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**WO 2012/141607 A1**

(54) **Title:** GOLD AND SILVER EXTRACTION TECHNOLOGY

(57) **Abstract:** The present invention relates to a process for chemical extraction of gold and silver from low grade and refractory pyritic concentrates containing minimum 1 ppm Au, by their leaching in enamelled cast iron reactors, steel plated lead or plastic coated steel, at room temperature, in ammoniac solutions (pH 8-10) of sodium thiosulfate (50-60 g/l  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ ) with a divalent copper salt as catalyst (3-4 g/l Cu). The suspension resulting after 2- 4 hours of reaction is filtered. The thiosulfate solution containing minimum 5 mg /l undergoes an electrolysis process with insoluble anodes. Copper, gold and silver is deposited in the cell as a sludge, and the electrolyte having a maximum content of Au of 1 mg/l, is recycled to the leaching operation of raw material, after correction of copper content and alkalinity to the baseline values. The copper, gold and silver deposit, separated as a sludge, is purified by leaching copper in a solution of 30-40% sulphuric acid at a solid: liquid ratio of 1:5 - 1:10, at a temperature of 85 - 90°C for 2-4 hours under air bubbling. The suspension is filtered. The copper leached as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  returns to the extraction process of gold and silver.

## GOLD AND SILVER EXTRACTION TECHNOLOGY

The present invention relates to a process for chemical extraction of gold and silver from ores, refractory pyritic concentrates, flotation tailings and metallurgical slag by using as reagent a sodium thiosulphate solution in the presence of ammoniac and of a bivalent copper salt as catalyst and their separation from the solution and the recycling the reagents used in the leaching process.

There are known methods for gold and silver extraction by leaching pyritic ores and concentrates in alkaline thiosulfate solutions by prior oxidation under oxygen pressure in basic or acid solutions, by biochemical reactions, oxidation reactions with chlorine or chlorates, by direct leaching in the presence of copper or nickel as activators. The separation of gold and silver from thiosulphate solutions is achieved by adsorption on ion exchangers, activate carbon, electrochemical processes, by cementation on copper, zinc or aluminium, by precipitation with alkaline sulphides. The extraction of pure metals is achieved by a reducing alkaline melting and electrochemical refining.

For example: in the Canadian patent 02412352/2002, the leaching of a Nevada ore type having 24.1 ppm Au (example 1) is performed in autoclaves with a suspension containing 25 g/l ammonium thiosulphate at a solid: liquid ratio of 1:3 and an oxygen pressure of 100 atm and a temperature of 20-60°C. The duration of the process is of 6 hours and the gold leaching efficiency is of 81%. Under the conditions of example 10, the gold ore with 2.48 ppm Au, coarse milled and placed in plastic columns, sprayed with an aerated solution containing 15 g/l ammonium thiosulphate at a spray rate of 12-130 l/h m<sup>2</sup> and a temperature of 22°C, a leaching efficiency of gold of 71% is achieved after 34 days.

In the Canadian patent 02209559/2001, the ore containing 6 ppm Au is oxidized in alkaline solution in autoclaves under an oxygen pressure at 210 -225°C. The suspension obtained is alkalized to pH 9 with ammonia solution and extracted with a solution containing 14.7 g /l thiosulphate and 1g/l copper. Gold and silver are leached with an efficiency of 80% and separated by cementation with zinc, copper or aluminium. The pure metals are extracted from the cement by conventional hydrometallurgical and pyrometallurgical processes.

In the U.S. patent 2003/0051581, gold leaching is done with a solution 0,1 m ammonium thiosulfate and 500 mg/l bivalent copper ions. The extraction of metals gold, silver and copper from the thiosulfate solution is achieved with ion exchange resin (IRA 93 or IRA 410), when gold concentrates to 9kg/t resin.

