(12) **PATENT ABRIDGMENT** (11) Document No. **AU-B-26797/88**
(19) **AUSTRALIAN PATENT OFFICE** (10) Acceptance No. **604389**

(54) Title
PROCESS FOR LEACHING GOLD AND/OR SILVER FROM ORES OR ORE CONCENTRATES AND FROM NOBLE-METAL WASTE OR NOBLE-METAL SCRAP BY USING CYANIDE-CONTAINING LEACHING SOLUTIONS

International Patent Classification(s)
(51)⁵ **C22B 011/08**
(51)⁴ **C22B 003/00**

(21) Application No. : **26797/88** (22) Application Date : **12.12.88**

(30) Priority Data

(31) Number	(32) Date	(33) Country
3801741	**22.01.88**	**DE FEDERAL REPUBLIC OF GERMANY**

(43) Publication Date : **27.07.89**

(44) Publication Date of Accepted Application : **13.12.90**

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(56) Prior Art Documents
US 3826723

(57) Claim

1. Process for leaching gold and/or silver from ores or ore concentrates and from noble-metal waste or noble-metal scrap by using cyanide-containing leaching solutions having a pH of from 7 to 13 with addition of aqueous hydrogen peroxide solution,

characterized in that

a) the total amount of hydrogen peroxide solution required for the leaching process is added to the leaching pulp on commencement of leaching,

b) the hydrogen peroxide is added to the leaching pulp in a stoichiometric ratio of 0.6 to 2.5 times the cyanide concentration, and

c) the pH of the leaching pulp is set to and held at between 7 and 10 or 11 and 13.

5. Process according to any one of the preceding

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claims, characterized in that the H_2O_2 solution is added in an amount such that the amount of H_2O_2 per tonne of ore is 0.1 to 2.5 kg at cyanide concentrations of from 0.1 to 3.0 kg of NaCN/t of ore.

9. Process according to any one of the preceding claims, characterized in that, in the case where ores or ore concentrates having relatively high contents of cyanide-soluble iron and/or copper, are used, flotation reagents for sulphide ores or anionic polymers are added to the leaching pulp in an amount of from 5 to 1,000 g of reagents per tonne of ore for passivation or masking of the copper or iron minerals.

13. Process according to any one of claims 9 to 12, characterized in that the masking or passivation agents added to the leaching pulp are thiocarbonates, thiophosphates, thiocarbamates, or anionic polymers in the form of acrylates, starches or carboxymethylcelluloses.

S & F Ref: 80179

604389

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

This document contains the amendments made under Section 49 and is correct for printing.

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Complete Specification for the invention entitled:

Process for Leaching Gold and/or Silver from Ores or Ore Concentrates and from Noble-Metal Waste or Noble-Metal Scrap by Using Cyanide-Containing Leaching Solutions

The following statement is a full description of this invention, including the best method of performing it known to me/us

Abstract

In the process for leaching gold and/or silver from ores or ore concentrates by using cyanide-containing leaching solutions by addition of an aqueous H_2O_2 solution, it is proposed, in order to accelerate the leaching process, to add the entire amount of hydrogen peroxide solution required for the leaching process to the leaching pulp on commencement of leaching, the amount of H_2O_2 solution being determined from the fact that H_2O_2 is added to the leaching pulp in a stoichiometric ratio of 0.6 to 2.5 times the cyanide concentration. In this process, the pH of the leaching pulp is set to and held at between 7 and 10 or 11 and 13.

Process for leaching gold and/or silver from ores or ore concentrates and from noble-metal waste or noble-metal scrap by using cyanide-containing leaching solutions

The invention relates to a process for leaching gold and/or silver from ores or ore concentrates and from noble-metal waste or noble-metal scrap using cyanide-containing leaching solutions having a pH of from 7 to 13 by addition of an aqueous H_2O_2 solution.

In the industrial processes customary hitherto for leaching noble metals from ores or ore concentrates, the ore, in finely ground form, is slurried in water, the pH of the ore pulp is raised into the basic pH range by adding lime or milk of lime, and the cyanide acting as a complexing agent is subsequently added, generally as NaCN in the form of an aqueous, approximately 5 to 20% strength solution. The ore pulp is subsequently agitated in stirred or Pachuca tanks for 24 to 48 hours while passing air into the tanks.

