bearing chloride complex and a base metal complex; and
- recovering said precious metal from said chloride complex.

In another of its aspects, the invention provides a method for leaching a precious metal from a host material, comprising the steps of:

- subjecting said host material to an oxidative pressure leach process, in the presence of a chloride ion constituent at a temperature of at least 170 degrees Celsius in order to form a leach solution in which the leached precious metal is exclusively contained in a chloride complex; and

- recovering said precious metal from said chloride complex .

Preferably, the leach solution is at a pH of between 0 and 1, more preferably between 0 and 0.5.

Preferably, the temperature ranges from about 170 to about 275 degrees Celsius, more preferably 195 to 275 degrees Celsius. Alternatively, the temperature may be at least 180 degrees Celsius, more preferably 180 to 275 degrees Celsius.

In still another of its aspects, the invention provides a method for leaching a precious metal and a base metal from a host material in a single step by subjecting the host material to an oxidative pressure leach process, in the presence of a chloride ion constituent and at a temperature of at least 170 degrees Celsius in order to form a leach solution containing at least one precious metal- bearing chloride complex and the base metal.

In yet another of its aspects, the invention provides a method for economically leaching a precious metal from a host material, comprising the step of leaching said host material with salt water at a temperature of at least 170 degrees Celsius, in the presence of an oxidant and at sufficient pressure to form, in the leach solution, a chloride complex containing the precious metal.

If desired, the salt water can be ground water, sea water or otherwise naturally formed or may simply be a prepared.

In one embodiment, the base metal is contained in a base metal sulfate complex and the precious metal bearing chloride complex is a platinum-, palladium- or a gold-bearing complex.

In another of its aspects, the invention provides a method for recovering a precious metal from a host material, comprising the steps of:

- subjecting the host material to an oxidative pressure leach process, in the presence of a leach solution bearing a halide ion constituent which is reactive with the precious metal. and at a temperature sufficient to cause at least a portion of the precious metal to be extracted by said leach solution; and

- recovering the precious metal from the leach solution.

Preferably, the halide ion is selected from the group chloride, iodide or bromide. In this case. fluoride is not included because it is not sufficiently reactive with (or does not effectively complex with) gold and other precious metals. Chloride is particularly preferable because of its convenience and ease of handling as a salt, although chloride is generally inefficient, at lower concentrations (such as 20 g/L at 200 degrees Celsius) to recover silver. For the purposes of this process, the term 'precious metal' as used herein refers to both gold and the platinum group metals that are present in the host material either as single elements or in any combination thereof. Thus, for host materials which have an economical quantify of silver, it may be appropriate to increase the chloride levels to above 50 g/L.

Preferably, the halide ion originates from a halide salt which is added to the leach solution. Still more preferably, the halide ion is a chloride ion provided to the leach solution by a chloride salt. In this case, the chloride salt may include sodium chloride, calcium chloride or potassium chloride, as well as ferrous or ferric chloride, hydrochloric acid, cupric or cuprous chloride, lithium chloride, magnesium chloride and ammonium chloride, among still others.

Preferably, sufficient chloride salt constituent is present in solution to provide a chloride ion concentration ranging from about 0.5 g/L to about 100 g/L, more preferably from 1 to 20 g/L, still more preferably from 1.5 to 10 g/L. Still more preferably, the chloride ion constituent is present at a concentration ranging from about 3 to about 6 g/L. In one embodiment, the chloride salt is sodium chloride which itself is provided at a concentration of about 10 g/L.

In another aspect of the present invention, there is provided a method for recovering a precious metal from a host material. comprising the steps of:

- placing the host material in a pressure leaching vessel;

- subjecting the host material to an oxidative pressure leach process, in the presence of a halide ion constituent which is reactive with the precious metal, and at a temperature sufficient to cause at least a portion of the precious metal to be extracted by a leach solution; and

- recovering the precious metal from the leach solution.

Preferably, before recovering the precious metal from the leach solution, barren solid is separated from the leach solution, although it may be desirable in some cases to recover the precious metal from the leach solution before separating the barren solid, for example to minimize the loss of precious metals contained in the residual leach solution which can be lost with the separated barren solids.

In one embodiment, the oxidative pressure leach process takes place in the presence of a gaseous oxidant. Preferably, the gaseous oxidant is oxygen gas. The oxygen gas is preferably injected into the vessel at an oxygen partial pressure of between 1 and 500 psig, still more preferably between 10 and 200 psig and still more preferably between 50 and 100 psig. Other oxidants may also be effective including chlorine, the ferric ion, hydrogen peroxide and Caro's acid, though these may not in some cases be as economical as oxygen gas.

Preferably, the temperature ranges from about 170 degrees Celsius to about 300 degrees Celsius, more preferably from about 180 degrees Celsius to about 295 degrees Celsius, more preferably from about 195 degrees Celsius to about 275 degrees Celsius, more preferably from 200 degrees Celsius to 250 degrees Celsius, still more preferably from 210 degrees Celsius to about 230 degrees Celsius. However, the upper limit of 300 degrees Celsius is limited to the physical constraints of the pressure leaching systems currently available.

Preferably, the leach solution is acidic. Still more preferably, the acid constituent is sulphuric acid at a concentration ranging from 1 to 500 g/L. More preferably, the sulphuric acid is at a concentration ranging from about 5 to about 250 g/L, more preferably at a concentration ranging from about 10 to about 100 g/L.

It is important to maintain an elevated oxidation potential in solution during the leach (for example at levels greater than 500 mV versus Ag/AgCl) for maintaining precious metal leaching efficiencies in the process. This can be done by oxidizing, as completely as possible, any reduced species such as sulphide ions or sulphur in the feed to the process, for example.

It may also be done by converting most of the ferrous ion in solution to ferric ion. In addition, a tramp ion constituent, which is added as a consequence of grinding or re-grinding the feed to the process, may also contribute to a reduction in the precious metal recovery. This is especially true in the case of gold.

The host material may be in any one of a number of forms, including a primary sulphide or oxide ore body which has been processed by grinding and the like, an ore concentrate, or a secondary material containing precious metals, such as for example a spent oxidation catalyst. An example of a primary oxide ore body would be a laterite, which contains nickel and cobalt as well as PGMs in some cases, and which is normally treated by pressure acid leaching to recover the nickel and cobalt. The host may also be a matte material from a smelting operation which, in contrast to the ore concentrates, can have precious metal concentrations of up to 10 percent, with the balance being base metals and sulphide. The host may also, in some cases, be a mixture of matte material and flotation concentrate. In these cases, it may be desirable either to recover the precious metals and base metals together into the leach solution or, alternatively, use a multiple step process to recover the base metals first and then the precious metals second. For example, in a first step, the base metals can be recovered to a first leach solution as in the prior art using concentrations of oxygen and suitable temperatures to obtain a first leach solution of base metals with residual amounts of sulphuric acid. The precious metals will be retained in the residue and may then be removed in a second phase at the conditions disclosed herein to recover the precious metals to a second leach solution.

The first phase may be carried out using just air or oxygen in the absence of a halide ion constituent to recover the base metal constituents as in the form of one or more sulphate complexes, such as copper(II)sulphate, nickel(II)sulphate and cobalt(II)sulphate. In this case, the oxidative leach autoclave of the first phase will likely be operating at relatively lower temperatures, than the oxidative leach process of the second phase which will have relatively higher temperature and be exposed to the halide ion constituent. Alternatively, the first phase may be carried out in the presence of a halide ion constituent at conditions as disclosed herein to recover the base and precious metal constituents simultaneously.