In the patent WO 2007/053947 the leaching process of gold from pyrites takes place in two phases, that is: in the first phase the ore compounds are oxidized with oxygen in autoclaves at 100 atm in a suspension of diluted sulphuric acid. The oxidized ore, washed with water and regenerated with a 0.1 m solution of sodium sulphite at a solid: liquid ratio of 1:2.5, according to Example 5, after 4 hours of stirring at a temperature of 70°C a solution of 7.39 g/l sodium thiosulphate is produced, which provides an efficiency of 81% of the gold leaching process.

In the patent WO 2007/098603, the leaching of ore having a content of 17g/l gold is done with an ammonium thiosulfate solution containing 0.2 m  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  300 mg / l and  $\text{NH}_4\text{OH}$  0.9 m lasts 24 hours at an efficiency of 90.7%. The leached gold is retained on the resin DOWEX21K and the thiosulfate consumption is of 17.8 kg/t ore.

These methods have the following disadvantages:

- in the first stage an oxidation process of pyritic ore or concentrates takes places at high temperatures and pressures in autoclaves in alkaline or acid solutions.
- the thiosulphate solution used for extraction of gold and silver is not recycled in the process, that means that a residual solution is produced that requires further purification.
- they provide a low concentration of gold in the final product.
- they are energy-intensive technologies.

The thermal problem that the present invention aims to solve is the exploitation of low-grade materials having a content of minimum 1 ppm Au and the recirculation within the system of the reagents used in the leaching process of gold and silver and finally to extract these pure metals.

The solution of the above-mentioned technical problem consists in the treatment of raw materials containing a minimum of 1 ppm Au, under stirring, with a solution resulting from the operation of electrochemical separation of gold, silver and copper, containing: 50 -60g/l  $\text{Na}_2\text{S}_2\text{O}_3$ , 5:20, 0.1 - 0.2 g/l Cu, 5-7g/l  $(\text{NH}_4)\text{SO}_4$ , 1g/l  $\text{NH}_3$ , corrected to 3- 4 g/l Cu and 3g/l  $\text{NH}_3$  (pH = 10), at a solid: liquid ratio of 1:1 - 1:1.5 for 2-4 hours at a temperature of 15-25°C. After filtering the resulting suspension results a residue which, in the absence of common metals, can be used as filler in construction, or otherwise as a raw material for their recovery. The solution resulting from the leaching process, after prior recirculation to a minimum of 10 ppm Au + Ag, undergoes an electrochemical extraction with insoluble electrodes when settles a copper cement that has a content of 5.000 -12.000 ppm Au and 25.000 -80.000 ppm Ag.

The solution resulting after the alkaline electrolysis process with 1 ppm Au and 0.2 g/l Cu, is corrected to the baseline values and recycled in the leaching process of gold and silver.

The copper cement and the precious metals separated from the electrolysis cell, undergo a chemical refinery process with a hot (70-90°C) acid leaching process in a sulphuric acid solution, bubbled with air, at a solid: liquid ratio of 1:5 - 1:10 for 2-4 hours.

By acid leaching, the copper contained in the cement goes into the solution with an efficiency of 80-90% resulting a solution of copper sulphate and gold and silver remain in the sludge which contains 5-7% Au and 12-15% Ag. The sludge is collected, filtered, washed with water and dried at 105°C. The processing method of this sludge in order to obtain Au-Ag alloy (dore alloy) is the classic alkaline melting and the refining to pure metal is done by the electrochemical method and the result is gold and silver of 99.9% purity.