Since cyanide hydrolyses in the acidic pH region to form highly toxic hydrocyanic acid, the pH of the ore pulp must be raised into the basic region and kept in this region, the process usually being carried out at a pH of from 10 to 11. This pH is usually produced by adding lime and milk of lime in the ratio 80:20.

Depending on the ore composition, the cyanide concentration of the leaching pulp is 0.025 to 0.25% by weight of NaCN. The cyanide here is metered in as an aqueous 2 to 20% strength solution into the first of up to ten leaching tanks arranged successively in a cascade arrangement and through which the pulp flows.

During introduction of air into the leaching pulp, the aim is, as far as possible, that the concentration of dissolved oxygen in the pulp should be at the maximum value, due to physical factors, of approximately 8 to 9 ppm, since diffusion of dissolved oxygen in the pulp determines the leaching rate at the cyanide concentration of from 0.3 to 3 kg/t of ore which is customary in industry.

Leaching of gold and silver in cyanide solutions using NaCN proceeds in accordance with the equation below.

$$2\ Au + 4\ NaCN + 1/2\ O_2 + H_2O$$
$$\text{--->}\ 2\ Na[Au(CN)_2] + 2\ NaOH.$$

The abovementioned reaction takes places in two steps.

$$2\ Au + 4\ NaCN^- + O_2 + H_2O$$
$$\text{--->}\ 2\ Na[Au(CN_2)] + H_2O_2 + 2\ NaOH$$

$$2\ Au + 4\ NaCN + H_2O_2\ \text{--->}\ 2\ Na[Au(CN)_2] + 2\ NaOH.$$

The peroxide formed in the first reaction step increases the concentration of dissolved oxygen in the pulp as a consequence of its decomposition into oxygen and water. It is also possible, without hesitation, to replace the NaCN mentioned above and below by KCN.

It is known to use hydrogen peroxide in the recovery of noble metals using cyanide-containing leaching solutions. A use of this type comprises not using the hydrogen peroxide for oxidation of the noble metals, but instead for decontamination of the leaching pulps before they are passed on into the receiving water. In this case, the cyanide present in the pulps is broken down by the addition of hydrogen peroxide into nontoxic cyanate and ammonia. Degradation of the cyanide here only occurs relatively quickly in the pH range 9.5 to 11.5. This pH range matches the preferred pH range for the known leaching processes of the type mentioned in the introduction, in which oxygen is introduced into the leaching pulp by air bubbles.

A further known process (US Patent 3,826,723) proposes adding aqueous H_2O_2 solution as an oxidant for noble-metal leaching by means of cyanide-containing leaching solutions; however, this process is uneconomic due to the extremely high cyanide consumption and cannot be introduced into industry. In order to achieve a shorter leaching time in this known process, the cyanide concentration should be 1 to 600 g of NaCN/l of leachate, and in an illustrative embodiment 60 g of NaCN/l of leachate, and 5 ml of stabilized 50% strength H_2O_2 should be added to each litre of leachate. In addition, it is necessary in the known process to add 1 g of ligninsulphonate per litre of leaching solution.

The NaCN:H_2O_2 molar ratio established in the abovementioned process indicates that, as in the above-described decontamination of the leaching pulps, this process is carried out at a pH between 9.5 and 11.5. Due to the considerable degradation of NaCN on reaction with the H_2O_2 added, only the NaCN added in excess is available for complexing the noble metals.

In German Patent 3,637,082, which is not a prior publication, a process is described in which, in order to leach gold and/or silver from ore or ore concentrates using an aqueous cyanide leaching solution having a pH of from 8 to 13 with addition of an aqueous H_2O_2 solution, the addition of the H_2O_2 solution mentioned is regulated via the concentration of the oxygen dissolved in the leaching solution, and an oxygen content of from 2 to 20 mg/l is established in the leaching solution. The leaching process is thereby intended to be carried out more economically, in particular due to a reduction in the consumption of H_2O_2, without causing a higher sodium cyanide consumption compared with the previously known leaching technique involving aeration.

The invention has the object of improving the process mentioned in the introduction in a manner such that, at the customary concentration of NaCN in the leaching pulp and with a low consumption of H_2O_2, the leaching time is considerably reduced compared with the known process and the cost of carrying out the process is thereby significantly reduced.

The above object is achieved by a process in which

a) the total amount of hydrogen peroxide solution required for the leaching process is added to the leaching pulp on commencement of leaching,

b) the hydrogen peroxide is added to the leaching pulp in a stoichiometric ratio of 0.6 to 2.5 times the cyanide concentration, and

c) the pH of the leaching pulp is set to and held at between 7 and 10 or 11 and 13.