Thus, in yet another of its aspects, the present invention provides a method for recovering a precious metal from a smelt matte material, wherein said matte material includes a precious metal constituent and a base metal constituent, comprising the steps of:

- subjecting said matte material to a first oxidative pressure leach process, with sufficient oxidant and at a selected temperature to recover substantially all of said base metal constituent in the form of at least one sulphate complex into a first leach solution; and then

- subjecting said host material to a second oxidative pressure leach process, in the presence of a halide ion constituent which is reactive with said precious metal, and at a temperature sufficient to cause at least a portion of said precious metal to be recovered into a second leach solution; and then

- recovering said precious metal from said leach solution.

Preferably, the first oxidative pressure leach process occurs at a temperature ranging from 100 to 190 degrees Celsius, more preferably from 120 to 170 degrees Celsius, still more preferably from 130 to 150 degrees Celsius. Preferably, the second oxidative pressure leach process occurs at temperature ranging from about 170 degrees Celsius to about 300 degrees Celsius, more preferably from about 180 degrees Celsius to about 260 degrees Celsius, more preferably from about 195 degrees Celsius to about 275 degrees Celsius, more preferably from 200 degrees Celsius to 250 degrees Celsius, still more preferably from 210 degrees Celsius to about 230 degrees Celsius.

In still another of its aspects, the present invention provides a method for recovering a precious metal from a smelt matte material, wherein said matte material includes a precious metal constituent and a base metal constituent, comprising the steps of:

- subjecting said matte material to a single oxidative pressure leach process, in the presence of a halide ion constituent which is reactive with said precious metal constituent, and at a temperature sufficient to cause substantially all of said base metal and precious metal constituents to be recovered into a first leach solution; and

- recovering said base and precious metal constituents from said leach solution.

Preferably, the halide is chloride, though the other halides as disclosed herein are also contemplated.

In still another of its aspects, the invention provides a method for recovering a platinum group metal or gold from a host material, comprising the steps of:

- subjecting the host material to an oxidative pressure leach process, in the presence of a leach solution bearing a halide ion constituent which is reactive with the platinum group metal or gold, and at a temperature sufficient to cause at least a portion of the platinum group metal or gold to be extracted by said leach solution; and

- recovering the platinum group metal or gold from the leach solution.

## BRIEF DESCRIPTION OF THE DRAWINGS

Several preferred embodiments of the present invention will now be described, by way of example only, with reference to the appended drawings in which:

Figure 1 is a schematic view of a method for recovering precious metals;

Figures 2a, 2b and 2c are Eh – pH diagrams for several process examples;

Figure 3 is a plot of percent extraction versus temperature for several process examples;

Figure 4 is a plot of percent extraction versus chloride concentration for several process examples;

Figure 5 is a Cu extraction isotherm for one process example;

Figure 6 is a flowsheet for gold, PGM and base metal recovery for one process example; and

Figure 7 is a flowchart for another process example.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present method is based, in part, on the discoveries that:

i) one or a number of the precious metals and base metals may be leached from a host material in a single oxidative pressure leach process, whose leach solution may be treated to recover the individual precious and base metals, as desired; and

ii) this reaction can occur successfully with a relatively low concentration of halide ion in the leach solution , provided the selected halide ion is sufficiently reactive with the precious metals being recovered.

The present method involves the following steps:

i) subjecting the host material to an oxidative pressure leach process, in the presence of a leach solution bearing halide ion constituent which is reactive with the precious metal, and at a temperature sufficient to cause at least a portion of the precious metal to be extracted by the leach solution; and

ii) recovering the precious metal from the leach solution.

In one embodiment, the host material is a sulphide ore body or ore concentrate. During pressure leaching in the presence of oxygen, the sulphide component of the host material is oxidized to sulphuric acid. In this case, the process takes place in an acidic environment ranging from 20 to 100 g/L sulphuric acid. In other words, the acid is produced during the reaction to solubilize the copper and nickel.

In one embodiment, the successful leach of precious metals and base metals from a host material occurs in the presence of an acid, in this case, sulphuric acid and at a temperature of at least 200 degrees Celsius. It is believed that the process may also function at temperatures below 200 degrees Celsius and to temperatures as high as economically achievable. It is also believed that the presence of acid in the leach solution has a desirable effect of increasing the overall recovery of precious metals from the host material. Thus, the temperature selected for the pressure leach reaction of the present process will depend on the mineralogical characteristics and particle size of the feed material, the concentration of precious metals in the feed material, the acid strength, the oxygen partial pressure and the residence time in the pressure leaching vessel.

When the halide ion is a chloride, the chloride salt may be preferably selected from sodium chloride, calcium chloride or potassium chloride. More preferably, the salt is sodium chloride and is provided at a concentration ranging from about 1 g/L to about 100 g/L, still more preferably from 2 to 20 g/L, still more preferably from 5 to 15 g/L, still more preferably from 8 to 12 g/L.

In one embodiment, the chloride salt is sodium chloride at a concentration of about 10 g/L in solution. The optimum concentration of the chloride ion will likely tend to be higher with increasing concentration of the precious metal being recovered.

In one embodiment, the oxidative pressure leach process takes place in the presence of a gaseous oxidant. Preferably, the gaseous oxidant is oxygen gas. The oxygen gas is preferably injected into the vessel at an oxygen partial pressure of between 1 and 500 psig, still more preferably between 10 and 200 psig and still more preferably between 50 and 100 psig.

When using an autoclave for the oxidative pressure leach and chloride ions as the halide, it has been discovered that the addition of chloride at concentrations as low as ~3 g/L (5 g/L NaCl) in some cases resulted in the dissolution of most of the precious metals in the autoclave. For example, by conducting the chloride leach in the autoclave, not only does Pt recovery improve from <50% to ~98% under optimum conditions, but significant capital and operating cost savings will be achieved by leaching the precious metals in the same vessel and within the same reaction time as the base metals Cu and Ni, when present, under essentially the same conditions as required for efficient base metal recovery. Apart from the fairly minor cost of chloride losses to the tailings, and the fact that it will be necessary to select autoclave materials that will withstand the increased corrosive autoclave environment, the precious metals leaching costs should be absorbed in the base metal leaching costs. Moreover, the present process does not require catalysts such as ammonia to promote the reaction to form a precious metal-bearing complex.

The high temperature autoclave oxidation process converts metal sulfide minerals into metal sulfates and iron hydrolysis products (primarily hematite). The oxidation of gold, palladium, platinum and other precious metals is favoured by the presence of relatively small amounts of chloride in solution. The chloride stabilizes the various platinum group elements as dissolved chloro complexes.

The chemical reactions believed to occur during the present process, for example in an autoclave, are shown below. The mineralogy of the precious metals may be very complex, but for simplicity only the metallic species are considered.