The reactions taking place in the process are:

1.  $\frac{1}{2} \text{O}_2 \rightarrow \frac{1}{2} \text{O}^{2-} + 2e$
2.  $\text{Cu}(\text{NH}_3)_2^{2+} + 2\text{H}_2\text{O} + e \rightarrow \text{Cu}(\text{NH}_3)_2^+ + 2\text{NH}_4\text{OH}$
3.  $\text{Cu}(\text{NH}_3)_2^+ + 2\text{S}_2\text{O}_3^{2-} + 2\text{H}_2\text{O} \rightarrow \text{Cu}(\text{S}_2\text{O}_3)_2^{3-} + 2\text{NH}_4\text{OH}$
4.  $\text{Cu}(\text{S}_2\text{O}_3)_2^{3-} + \text{Au} \rightarrow \text{Au}(\text{S}_2\text{O}_3)_2^{3-} + \text{Cu}$
5.  $\text{Cu}(\text{S}_2\text{O}_3)_2^{3-} + \text{Ag} \rightarrow \text{Ag}(\text{S}_2\text{O}_3)_2^{3-} + \text{Cu}$
6.  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-} - e \rightarrow \text{Au} + (\text{S}_2\text{O}_3)_2^{2-}$
7.  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-} - e \rightarrow \text{Ag} + (\text{S}_2\text{O}_3)_2^{2-}$
8.  $\text{Cu}(\text{S}_2\text{O}_3)_2^{3-} - e \rightarrow \text{Cu} + (\text{S}_2\text{O}_3)_2^{2-}$
9.  $\text{Cu-Au-Ag} + \text{H}_2\text{SO}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{Cu SO}_4 + \text{Au-Ag} + \text{H}_2\text{O}$
10.  $\text{CuSO}_4 + \text{NH}_4\text{OH} \rightarrow \text{Cu}(\text{NH}_3)_2^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O}$

We give below two examples on the implementation of the invention:

#### Example 1.

In a reactor made of plastic or enamelled cast iron with a capacity of 4 cubic meters, equipped with a stirring system are placed 3 cubic meters of a solution resulting from alkaline electrolysis, containing: 0.1-0.2 g / l Cu , 5-10 g / l  $(\text{NH}_4)_2\text{SO}_4$ , 1.5 - 3.0 g / l  $\text{NH}_4\text{OH}$ , 50-60 g / l  $\text{Na}_2\text{S}_2\text{O}_3$ , 5:20. It is corrected to 3-4 g / l Cu, 50-60 g /  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ , 3g/l  $\text{NH}_4\text{OH}$  and 2500 kg siliceous ore containing 1.8 ppm Au and 18.6 ppm Ag. The suspension is stirred for 3 hours with by bubbling 5 cubic meter/h air and filtered on a rotary vacuum filter.

The resulting sludge (2500 kg) is washed with 0.2-0.3 cubic meter water and it results a siliceous residue without toxic impurities. The filtrate solution is adjusted with  $\text{NH}_4\text{OH}$  to pH 9-10 and returned to the leaching process of the siliceous ore, up to a minimum content of 5mg/l Au, and then it undergoes an electrolysis on high-alloyed steel anodes at a current density of 3-3.5 A/dm<sup>2</sup>.

The electrolysis process is considered as finished, when the gold concentration of the electrolyte does not exceed 1 mg/l (12-14 hours).

After a number of 5 cycles of electrolysis, the sludge containing copper, gold and silver, that drops from the cathode in the electrolytic cell undergoes a leaching process for copper in sulphuric acid. The operation is performed in a reactor with stirring and heating jacket, made of enamelled cast iron or steel antacid protected with lead. The operation is performed at a temperature of 85-95°C and a solid: liquid ratio of 1:5 -1:10, using a sulphuric acid solution with a concentration of 30-40%, bubbled with air. The suspension resulting after 2-4 hours of reaction is filtered hot (50°C). The resulted acid solution of copper sulphate having a content of 95-120 g/l Cu and 30-200 g/l H<sub>2</sub>SO<sub>4</sub> is crystallized by cooling it when CuSO<sub>4</sub>•5H<sub>2</sub>O is separated as a crystalline product. The copper sulphate resulted is used in the leaching process of the raw material in order to correct the copper content of the solution resulting after the electrochemical separation of the cement containing copper, gold, silver. The sludge resulting from filtering the suspension is filtered, washed with water and dried at 105°C and it has a content of 6.2% Au and 13.5% Ag.

