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The extractive metallurgy of gold

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Mössbauer spectroscopy has been successfully used in investigation of the gold compounds present in ores and the gold species which occur during the process metallurgy of this metal. This paper is a survey of the basic recovery methods and techniques used in extractive metallurgy of gold. Process fundamentals on mineral processing, ore leaching, zinc dust cementation, adsorption on activated carbon, electrowinning and refining are examined. The recovery of gold as a by-product of the copper industry is also described. Alternative processing methods are indicated in order to shed light on new interesting research topics where Mössbauer spectroscopy could be applied.

1. Introduction

The methods used to recover metals from their ores strongly depend on their physical and chemical properties, their mineralization and mode of occurrence in ore deposits. Of the various gold-bearing minerals existing in nature, the most important in extractive metallurgy are: native gold, electrum and tellurides. Gold is often hosted in sulphide minerals like pyrite and arsenopyrite and in compounds of the elements selenium and antimony [1]. Native gold is the main form of gold occurring in nature, with a gold content of 90% or more and frequently accompanied by silver. In combination with silver, it is found in an alloy type compound called "Electrum" which contains 15–35% Ag. Copper and iron are most common impurities in gold ores. Also of metallurgical importance are the telluride compounds: Calverite (Au, Ag)Te_2, Sylvanite (Au, Ag)Te_4, Petzite $(Au, Ag)_2Te$, Kalgoorlite $HgAu_2Ag_6Te_6$, ... which are frequent in Australian ore deposits. Gold content in gold ores normally ranges up to 30 g/t, but today processing of low-grade ores of less than 5 g/t is common practice.

Gold production mainly comes from hard rock ore deposits. This kind of deposit is found in the Witwatersrand region in South Africa which is the major gold producer of the world. Outside South Africa, a large proportion of gold is produced from gold placers, especially in the former USSR. A significant amount of gold is produced as a by-product, mainly from copper refineries [2].

The basic processing flow sheet for the recovery of gold from its ores and from gold-bearing copper ores is shown in figure 1. Process fundamentals, methods and techniques used are examined in detail in this paper.