*Chalcopyrite Oxidation/Iron Hydrolysis:*

$$CuFeS_2 + 17/4O_2 + H_2O \rightarrow CuSO_4 + 1/2Fe_2O_3 + H_2SO_4 \tag{1}$$

*Pyrite Oxidation:*

$$FeS_2 + 15/4O_2 + 2H_2O \rightarrow 1/2Fe_2O_3 + 2H_2SO_4 \tag{2}$$

*Pyrrhotite Oxidation:*

$$FeS + 8/4O_2 + H_2O \rightarrow 1/2Fe_2O_3 + H_2SO_4 \tag{3}$$

*Nickel Sulfide Oxidation:*

$$NiS + 2O_2 \rightarrow NiSO_4 \tag{4}$$

*Gold Oxidation/Chlorocomplex Formation:*

$$Au + 1/4O_2 + 1/2H_2SO_4 + 4NaCl \rightarrow Na_3AuCl_4 + 1/2Na_2SO_4 + 1/2H_2O \quad (5)$$

***Platinum Oxidation/Chlorocomplex Formation:***

$$Pt + O_2 + 2H_2SO_4 + 6NaCl \rightarrow Na_2PtCl_6 + 2Na_2SO_4 + 2H_2O \quad (6)$$

***Palladium Oxidation/Chlorocomplex Formation:***

$$Pd + 1/2O_2 + H_2SO_4 + 4NaCl \rightarrow Na_2PdCl_2 + Na_2SO_4 + H_2O \quad (7)$$

Referring to figure 1, once the precious metals are in solution, a number of approaches can be selected to recover the precious metal constituent first, such as by the use of activated carbon adsorption or ion exchange resin adsorption, or reduction with of sulphur dioxide and a precipitation with sodium hydrosulfide and other suitable sulfide containing compounds such as $Na_2S$ and $H_2S$, as well as copper cementation. In the case of adsorption on activated carbon or ion exchange resins, the precious metals constituent can be recovered directly, if desired, from the acidic pulp phase prior to solid liquid separation, which may be advantageous in some circumstances.

While a number of ranges have been provided herein above for a chloride concentration, there may be, in some cases, other ranges that are suitable, given changes in the composition of the feed, particularly changes in the concentrations of the precious metals.

Embodiments of the present invention will be described with reference to the following examples which are presented for illustrative purposes only and are not intended to limit the scope of the invention.

| TEST No | CONCENTRATE REGRIND | REGRIND MEDIA | LEACH TEMP (°C) | NaCl ADDED (g / L) | ANALYZED | GOLD (g / L) | PLATINUM (g / L) | PALLADIUM (g / L) |
|---|---|---|---|---|---|---|---|---|
| 0 | | | | | FEED | 2.24 | 1.75 | 8.91 |
| 1 | NO | | 220 | 0 | RESIDUE | 3.32 | 1.97 | 5.44 |
| | | | | | EXTN , % | 7 | 29 | 61 |
| 2 | NO | | 220 | 10 | RESIDUE | 0.27 | 0.49 | 1.37 |
| | | | | | EXTN , % | 91 | 79 | 88 |
| 3 | YES | STEEL | 220 | 10 | RESIDUE | 0.74 | 0.18 | 0.47 |
| | | | | | EXTN , % | 79 | 93 | 96 |
| 4 | YES | STEEL | 220 | 5 | RESIDUE | 0.64 | 0.16 | 1.01 |
| | | | | | EXTN , % | 79 | 93 | 92 |
| 5 | YES | STEEL | 200 | 10 | RESIDUE | 2.71 | 1.97 | 10.9 |
| | | | | | EXTN , % | 0 | 4 | 0 |
| 6 | YES | CERAMIC | 220 | 10 | RESIDUE | 0.13 | 0.06 | 0.72 |
| | | | | | EXTN , % | 96 | 98 | 94 |
| 7 | YES | CERAMIC | 220 | 10 | RESIDUE | 0.13 | 0.06 | 0.64 |
| | | | | | EXTN , % | 96 | 98 | 95 |

| | | |
|---|---|---|
| CONCENTRATE PARTICLE SIZE | $R_{80}$ | 32 MICRONS |
| REGROUND CONCENTRATE | $R_{80}$ | 15 - 20 MICRONS |
| OXYGEN PARTIAL PRESSURE | 100 PSI | |
| LEACH TIME | 2 HOURS | |

TABLE 1

| SAMPLE | METAL CONCENTRATION ( ppm UNLESS STATED OTHERWISE ) | | | | | |
|---|---|---|---|---|---|---|
| | Cu | Ni | Fe | Au | Pt | Pd |
| LEACH SOLUTION | 15200 | 18500 | 1500 | 0.32 | 0.24 | 1.24 |
| BARREN SOLUTION | 14300 | 18200 | 1340 | 0.01 | 0.00 | 0.01 |
| PRECIPITATE | 61.8 % | 0.2 % | 0.4 % | 92 | 102 | 484 |

TABLE 2

EXAMPLES:

Tests were conducted with 5 and 10 g/L NaCl added to the pressure leach solution for a precious metal-bearing ore flotation concentrate, including gold, platinum and palladium. In this case, the pressure leach was carried out in an autoclave.

The results pertaining to gold, platinum and palladium are shown in table 1 for several tests under different conditions. It can be seen that 91 to 96 percent of the resident gold, 93 to 98 percent of the resident platinum and 94 to 96 percent of the resident palladium were successfully recovered into the leach solution, using different temperatures and concentrations of NaCl in solution. Recoveries of copper and nickel to the leach solution were over 94 percent in all the tests.

The efficacy of the process may be improved with an increase in surface area of the host material to the pressure leach solution and, desirably, the ore may be ground to 75% passing 75 microns or a concentrate may be re-ground to 75 percent passing 20 microns.

It can also be seen that the presence of a tramp ion constituent, as a consequence of grinding or re-grinding the feed to the process, appears to have contributed to a reduction in the precious metal recovery. This reduction can be seen in tests 3 to 5 whose samples were re-ground using steel ball media in comparison with tests 6 and 7 whose samples were re-ground using inert ceramic ball media.

However, it will also be seen that, in the case of experiment 5, essentially no precious metals were recovered from the concentrate wherein the temperature was 200 degrees Celsius, wherein the concentrate was re-ground, despite the presence of 10 g/L NaCl in solution. Therefore, temperature may, in some cases, have a significant influence on the successful recovery of precious metals using the present process.

In one test, the acidic leach solutions from tests 6 and 7 was combined and treated by a process to recover the precious metals into a precipitate. The leach solution was first reduced with sodium metabisulphite from a potential of 570 mV to 340 mV (versus Ag/AgCl). Sodium hydrogen sulphide was then added to the reduced leach solution at a concentration of 2.5 g/L NaHS. The results of this test are shown in table 2.

The thermodynamic stability at 25°C of the chloro-complexes of gold, platinum and palladium, at concentrations similar to those encountered during these examples, is graphically presented as Eh-pH in Figures 2. These equilibrium diagrams indicate that the oxidizing potential required to form the chloro-complex of Pd in the acidic domain is lower than those of platinum and gold.

Cu and Ni recovery was high in all the tests, but PGM and gold recovery was found to be a sensitive function of the operating conditions. For example, it was observed that regrinding the float concentrate from a $K_{80}$ of 32 microns (Test 2) to 15-20 microns (Test 3) improved Pt recovery from 79 to 93% and Pd from 88 to 96%, but actually resulted in a decrease in gold recovery from 91 to 79%. This was thought to be due to the cementation of gold chloride onto residual flakes of iron powder (introduced during fine grinding in a stirred mill with steel grinding media).