After drying, the sludge is mixed with sodium carbonate and active coal at a ratio of 1:3:0.5 and melted in a graphite crucible at a temperature of 1150-1200°C. The Au-Ag alloy (dore alloy) is casted as anodes and undergoes the conventional electrochemical and thermal refining operations in order to obtain pure gold and silver.

The global efficiency of operation ore - metal is of 78.2% for gold and of 76.1% for silver.

#### Example 2.

The operations ensue in the same way as in example 1 excepted that the raw material is a pyritic concentrate containing 10 ppm Au and 40 ppm Ag.

The global efficiency ore-pure metal is in this case of 82.2% for gold and of 81.5% for silver.

The gold and silver extraction method is not toxic, it does not generate wastewater or toxic gas emissions.

The method is applicable for obtaining gold and silver from refractory low-grade pyritic ores and concentrates in alkaline cyanide extraction, ensuring the recirculation of all reagents in the raw material leaching process.

## Claims

1. Method for gold and silver extraction from low-grade refractory ores and concentrates, **characterized by the fact that** it leaches gold and silver in sodium thiosulfate solutions of 50-60 g/l  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$ , alkalized with ammonium hydroxide at pH 8-10, with a bivalent copper salt of 3-4 g / l Cu at activator, at ambient temperature while stirring for a time of 2-3 hours.
2. The method according to claim 1, **characterized by the fact that** it extracts gold and silver together with copper from the thiosulfate solution having a minimum content of 5 ppm Au, by electrolysis in alkaline solution (pH 8-10) by using high-alloyed steel electrodes at a current density of 3.0 - 3.5  $\text{A}/\text{dm}^2$ , providing also the recirculation of the reagents in the process of leaching gold and silver contained in the raw material.
3. Method according to claims 1 and 2, **characterized by the fact that** it separates the copper from the Cu-Au-Ag sludge by leaching it in sulphuric acid solution of 30-40%, at a solid: liquid ratio of 1:5 - 1:10 at a temperature of 85-95°C and under air bubbling. The copper sulphate formed in the process is returned to the raw material leaching process.

**INTERNATIONAL SEARCH REPORT**

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**A. CLASSIFICATION OF SUBJECT MATTER**  
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According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
 C22B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2007/098603 A1 (METAL ASIA INTERNAT LTD [CN]; XIA CHEN [CA]; YEN WAN-TAI [CA]) 7 September 2007 (2007-09-07) cited in the application the whole document	1-3
A	US 5 785 736 A (THOMAS KENNETH G [CA] ET AL) 28 July 1998 (1998-07-28) the whole document	1-3
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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 of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/R02012/000005

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>LANGHANS JR J W ET AL: "COPPER-CATALYZED THIOSULFATE LEACHING OF LOW-GRADE GOLD ORES", HYDROMETALLURGY, ELSEVIER SCIENTIFIC PUBLISHING CY. AMSTERDAM, NL, vol. 29, no. 1 / 03, 1 June 1992 (1992-06-01), pages 191-203, XP000384549, ISSN: 0304-386X, DOI: 10.1016/0304-386X(92)90013-P the whole document</p> <p style="text-align: center;">-----</p>	1-3
A	<p>BREUER P L ET AL: "The reduction of copper(II) and the oxidation of thiosulfate and oxysulfur anions in gold leaching solutions", HYDROMETALLURGY, ELSEVIER SCIENTIFIC PUBLISHING CY. AMSTERDAM, NL, vol. 70, no. 1-3, 1 July 2003 (2003-07-01), pages 163-173, XP004427443, ISSN: 0304-386X, DOI: 10.1016/S0304-386X(03)00078-1 the whole document</p> <p style="text-align: center;">-----</p>	1-3

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/R02012/000005
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Patent document cited in search report		Publication date		Patent family member(s)	Publication date
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			CA	2644407 A1	07-09-2007
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