The invention is based on the knowledge that reaction of NaCN with H_2O_2 is considerably inhibited, i.e. proceeds more slowly, in the alkaline pH region of the leaching pulp below 10 or above 11 up to pH 13, so that more NaCN is retained as a complexing agent and the intended concentration of dissolved oxygen in the pulp necessary, in accordance with the introductory comments, for reaction of the NaCN with the noble metal is simultaneously achieved through decomposition of the H_2O_2. By adding the total amount of H_2O_2 solution required for the leaching process to the leaching pulp on commencement of leaching, an optimum ratio between the H_2O_2 concentration, the amount of noble metal to be leached and the NaCN concentration is achieved over the entire leaching period. In the case of very high contents in the leaching pulp of noble metals to be leached and of cyanogen, a very high supply of H_2O_2 is also ensured at the beginning of the leaching process. As bonding of the noble metal to CN increases, the content of H_2O_2 in the leaching pulp also adjusts automatically to the reduced demand.

In order to accelerate the leaching process, it is important that it is ensured that the H_2O_2 solution is distributed homogeneously in the leaching pulp as early as the stage of introduction, since otherwise local NaCN:H_2O_2 molar ratios which result in accelerated decomposition of the NaCN occur in the leaching pulp and result in either a reduction in the recovery of noble metals or in an increase in the necessary amount of NaCN added. For this reason, it is expedient for the hydrogen peroxide solution to be added continuously to a leaching pulp stream distributed homogeneously over the cross-section thereof. In addition, the homogeneous distribution of the H_2O_2 solution in a leaching pulp stream results in a uniform reaction over the stream cross-section from the moment of addition onwards, which in turn contributes to a shortening of the leaching time.

Particularly favourable ratios and leaching times are achieved if the pH of the leaching pulp is set to and held at between 8 and 9.5 or 11.5 and 12.3.

The H_2O_2 solution can be added to the leaching pulp either before or after addition of the cyanide. Addition of the H_2O_2 solution is expediently carried out before addition of cyanide to the leaching pulp, since this results in an increase in the concentration of O_2 and distribution thereof in the pulp even before addition of the cyanide.

As in the customary processes, the NaCN concentration is about 0.25 to 1 g/l of the leaching pulp. It has been determined in a series of experiments that virtually 100% of the noble metals were recovered after approximately 100 minutes on addition of 0.5 g of NaCN and 1 g of a 35% strength H_2O_2 solution per litre of leaching pulp at a pulp pH of 9, it being possible to remove the noble metals by charcoal adsorption without difficulties.

Through the novel process, the time span for leaching of the noble metals is reduced compared with the customary process to between 1/5 and 1/20 of the values of this prior art. Instead of the leaching times of from 24 to 48 hours used hitherto, times of from 2 to 4 hours are sufficient in the novel process.

The amount of H_2O_2 solution added is not limited by the amount of NaCN in the leaching pulp. Instead, the amount of H_2O_2 can be significantly above the amount necessary for complete decomposition of the NaCN without undesired degradation of the NaCN having to be accepted. Practical experience has shown that it is favourable for the H_2O_2 solution to be added in an amount such that the amount of H_2O_2 per tonne of ore is 0.1 to 2.5 kg per tonne of ore at the customary cyanide concentrations of from 0.1 to 3 kg of NaCN/t of ore.

An expedient form of introduction of the H_2O_2 solution into the leaching pulp stream is to introduce the H_2O_2 solution into the leaching pulp stream as a crosscurrent at a flow rate of from 10 to 50 times that of the leaching pulp stream. A preferred embodiment is characterized in that the leaching pulp flows at a rate of from 1 to 3 m/sec in the region of addition of the H_2O_2 solution, and the H_2O_2 solution crosscurrent is set to a flow rate of from 10 to 100 m/sec. The H_2O_2 solution is supplied to the leaching pulp stream using customary supply devices, preferably via slot nozzles in the micron region. The abovementioned measures result in the H_2O_2 being distributed uniformly in the leaching pulp stream after only fractions of seconds. When slot nozzles are used, those having slot openings of from 5 to 100 μm should be used if the H_2O_2 solution is added to the leaching pulp in the region of a tubular cross-section having a diameter of not greater than 10 cm.