Supporting this theory was the observation that gold recovery improved to ~96% (Tests 6, 7) when the regrind media were changed to ceramic balls. Pt and Pd recovery remained very high. The effects of temperature and salt addition (without regrind) are presented in Figures 3 and 4. The effect of acid concentration in the autoclave was not yet been assessed. Under the conditions tested, the feed to the autoclave contained ~25 g/L free $H_2SO_4$ (due to recycling a portion of the autoclave liquor after copper solvent extraction (hereinafter referred to as 'SX'), to build up Ni concentration and to provide autoclave coolant) and the discharge contained 55-65 g/L $H_2SO_4$. Salt addition had no effect on base metals recovery, but has a direct effect on precious metals extraction (Figure 4). Palladium is extracted to an extent without salt but this reaction is not easy to control.

## GOLD AND PGM RECOVERY FROM THE AUTOCLAVE PRODUCT

Two approaches have been tested; precipitation with sulphide ions and adsorption on activated carbon. In both cases, the autoclave liquor was treated directly without neutralization of the 55-65 g/L $H_2SO_4$ in solution. This may be an important requirement of a precious metal recovery process, as it was shown in the testwork that gold and the PGM's partially precipitated during neutralization. The sulphide precipitation flowsheet may require solid/liquid separation prior to precious metal recovery, whereas the activated carbon flowsheet could be applied to solutions or pulps.

Precipitation with sodium hydrogen sulphide (NaHS) was effective, particularly when the pregnant leach liquor was first treated with $SO_2$ or metabisulfite to reduce the $Fe^{3+}$ to $Fe^{2+}$ and lower the emf to ~400 mV (Ag/AgCl). Results from a precipitation test are presented in Table 5.

**Table 5. NaHS Precipitation of Gold and the PGM's from Pre-Reduced Pregnant Solution**

| | Cu | Ni | Fe | Au | Pt | Pd |
|---|---|---|---|---|---|---|
| Preg solution, mg/L | 17000 | 19900 | 1550 | 0.32 | 0.34 | 1.23 |
| Barren solution, mg/L | 14300 | 18200 | 1340 | 0.01 | 0.00 | 0.01 |
| Precipitate | 61.8% | 0.19% | 0.37% | 92 g/t | 102 g/t | 484 g/t |
| Precipitation efficiency, % | 16 | <0.1 | 1 | 97 | ~100 | 99 |

Further tests to optimize the amount of NaHS indicated that the concentration of copper in the final precipitate could be reduced quite significantly without compromising precious metal precipitation efficiency. The precious metal precipitate could either be sold directly to a copper smelter or, preferably, pretreated in a small pressure leach reactor to dissolve the copper and produce a very high grade precious metal residue (>10% precious metal's) for sale to a precious metal refinery.

A limited amount of testwork has been done on base metal recovery. Copper recovery by conventional solvent extraction/electrowinning was very efficient. In two stages of countercurrent extraction with 30% LIX984 in ISOPAR M (a Trademark), it was possible to reduce copper in solution from 9100 mg/L to less than 400 mg/L, producing an organic phase containing 16 g/L Cu. The presence of ~10 g/L NaCl in the pregnant solution had no adverse effect on copper extraction or selectivity, with the loaded organic containing copper at a purity of >99.98%. The extraction isotherm is presented in Figure 5.

Various alternatives were tested for the treatment of the copper SX barren solution to recovery nickel and cobalt (respectively ~17 and ~0.6 g/L at steady state). After purification of the bleed stream for iron and copper removal, the bleed could be processed for simultaneous nickel and cobalt SX, or stepwise cobalt SX, followed by nickel SX. Main issues concern elements such as zinc, magnesium and calcium, but the testwork demonstrated the technical viability of the two processes considered. The overall conceptual flowsheet is presented in Figure 6.

## APPLICATION OF THE PROCESS TO VARIOUS OTHER CU/NI CONCENTRATES

The present process was briefly tested on several other Cu/Ni concentrates from various mines in North America (USA + Canada) and South Africa. Analyses of the various concentrates tested are presented in Table 6.

**Table 6. Analyses of the Various Cu/Ni Concentrates Tested**

| Elements | Concentrate Type | | | | | | |
|---|---|---|---|---|---|---|---|
| % | A | B | C | D | E | F | G |
| Cu | 4.4 | 2.6 | 3.2 | 5.8 | 2.1 | 12.0 | 4.2 |
| Ni | 9.9 | 4.7 | 5.7 | 4.1 | 3.1 | 3.01 | 7.7 |
| Fe | - | 19.0 | 23.8 | 17.1 | 12.6 | 33.9 | 35.9 |
| S | - | 33.7 | 14.1 | 16.3 | 7.3 | 24.5 | 34.1 |
| Au, g/t | 2.5 | 3.6 | 4.0 | 12.4 | 5.0 | 0.9 | 0.5 |
| Pt, g/t | 6.0 | 24.6 | 81.1 | 12.3 | 490 | 0.8 | 1.4 |
| Pd, g/t | 14.4 | 38.9 | 59.8 | 143 | 294 | 2.8 | 2.0 |
| Rh, g/t | 1.8 | 4.1 | 14.2 | - | 103 | - | - |
| $Cr_2O_3$ | - | 0.20 | 0.35 | 0.20 | 2.2 | - | - |
| $Al_2O_3$ | - | 3.22 | 2.04 | 9.3 | 6.2 | - | - |
| MgO | - | 15.3 | 14.4 | 4.5 | 17.6 | - | - |
| CaO | - | 4.5 | 1.8 | 6.6 | 2.8 | - | - |
| $SiO_2$ | - | 33.7 | 28.3 | - | 39.3 | - | - |

With the exception of Sample A, these were all "one-off" leaches, using the test conditions according to table 7. Metal extractions are summarized in Table 7.

**Table 7. Performance of the Process on Various Cu/Ni Concentrates Tested - Scoping Tests**

*10-20 g/L NaCl; 220°C; 50 g/L $H_2SO_4$ initial; 100 psi $O_2$ overpressure*

| | % Extraction in Leach | | | | | | |
|---|---|---|---|---|---|---|---|
| Elements | A | B | C | D | E | F | G |
| Cu | 99.9 | 98 | 99.9 | 99.9 | 99.9 | 99.3 | 99.0 |
| Ni | 99.9 | 99 | 99.9 | 99 | 99 | 93.8 | 99.6 |
| Au | 93 | 83 | 96 | 99 | 83 | 97.1 | 84.3 |
| Pt | 72 | 80 | 76 | 95 | 51 | 97.4 | 98.2 |
| Pd | 97 | 93 | 94 | 94 | 80 | 98.1 | 93.9 |
| Rh | 95 | 77 | 92 | - | - | - | - |

As expected, base metal extractions are excellent in all cases. The results for these tests are quite promising for the precious metal's recovery. Without optimization, gold recovery is higher than 83% in all cases, and higher than 93% in several cases. Palladium recovery is usually higher than 93%, while platinum extraction is more difficult. The high grade precious metal concentrate (Concentrate E) requires further study.

## OTHER SULPHIDE FEEDSTOCKS

The present process has a wide range of application. It can be applied to feeds other than Cu/Ni concentrates, for example mattes and copper-gold concentrates. Table 8 presents head assays of samples of matte and copper concentrate submitted to the present process to the test conditions of table 7.