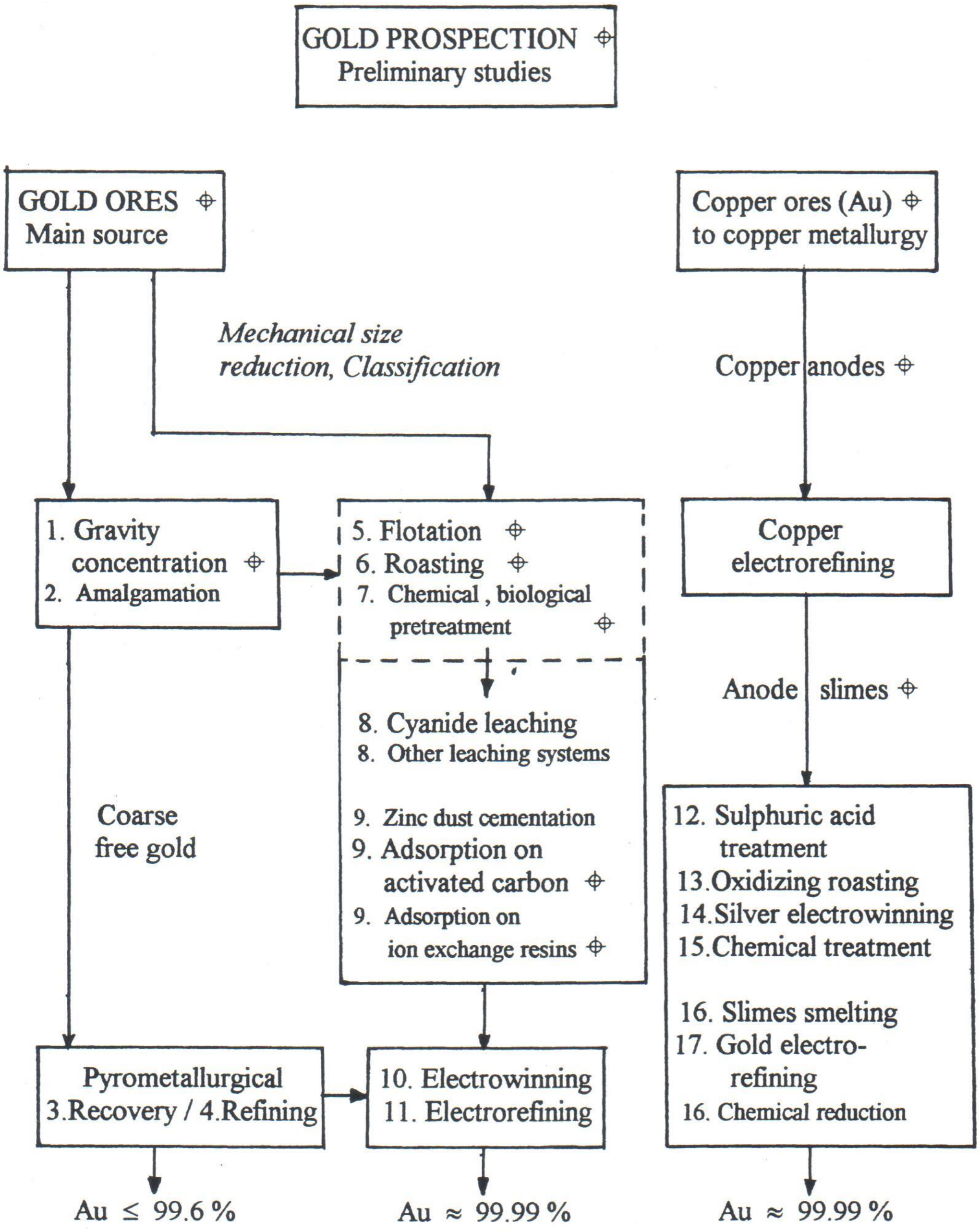

Figure 1. Basic processing flowsheet for gold bearing copper ores. Mössbauer Spectroscopy can be applied to gold bearing solid substances at all processing stages. ⊕ Interesting fields for Mössbauer studies.

2. Gravity concentration of gold

Gravity concentration methods are soundly based upon the density difference between the constituent minerals of an ore for their separation [2]. The motion of two mineral particles of different densities in a fluid will be different. The heavier mineral will rapidly settle down, while the light one will be suspended in the fluid or washed away by the moving fluid. Because of the great density difference between gold (density 19.3) and the gangue minerals (average density 2.7–3.5) which are present in the ore, gravity separation operations are widely used for gold concentration. The mineral particles must be sufficiently liberated for a good separation. Generally, liberation of the constituent minerals is achieved by communition and grinding. Overgrinding would be detrimental to both the separation efficiency and energy consumption. Gravity separation efficiency significantly decreases with decreasing particles size, although new technological improvements of gravity concentration devices have led to improved separation efficiency when treating fine-grained minerals. In practice, the coarser-grained particles range from a few mm (e.g., 2 mm) down to approximately 40 µm. Such good liberated free gold particles are suitable for gravity concentration, which is then preferred for a faster recovery of values. Gold from placer deposits is recovered mainly by using gravity concentration methods.

The most used gravity concentration devices in today practice include sluices, shaking tables, jigs, ... They all exploit the fluid (water) movement, flowing by sluices and tables or pulsating by jigs, to enhance the separation of different minerals. More developed technological equipment like the "Knelson concentrator" even makes use of centrifugal force. The centrifugal separators can efficiently operate at very small particle size down to 30 µm [3].

Gravity concentration flow sheets generally include in different combinations the following operations: communition, wet grinding, granulometric classification of the mineral particles, multi-stage concentration, concentrate recovery and residue discard.