If high contents of cyanide-soluble iron or copper, in particular in the form of sulphides, are present in the noble-metal ores or in the ore concentrates, spontaneous decomposition of the H_2O_2 in the leaching pulp and, as a consequence, rapid decomposition of the cyanide too, can take place due to the catalytic action of the Cu(II) or Fe(III) ions. These reactions proceed over the entire pH range of from 7 to 13, also in the abovementioned pH range between 7 and 10 or 11 and 13.

The abovementioned disadvantages can be avoided if flotation reagents for sulphide ores or anionic polymers are added to the leaching pulp in an amount of from 5 to 1,000 g/t of ore, preferably 25 to 250 g/t, for passivation or masking of the copper or iron minerals. The flotation reagents or polymers are preferably added after adjusting the pH of the leaching pulp and before addition of the H_2O_2 solution and of the cyanide. The masking or passivation agents added to the leaching pulp are preferably thiocarbonates, thiophosphates, thiocarbamates or anionic polymers in the form of acrylates, starches or carboxymethylcelluloses. The masking or passivation agents are generally added to the leaching pulp in the form of a 0.1 to 10% strength by weight aqueous solution.

The reagents described in these claims should expediently likewise be added distributed homogeneously over the cross-section of the pulp stream. If aqueous solutions are used, this can be achieved using slot nozzles as described above in connection with supply of the H_2O_2 solution. Homogeneous and rapid distribution of the passivation or masking agents results in a shortening of their reaction times with the Cu or Fe minerals.

Examples

The following results were achieved in the experiments carried out, each in a 2 l beaker:

A) Leaching by the customary process using NaCN without addition of H_2O_2.

A malachite/azurite-rich gold ore - the leaching residue from a relatively old gold treatment plant - contains about 3 ppm of gold and, as an important accompanying element, 1.2% of copper. The ore is ground to a d_{80} value of 200 μm.

The ore is leached at a pulp density of 500 g of ore/l of leachate with vigorous stirring and addition of 0.02 to 0.2% by weight of NaCN. The pH of the leaching pulps are varied between 9 and 12.

The gold yield achieved does not exceed 87% in any of the experiments carried out. The maximum recovery is in each case not achieved until a leaching duration of about 20 hours.

B) Leaching of the same ore as indicated in A), but with addition of an H_2O_2 solution.

0.6 ml of 35% strength H_2O_2 solution per litre of pulp is introduced via slot nozzles into the ore pulp having a pulp density of 500 g of ore/l of leachate; this is done before addition of NaCN. The latter is added in an amount such that an NaCN concentration of 0.05% by weight is achieved. In the case of the addition of H_2O_2 solution as described, an H_2O_2 concentration in the leachate of 0.02% by weight is produced.

After an experimental time of three hours, recovery rates for gold of greater than 97% are achieved in the case of leaching pulp of pH 8 to 9. In the case of leaching pulp of pH 12, the recovery rates are likewise greater than 90%, namely 93%. A gold yield of less than 87% is only observed in the region between the pH values mentioned.

C) Leaching of a partially refractory pyrite-containing gold ore from Western Australia using NaCN without addition of hydrogen peroxide (gold content 1.3 ppm)

The ore, ground to a d_{80} value of 200 µm, is treated with 0.7 kg of NaCN per tonne of ore at a pulp density of 500 g of ore/l of leachate, and aerated by blowing in air. The pH of the pulp was adjusted to 11.

The maximum gold recovery of about 82% is achieved after 24 hours. After 3 hours, the gold recovery rate is 45%.

D) Leaching of the ore of C) with addition of an H_2O_2 solution.

The peroxide solution is introduced into the pulp mentioned under C) and having the same content of NaCN after the pH of the pulp has been adjusted to pH 8. The peroxide addition is continued until the amount of H_2O_2 per tonne of ore is 1.6 kg.

After a leaching time of three hours, a gold recovery rate of 91% is achieved.

E) Leaching of a gold ore from south-east Asia containing copper sulphide and iron sulphide (gold content about 6 ppm).

Comparative experiments were carried out on leaching the ore by adding an H_2O_2 solution with and without addition for passivation/masking of the copper sulphide/iron sulphide minerals, and the values given in the table below were achieved.

Au recovery	pH 11 air	pH 9 H_2O_2	pH 9 H_2O_2 AX	pH 9 H_2O_2 CMC	pH 9 H_2O_2 TTC
after 3 h	25%	55%	90%	92%	>97%
after 24 h	68%	58%	91%	93%	97%

In all the experiments, the pulp density was 500 g of ore/l of leachate, and 0.8 kg of NaCN were added per tonne of ore. H_2O_2 solution was added until 1 kg of H_2O_2 was achieved per tonne of ore.