**Table 8. Analyses of Other Feedstocks**

| Elements | | Feedstock | |
|---|---|---|---|
| | | Matte | Cu Conc |
| Pt | g/t | 16.3 | - |
| Pd | g/t | 34.6 | - |
| Au | g/t | 9.2 | 5.7 |
| Cu | % | 73.0 | 28.9 |
| Ni | % | 17.3 | <0.01 |
| Fe | % | 0.2 | 28.3 |
| S | % | 9.5 | 33.3 |

The matte was produced in a SIROSMELT ( a trademark) furnace, while the copper concentrate was a typical chalcopyrite concentrate. The two samples were submitted the test conditions at table 7. The results are presented in Table 9.

**Table 9. Results for a Matte and a Au Chalcopyrite Concentrate**

| Elements | % Extraction in Leach | |
|---|---|---|
| | Matte | Cu Conc |
| Cu | 99.9 | 99.7 |
| Ni | 99.9 | - |
| Au | 80.9 | 95.9 |
| Pt | 99.4 | - |
| Pd | 99.4 | - |

These results show that the base metals (Cu+Ni) extraction from the matte was practically complete, as well as that of the platinum and palladium. Gold extraction was lower (81%) during that one-off test, and could likely be improved.

Recovery of copper and gold from the chalcopyrite concentrate was excellent (99.7 and 95.9%, respectively). The gold in solution was easily recovered on activated carbon (CALGON GRC-22) (a trademark) directly from the pressure oxidative leach liquor, without prior pH adjustment, generating a barren solution at less than 0.01 mg/L Au. A simplified flowsheet for copper-gold ores is presented in Figure 7. Gold recovery with the present process appears straightforward.

## LATERITES HOST MATERIALS

It is well known that certain laterites do contain measurable amounts of platinum (for example the Syerston deposit in Australia). A sample of laterite assaying 1.48% Ni, 0.18% Co and 0.76 g/t Pt was leached for 90 minutes at 250°C with 450 kg/t sulphuric acid and an addition of 20 g/L NaCl; under those conditions, 98% of the Ni, >95% of the cobalt and 97% of the Pt were dissolved. Although demonstrated only on a low grade Pt laterite, the present process should also be applicable to higher grade platinum-bearing laterites.

The following references are incorporated herein by reference:

1. R.C. Hochreiter, et. al., "Platinum in South Africa", Journal of the South African Institute of Mining and Metallurgy, June 1985

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4. G.P. Demopoulos, "Refining of platinum-group metals", CIM Bulletin, March 1989

4. R.P. Schouwstra, "The slow-cooling process: A mineralogical perspective", CIM Bulletin No. 1036, Jan. 2000

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8. Anon, "Hartley adds platinum to Zimbabwe's portfolio", Metals Bulletin M, Nov. 1996

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11. G.J. Hodges, et. al., "Stillwater Mining Co.'s precious metals smelter: From pilot to production", Mining Engineering, July 1991

12. L. Newman, M. Makwana, "Commissioning of the Stillwater Mining Company base metals refinery" Nickel Cobalt 97, Vol. 1, Hydrometallurgy and Refining of Nickel and Cobalt, Cooper and Mihaylov, Eds. 27th Annual Hydrometallurgy Meeting, CIM, Sudbury 1997

13. J. Kolstad, L. Newman, "The BMR refinery at Stillwater", New Dimensions in

Hydrometallurgy, FDW Seminar, Vancouver, 1998

14. Anon, “Processing of UG-2 ores”, Mintek Bulletin No. 97, August 1996

CLAIMS

1. A method for recovering a precious metal portion and a base metal portion from a host material, comprising the steps of:

   - subjecting said host material to an oxidative pressure leach process, in the presence of a chloride ion constituent at a temperature of at least 170 degrees Celsius in order to form a leach solution containing at least one precious metal-bearing chloride complex and a base metal complex; and

   - recovering said precious metal from said chloride complex.

2. A method as defined in claim 1 wherein the base metal complex is a base metal-bearing sulfate.

3. A method as defined in claim 1 wherein the leach solution is at a pH of less than 0.5.

4. A method as defined in claim 1 wherein the temperature ranges from 195 to 275 degrees Celsius.

5. A method for leaching a precious metal from a host material, comprising the steps of:

   - subjecting said host material to an oxidative pressure leach process, in the presence of a chloride ion constituent at a temperature of at least 170 degrees Celsius in order to form a leach solution in which the leached precious metal is exclusively contained in a chloride complex; and

- recovering said precious metal from said chloride complex.

6. A method as defined in claim 5 wherein the temperature is at least 180 degrees Celsius.

7. A method as defined in claim 6 wherein the temperature ranges from about 180 degrees Celsius to 295 degrees Celsius.

8. A method as defined in claim 5 wherein the leach solution is at a pH of less than 0.5.

9. A method as defined in claim 5 wherein the temperature is at least 195 degrees Celsius.

10. A method as defined in claim 5 wherein the temperature ranges from 195 to 275 degrees Celsius.

11. A method for leaching a precious metal and a base metal from a host material in a single step by subjecting the host material to an oxidative pressure leach process, in the presence of a chloride ion constituent and at a temperature of at least 170 degrees Celsius in order to form a leach solution containing at least one precious metal-bearing chloride complex and the base metal.

12. A method for economically leaching a precious metal from a host material, comprising the step of leaching said host material with salt water at a temperature of at least 170 degrees Celsius, in the presence of an oxidant and at sufficient pressure to form, in the leach solution, a chloride complex containing the precious metal.

13. A method as defined in claim 12 wherein the salt water is ground water, sea water or otherwise naturally formed.

14. A method as defined in claim 12 wherein the precious metal bearing chloride complex is a platinum-, palladium- or a gold-bearing complex.

15. A method for recovering a precious metal from a host material, comprising the steps of:

- subjecting said host material to an oxidative pressure leach process, in the presence of a halide ion constituent which is reactive with said precious metal, and at a temperature sufficient to cause at least a portion of said precious metal to be extracted by a leach solution; and

- recovering said precious metal from said leach solution.

16. A method as defined in claim 15 wherein said precious metal includes a platinum group metal or gold.

17. A method as defined in claim 15, wherein the halide ion is provided by adding a halide salt to said leach solution.

18. A method as defined in claim 15 wherein said halide ion is selected from the group chloride, iodide or bromide.

19. A method as defined in claim 16 wherein the halide salt is a chloride salt.

20. A method as defined in claim 19 wherein the chloride salt includes sodium chloride, calcium chloride or potassium chloride.

21. A method as defined in claim 15 wherein said halide ion constituent is a chloride ion which is present at a concentration ranging from about 0.5 g/L to about 100 g/L.

22. A method as defined in claim 21 wherein said chloride ion constituent is present at a concentration ranging from 1 to 20 g/L.

23. A method as defined in claim 22 wherein said chloride ion constituent is present at a concentration ranging from 1.5 to 10 g/L.

24. A method as defined in claim 23 wherein said chloride ion constituent is present at a concentration ranging from about 3 to about 6 g/L.

25. A method as defined in claim 15 wherein said temperature ranges from about 170 degrees Celsius to about 300 degrees Celsius.

26. A method as defined in claim 25 wherein said temperature ranges from about 195 degrees Celsius to about 275 degrees Celsius.