Sometimes, the gravity gold concentrates are cleaned up by amalgamation [4]. During this process, the free gold particles are wetted by mercury and form an alloy type compound at room temperature and can thus be separated from most of impurities. Mercury is thereafter separated from gold by distillation. After cooling, it is recycled in the process. The method was once widely used in gold ores processing, but it is now virtually abandoned because of the health and environmental hazard due to the mercury handling.

3. Dissolving gold from ores

In many cases, the gold particles which are present in ore are too fine, less than 50 µm, or too low grade to be efficiently concentrated by gravity methods. The gold is then leached from the ore by cyanidation, according to the following reaction [5,6]:

$$4\mathrm{Au} + 8\mathrm{NaCN} + \mathrm{O_2} + 2\mathrm{H_2O} \rightarrow 4\mathrm{Na[Au(CN)_2]} + 4\mathrm{NaOH}. \qquad (1)$$

If present in the ore, silver is also dissolved in a similar manner. A dilute aqueous solution of sodium or potassium cyanide is used to dissolve the precious metals. Lime or sodium hydroxide is added to adjust the pH value at 10–11. Cyanide ions are subject to reaction (2) in solution.

$$CN^- + H^+ \rightarrow HCN. \qquad (2)$$

Accordingly, the concentration of free cyanide, needed for effective leaching, increases with solution alkalinity. Furthermore, protective alkalinity is necessary to avoid generation of a deadly HCN gas which occurs in acidic solution [5,8]. Equation (1) indicates that the presence of oxygen is necessary for gold dissolution. Gold must first be oxidized to Au^+ before it reacts with CN^- to form the dissolved gold cyanide complex ion $Au(CN)_2^-$. Under normal concentration conditions, this complex is stable in almost the entire pH range [9]. In contrast, the similar silver cyanide ion promptly precipitates as AgCN from acidic solutions, even if present in relatively low concentrations, i.e., 2.5 mmol/l [10].

The presence of cyanicides in the ore strongly reduces cyanide leaching efficiency and induces higher cyanide consumptions. Partially oxidized sulphides of Sb, Zn, Fe, Cu and As are known as interferent minerals which consume cyanide; carbonaceous materials adsorb prematurely the dissolved precious metal cyanides and organic substances consume the dissolved oxygen from the leach liquor.

In common practice, leaching of gold ores is carried out in large Pachuca tanks, in which air is blown to provide oxygen and to keep the solids in suspension in the ore pulp. Leaching time varies from 8 to 24 h or even more [7].

Too low grade ores, which were once considered waste, can economically be treated by using heap leaching, because of the lower capital and operating costs. Run-of-mine, crushed or agglomerated ores are mixed with NaOH and piled on a sloped, impervious pad. Cyanide solution is sprayed on, percolates through the oxygenated permeable ore heap and dissolves gold from the ores. The gold cyanide pregnant solution is collected at the bottom and drained to a storage basin [5,8]. From a gold ore containing as low as 1 g/t, 60–70% gold extraction can be achieved with this method after a treatment period of a few days. Absence of cyanicides and a good porosity in the ore are necessary conditions for efficient heap leaching.

Alternatively, thiourea leaching can be applied to dissolve gold from the ore [11].

4. Treatment of refractory gold ores

When gold is finely disseminated in a sulphide host mineral, commonly pyrite or arsenopyrite, or when gold tellurides are present, oxidation may be necessary prior to cyanidation. This is conventionally achieved by oxidizing roasting of a flotation concentrate, which breaks down the host mineral to produce a porous calcine, the latter being more amenable to cyanide leaching [13,14].

Due to environmental problems and a limited efficiency, roasting is no longer attractive. Hydrometallurgical oxidation methods are then preferred. Pressure oxidation is usually applied, using H_2SO_4 at elevated temperature ($\geqslant 170°C$). Alternatively, biochemical oxidation can be used to oxidize the metal sulphides by action of bacteria, mainly the Thiobacillus ferrooxidans, which oxidize both iron and sulphide under acidic media [15].