In the table, AX = amyl xanthogenate; TCC = trithiocarbonate, CMC = carboxymethylcellulose. These abovementioned passivation/masking agents were each added in an amount of 0.1 kg per tonne of ore.

It can be seen from the table that, without passivation/masking of the copper sulphide and iron sulphide, a maximum gold recovery rate of 68% is achieved at a pulp pH of 11, and of only 55% at a pulp pH of 9 with additional introduction of H_2O_2, whereas an increase in the recovery rate to 97% is achieved after a leaching duration of only three hours on addition of the passivation/masking reagents mentioned.

The claims defining the invention are as follows: 88 205 AO

~~Patent Claims~~

1. Process for leaching gold and/or silver from ores or ore concentrates and from noble-metal waste or noble-metal scrap by using cyanide-containing leaching solutions having a pH of from 7 to 13 with addition of aqueous hydrogen peroxide solution,
characterized in that

a) the total amount of hydrogen peroxide solution required for the leaching process is added to the leaching pulp on commencement of leaching,

b) the hydrogen peroxide is added to the leaching pulp in a stoichiometric ratio of 0.6 to 2.5 times the cyanide concentration, and

c) the pH of the leaching pulp is set to and held at between 7 and 10 or 11 and 13.

2. Process according to Claim 1, characterized in that the hydrogen peroxide solution is added continuously to a leaching pulp stream distributed homogeneously over the cross-section thereof.

3. Process according to Claim 1 or 2, characterized in that the hydrogen peroxide solution is added to the leaching pulp before addition of cyanide.

4. Process according to any one of the preceding claims, characterized in that the pH of the leaching pulp is set to and held at between 8 and 9.5 or 11.5 and 12.3.

5. Process according to any one of the preceding claims, characterized in that the H_2O_2 solution is added in an amount such that the amount of H_2O_2 per tonne of ore is 0.1 to 2.5 kg at cyanide concentrations of from 0.1 to 3.0 kg of NaCN/t of ore.

6. Process according to any one of the preceding claims, characterized in that the H_2O_2 solution is introduced into the leaching pulp stream as a crosscurrent at a flow rate of 10 to 50 times that of the leaching pulp stream.

7. Process according to Claim 6, characterized in that the leaching pulp flows at a rate of from 1 to 3 m/sec in the region of addition of the H_2O_2 solution, and the H_2O_2 solution crosscurrent is set to a flow rate of from 10 to 100 m/sec.

8. Process according to either Claim 6 or 7, characterized in that the H_2O_2 solution is supplied to the leaching pulp stream via slot nozzles having slot openings in the micron region.

9. Process according to any one of the preceding claims, characterized in that, in the case where ores or ore concentrates having relatively high contents of cyanide-soluble iron and/or copper, are used, flotation reagents for sulphide ores or anionic polymers are added to the leaching pulp in an amount of from 5 to 1,000 g of reagents per tonne of ore for passivation or masking of the copper or iron minerals.

10. Process according to claim 9, characterised in that the cyanide-soluble iron and/or copper is (are) in the form of sulphides.

11. Process according to Claim 9 or 10, characterized in that the reagents are added in amount of from 25 to 250 g/t.

12. Process according to any one of claims 9 to 11, characterized in that the flotation reagents or polymers are added after adjusting the pH of the leaching pulp and before addition of the H_2O_2 solution and of the cyanide.

13. Process according to any one of claims 9 to 12, characterized in that the masking or passivation agents added to the leaching pulp are thiocarbonates, thiophosphates, thiocarbamates, or anionic polymers in the form of acrylates, starches or carboxymethylcelluloses.

14. Process according to any one of Claims 9 to 13, characterised in that the masking or passivation agents are added in the form of a 0.1 to 10% strength aqueous solution to a leaching pulp stream distributed homogeneously over the cross-section.

15. Process for leaching gold and/or silver from ores or ore concentrates and from noble-metal waste or noble-metal scrap by using cyanide-containing leaching solutions having a pH of from 7 to 13 with addition of aqueous hydrogen peroxide solution, substantially as hereinbefore described with reference to any one of the Examples but excluding any comparative examples.

DATED this FOURTH day of SEPTEMBER 1990
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