27. A method as defined in claim 26 wherein said temperature ranges from 200 degrees Celsius to 250 degrees Celsius.

28. A method as defined in claim 27 wherein said temperature ranges from 210 degrees Celsius to about 230 degrees Celsius.

29. A method as defined in claim 15 wherein said leach solution is acidic.

30. A method as defined in claim 29 wherein said acid is sulphuric acid.

31. A method as defined in claim 30 wherein said sulphuric acid is at a concentration

ranging from 1 to 500 g/L.

32. A method as defined in claim 31 wherein said sulphuric acid is at a concentration ranging from about 5 to about 250 g/L.

33. A method as defined in claim 32 wherein said sulphuric acid is at a concentration ranging from about 10 to about 100 g/L.

34. A method as defined in claim 15 further comprising, before the recovering step, the step of separating barren solid residue from said leach solution.

35. A method for recovering a precious metal from a host material, comprising the steps of:

- placing said host material in a pressure leaching vessel;

- subjecting said host material to an oxidative pressure leach process, in the presence of a halide ion constituent which is reactive with said precious metal, and at a temperature sufficient to cause at least a portion of said precious metal to be extracted by a leach solution; and

- recovering said precious metal from said leach solution.

36. A method as defined in claim 35 wherein said oxidative pressure leach process takes place in the presence of a gaseous oxidant.

37. A method as defined in claim 36 wherein said gaseous oxidant is oxygen gas.

38. A method as defined in claim 37 wherein said oxygen gas is injected into said vessel

at an oxygen partial pressure of between 1 and 500 psig.

39. A method as defined in claim 38 wherein said oxygen partial pressure is between 10 and 200 psig.

40. A method as defined in claim 39 wherein said oxygen partial pressure is between 50 and 100 psig.

41. A method as defined in claim 15 wherein said host material is a processed ore body.

42. A method as defined in claim 15 wherein said host material is an ore concentrate.

43. A method as defined in claim 15 wherein said host material is a matte material from a smelting process.

44. A method for recovering a precious metal from a smelt matte material, wherein said matte material includes a precious metal constituent and a base metal constituent, comprising the steps of:

- subjecting said matte material to a first oxidative pressure leach process, with sufficient oxidant and at a selected temperature to recover substantially all of said base metal constituent in the form of at least one sulphate complex into a first leach solution; and then

- subjecting said host material to a second oxidative pressure leach process, in the presence of a halide ion constituent which is reactive with said precious metal, and at a temperature sufficient to cause at least a portion of said precious metal to be recovered into a second leach solution; and then

- recovering said precious metal from said leach solution.

45. A method as defined in claim 44 wherein the first oxidative pressure leach process occurs at a temperature ranging from 100 to 190 degrees Celsius.

46. A method as defined in claim 45 wherein the first oxidative pressure leach process occurs at a temperature ranging from 120 to 170 degrees Celsius.

47. A method as defined in claim 44 wherein the first oxidative pressure leach process occurs at a temperature ranging from 130 to 150 degrees Celsius.

48. A method for recovering a precious metal from a smelt matte material, wherein said matte material includes a precious metal constituent and a base metal constituent, comprising the steps of:

- subjecting said matte material to a single oxidative pressure leach process, in the presence of a halide ion constituent which is reactive with said precious metal constituent, and at a temperature sufficient to cause substantially all of said base and precious metal constituents to be recovered into a first leach solution; and

- recovering said precious metal from said leach solution.

49. A method as defined in claim 48 wherein the halide is chloride.

50. A method as defined in claim 15 wherein the host material includes a laterite.

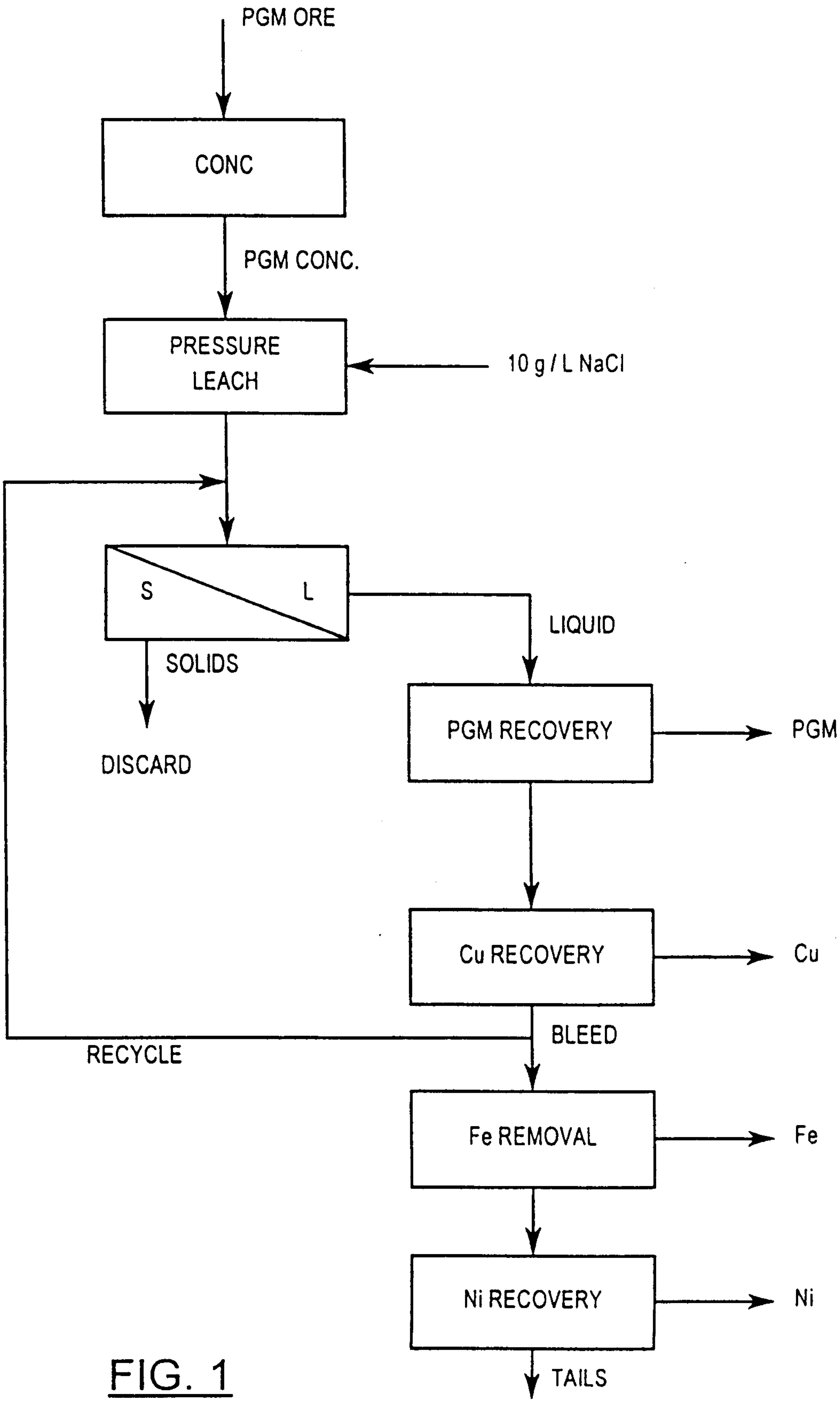
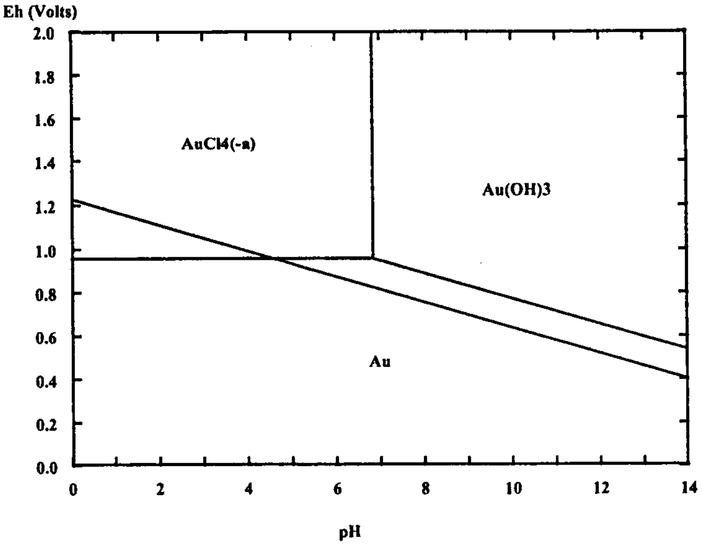
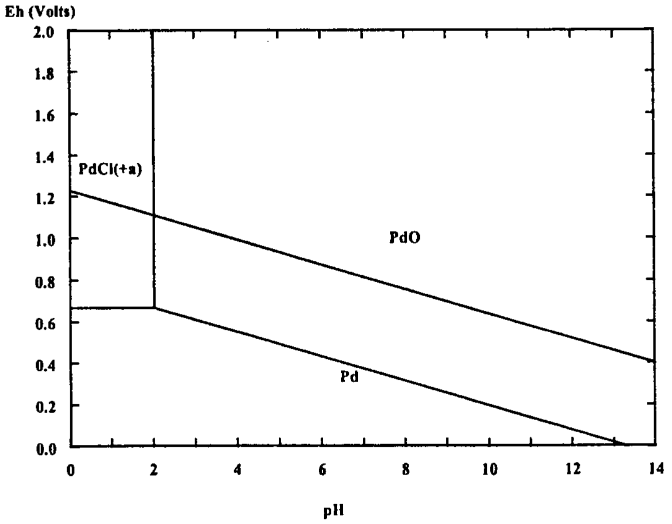