5. Recovery of gold from solution

5.1. Zinc dust cementation

Gold can be recovered from cyanide solutions by cementation (precipitation) with zinc dust which acts as a reducing agent according to the following overall reaction [5,6,8,12]:

$$2NaAu(CN)_2 + Zn \rightarrow Na_2Zn(CN)_4 + 2Au. \tag{3}$$

This method called the "Merril–Crowe Process" has been used worldwide since the 1890s. If present, silver is also precipitated in a similar way.

The clarified pregnant solution from the filter plant is de-aerated in a Crowe tower before addition of zinc dust and lead nitrate. Thereafter, the solid–liquid mixture is pumped into a Merrill filter unit where the pregnant solution flows through a zinc bed. This method is preferred for the treatment of gold high-grade solutions, or for solutions which contain a large amount of silver.

The presence of sulphides, sulphates, thiosulphates and ferrocyanides in solution, which passivate the zinc surface, causes inhibition of the cementation process. Arsenic and antimony in even low concentration (1 ppm) reduce gold extraction efficiency. A minimum concentration of free cyanide in solution is also needed during the process.

5.2. Adsorption on activated carbon

Gold can also be recovered from cyanide solutions by adsorption on activated carbon. Because of its technical and economical advantages, the "Carbon-In-Pulp" (CIP) process has been established as the standard method for the recovery of gold from cyanide solutions. Especially when treating fine ground ores, the separation of slimy solids from liquid may be difficult and expensive for the zinc dust cementation method to be efficiently used. The CIP process is then indicated. Furthermore, gold extraction by CIP is more selective toward the other species which may be present in solution.

After leaching, activated carbon is mixed and agitated with the pulp in a series of normally 5–7 tanks. The loaded carbon is separated from the pulp by sieving. The contact is performed stepwise in the tanks in a countercurrent flow of activated carbon and pulp. Granular activated carbon made from coconut shell is preferred in industrial practice because of its resistance to abrasion which may cause gold loss with the small carbon particles which may pass through the sieves.

When treating ores which contain carbonaceous materials, which adsorb gold prematurely from the leach liquor, adsorption on activated carbon is efficiently performed in the leaching tanks (Carbon-in-leach, CIL Process).

Silver removal from solutions prior to gold adsorption is recommended when treating ores of high silver-to-gold ratios. Silver can be eliminated by a sulphide precipitation method using sodium sulphide [8].

Elution of the adsorbed gold cyanide is performed by treating the loaded carbon with a sodium cyanide (0.1–0.2%) and sodium hydroxide (1%) solution at high temperature (90°C). A minimum concentration of free cyanide in solution is needed. Different organic solvants (alcohols) can be added to the strip solution for fast elution. Stripping time is then reduced from 48–72 h to nearly 6 h. Elution at elevated pressure is also helpful.

The loaded carbon is packed in a fixed bed column where the elution solution is pumped through. The eluate is sent to gold electrowinning. Sometimes, gold is recovered from the eluate by zinc dust cementation.

After elution, carbon is acid washed, reactivated by heating in a rotary kiln at 600–900°C and sent back to the process, while the eluate is sent to gold electrowinning. The electrolysis cell comprises stainless steel sheet anodes and steel wool cathodes at a negative potential of maximum 3 volts where gold is electroplated with some impurities (copper, lead, mercury, ...). Usually, the current efficiency averaged 30%. Steel wool cathodes or zinc dust precipitates may be smelted to doré bullion [12].

Alternatively, gold can be recovered from solution by adsorption on ion exchange resin or by solvent extraction [11].