PGM ORE
CONC
PGM CONC.
PRESSURE LEACH
10 g / L NaCl
S
L
LIQUID
SOLIDS
DISCARD
PGM RECOVERY
PGM
Cu RECOVERY
Cu
BLEED
RECYCLE
Fe REMOVAL
Fe
Ni RECOVERY
Ni
TAILS

FIG. 1

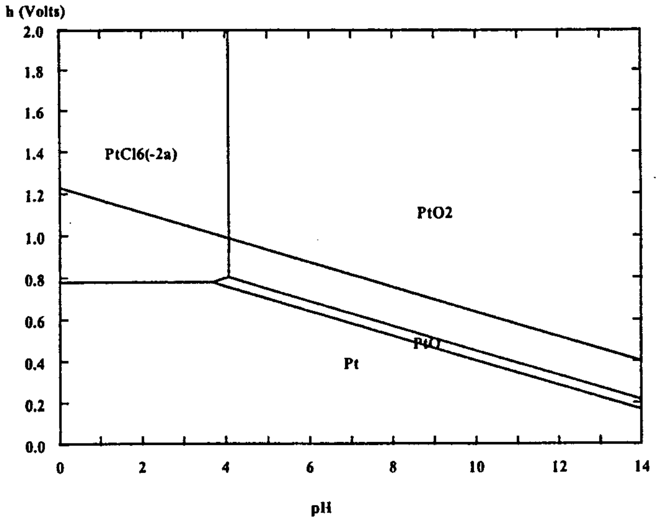
Figure 2 (a, b and c) Eh – pH Diagram



(a) Eh – pH Diagram for the Au-Cl system at 25 C. [Au] = 0.00001 M. [Cl] = 0.2 M.



(b) Eh – pH Diagram for the Pt-Cl system at 25 C. [Pt] = 0.00001 M. [Cl] = 0.2 M.



(c) Eh – pH Diagram for the Pd-Cl system at 25 C. [Pd] = 0.00001 M. [Cl] = 0.2 M.

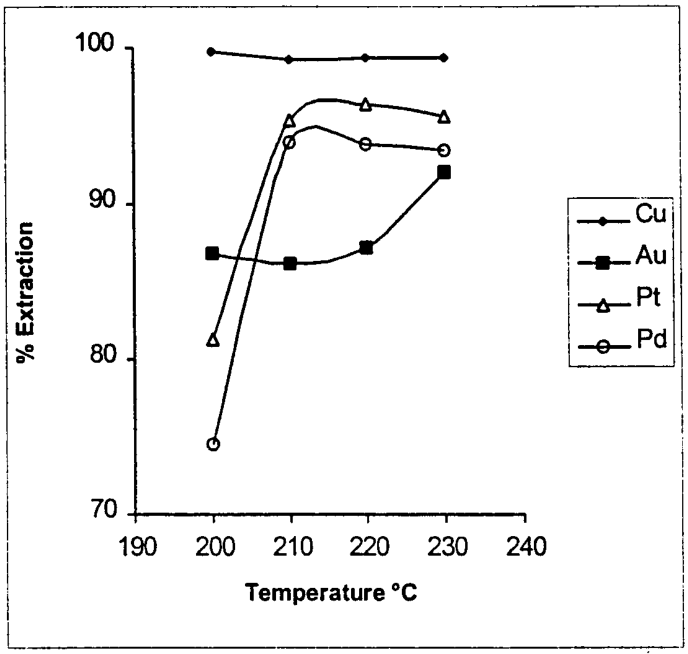


Figure 3. Effect of temperature on metal dissolutions

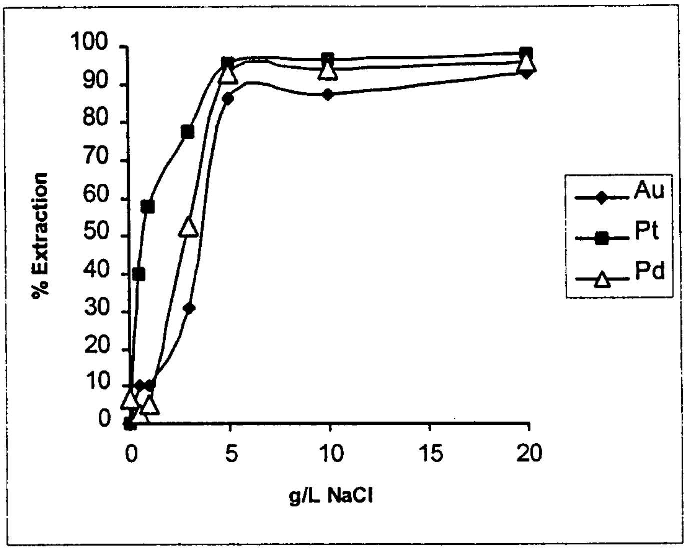


Figure 4. Effect of chloride additions on metal extractions

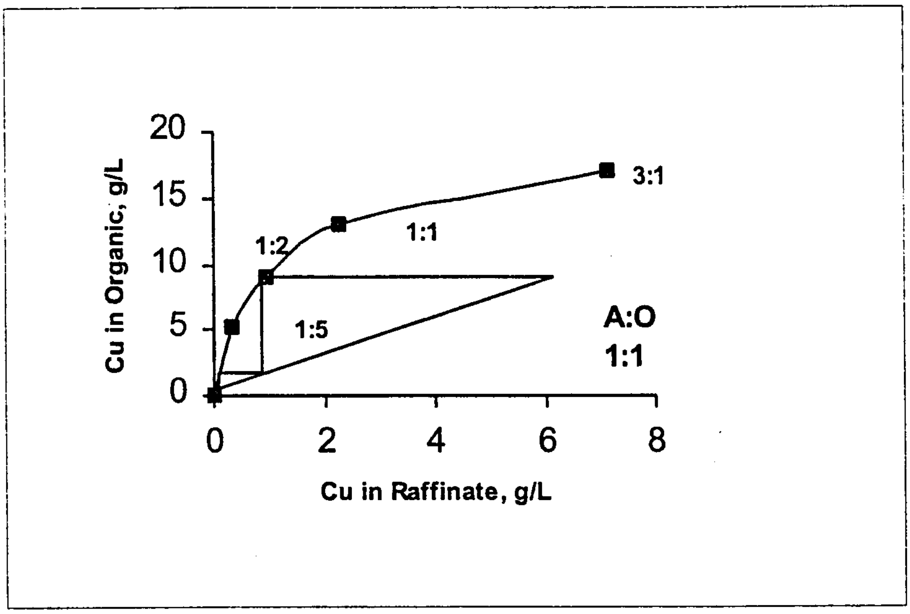


Figure 5. Cu Extraction isotherm

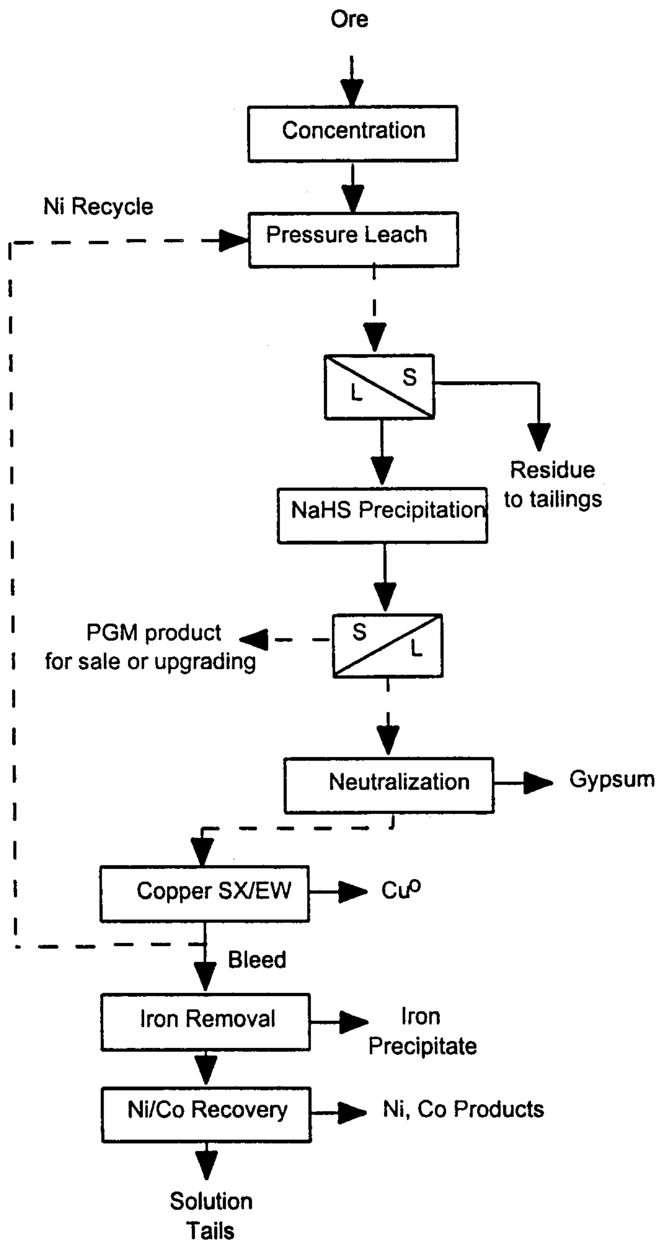


Figure 6 Conceptual flowsheet for gold, PGM and base metal recovery from Polymet concentrate

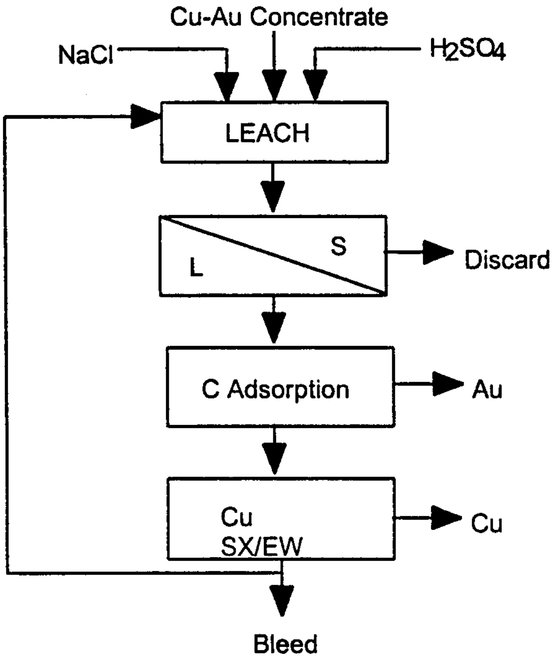


Figure 7. Simplified flowchart for chalcopyrite concentrates.

# INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 00/00438

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 7 C22B11/00 C22B11/06 C22B3/08 C22B3/10 C22B7/04
C22B23/00

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)
IPC 7 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 practical, search terms used)

WPI Data, EPO-Internal, PAJ, COMPENDEX

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | GB 2 128 597 A (DAVY MCKEE)<br>2 May 1984 (1984-05-02)<br>page 1, line 20 - line 24; table 1 | 1,4-7,<br>9-21,<br>25-29,<br>34-42 |
| Y | page 5, line 20 - line 35; claims 1-9<br>--- | 3,8,<br>22-24,<br>30-33,<br>44-50 |
| Y | US 5 542 957 A (HAN KENNETH N ET AL)<br>6 August 1996 (1996-08-06)<br>column 3, line 35 -column 4, line 20;<br>claims 1-8; examples I-VIII<br>---<br>-/-- | 3,8,<br>22-24,<br>30-33 |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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| Date of the actual completion of the international search<br>1 September 2000 | Date of mailing of the international search report<br>08/09/2000 |
| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Bombeke, M |

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# INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 00/00438

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication,where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | US 4 378 275 A (ADAMSON DAVID V ET AL)<br>29 March 1983 (1983-03-29) | 3,8,<br>22-24 |
| X | column 3, line 15 -column 4, line 5;<br>claims 1-6 | 1,5,6,<br>15-18,<br>35-42 |
| Y | US 3 652 265 A (MARSCHIK JOHN F ET AL)<br>28 March 1972 (1972-03-28)<br>column 4 -column 6; figure 1 | 2,44-50 |
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