6. Refining of gold

One of the most used refining methods is the "Miller Process" [17]. This method is preferred for the treatment of large gold quantities with negligible content of other precious metals. Crude gold is smelted under a borax–silica slag and treated with chlorine gas at elevated temperature (1150°C). The chlorine gas rapidly reacts with impurities. Iron, lead and zinc are removed as chloride gases. Copper and silver dissolve as chlorides in the slag which is separated from gold by gravity. The silver rich slag is thereafter treated with a HCl and $NaClO_3$ aqueous solution to dissolve silver which is finally precipitated by zinc dust addition. Refined gold assaying 99.6% can be produced by using this process. If necessary, a subsequent treatment by electrorefining can be applied for higher purity.

Electrorefining is necessary to achieve higher gold quality and to separate gold from the other precious metals. Molten crude or fire refined gold is cast into gold anodes for electrorefining in HCl media, containing 50–80 g/l Au and 5–7% free HCl (Wholwill Process). Electrolysis is conducted at 600–700 A/m^2 and 0.6 V. Gold of very high quality (99.99%) is produced. Platinum and Palladium are recovered from solution, while Osmium and Iridium are extracted from the anode slimes. Rhodium and Ruthenium are present both in solution and in slimes [17].

7. Recovery of gold as a by-product of the copper metallurgy

As a by-product, gold comes mainly from sulphide copper metallurgy. In common practice, the gold bearing sulphide copper ores are first concentrated by flotation. The concentrates are then treated pyrometallurgically for blister copper production, where most of gold is accumulated. Blister copper is fire refined and subsequently electrorefined to produce copper of very high quality. During copper electrorefining, copper anodes are dissolved in solution, while the Cu^{2+} ions are reduced and electrodeposited as pure copper at the cathode. The precious metals (gold, silver, platinum group metals, selenium), which are present in the copper anodes as impurities, remain undissolved in the anode slimes. Approximately, 0.5–1% of anode is precipitated as anode slimes, typically assaying 20–40% Au. The precious metals are recovered in the precious metals refinery [16,17].

The extraction methods used are somewhat different depending on the slimes composition. Generally, copper and selenium are removed from the anode slimes by sulphuric acid leaching and oxidizing roasting respectively, prior to smelting of slimes to doré metal and casting into anode for silver electrolysis. Silver is electroextracted in a HNO_3 solution, typically containing 30–40 g/l Ag and 0.5–3.0 g/l HNO_3. Electrolysis is conducted at current density of 400–650 A/m^2 and cell voltage of 2.5–3.5 V. Gold remains in the silver anode slimes (80–90% Au) which are further treated with sulphuric acid and ammonium acetate to dissolve some impurities (Ag, Fe, Ni, Pb, ...) [16]. Finally, the slimes are smelted to gold anodes for gold electrorefining in HCl according to the Wholwill Process as previously described.

Alternatively, after silver electrowinning, the silver anode slimes are treated with sulphuric acid and aqua regia ($HCl–HNO_3$) followed by reduction with Na_2SO_4. In this case also, gold of very high quality is produced. The platinum metals are subsequently precipitated in a similar manner [18].

8. Application of Mössbauer spectroscopy in gold metallurgy

Mössbauer spectroscopy with the 77 keV gamma rays of ^{197}Au has been successfully used in the investigation of the gold compounds present in ores and the gold species which occur during the mineral and metallurgical processing operations [19–25]. This method can in principle be applied to gold bearing solid substances at all processing stages. Interesting fields for Mössbauer studies are indicated ($\oplus$) in figure 1. During the preliminary period of mineral deposit prospection, valuable information on the type of the gold compounds can be provided by Mössbauer spectroscopic measurements. Sometimes, they are performed in combination with other analytical methods for complementary information [22]. The provided data can then be used for the determination of the best processing route with regard to the characteristics of the material under investigation. As for industrial operations, Mössbauer spectroscopy can contribute to an improved understanding of the process mechanism [21,23–25]. This knowledge is necessary for an optimization of the process operating conditions.

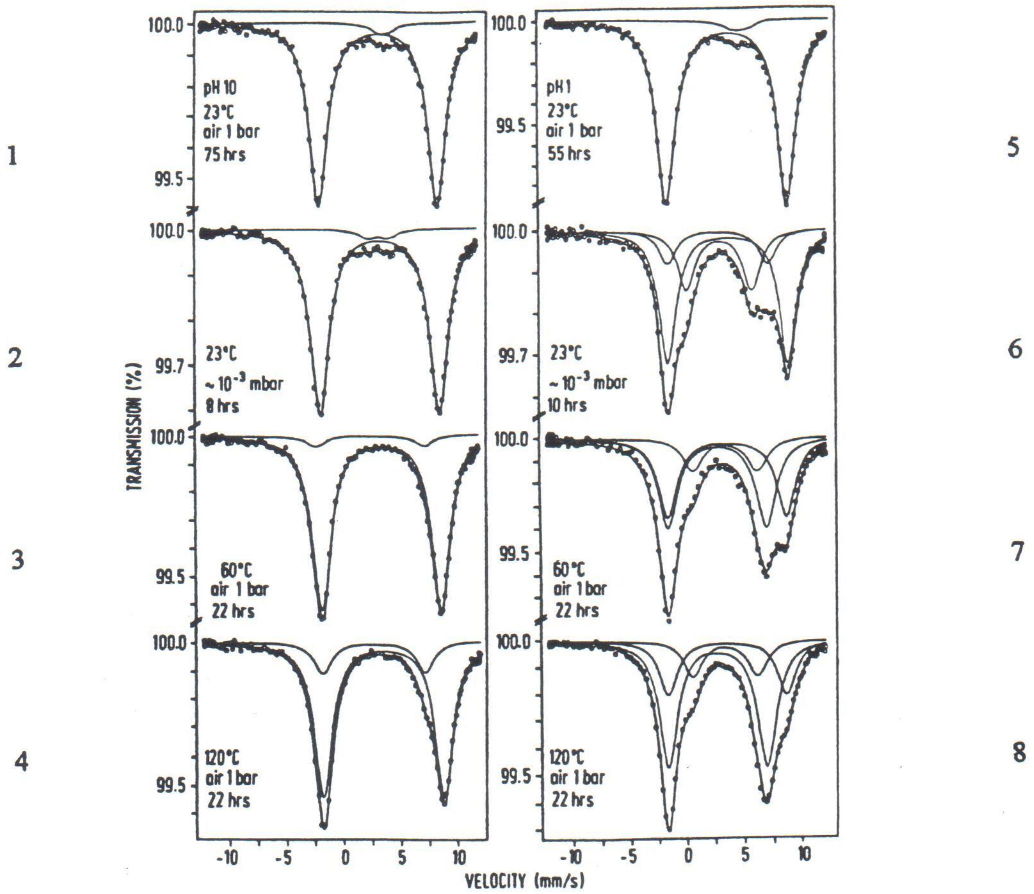

Figure 2. ^{197}Au Mössbauer spectra of activated carbon loaded from KAu(CN)$_2$ solutions at pH values of 10 (left) and 1 (right) and then treated in different manners as indicated. The gold loading was 60 mg/g in all cases. The following adsorbed species have been identified: Au(CN)$_2^-$ in samples 1 to 8, AuCN in samples 4, 6 to 8 and Au(CN)$_2$Cl$_2^-$ in samples 6 to 8.

An example of application of the Mössbauer effect in extractive metallurgy of gold is illustrated in figure 2, where ^{197}Au Mössbauer spectra of activated carbon loaded from KAu(CN)$_2$ solutions are recorded. The adsorbed species have been unambiguously identified as indicated in the figure caption.

9. Conclusion

Extractive metallurgy of gold has been described in this survey and the main challenges facing the metallurgists were mentioned. Application of Mössbauer spectroscopy in this field has provided useful information. The use of this investigation method is therefore recommended, especially in solving metallurgical problems or for the development of effective recovery methods.

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