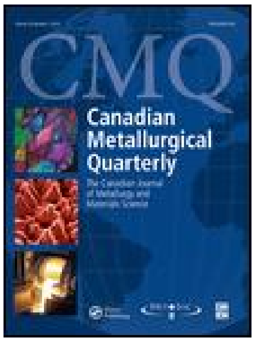

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GOLD METALLURGY—A HISTORICAL PERSPECTIVE

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Abstract—The extractive metallurgy of gold is reviewed starting with the introduction of cyanide leaching in 1887.

Cyanidation procedures involving the loading and stripping of gold from activated carbon are described. Recent developments including treatment of refractory ores, biological processes and alternative leachants are summarized with references.

INTRODUCTION

Gold is undoubtedly the brightest spot in the world of mining today, especially in North America, where many other metal industries are struggling. The approximately 115.1×10^3 kg (3,700,000 oz) of gold produced in the United States in 1986 had a value of U.S. $1,374,710,000. Canada had a similar output of over 105.8×10^3 kg (3,400,000 oz) of gold, making it the fourth largest world producer. Although 100×10^3 kg (3.5 million oz) of gold seems like a large amount, it is small compared to the 638×10^3 kg (20.5 million oz) produced by South Africa, equivalent to 40% of the total world production of 1.6×10^6 kg (51 million oz).

In the Western United States gold production has increased rapidly in the last 5 yr. In 1981, Nevada produced 16.3×10^3 kg (525,000 oz) of gold. In 1986 it produced 65.3×10^3 kg (2,099,000 oz), again putting it in first place of the gold producing regions of the United States. In Canada, gold production increased, but not as dramatically, from 52×10^3 kg (1,673,000 oz) in 1981 to 104.7×10^3 kg (3,365,000 oz) in 1986. A good part of this increase came from the Hemlo deposits in Ontario.

Where did this gold come from, and how was it processed? This review looks at the processing changes in the last 100 yr, and defines some areas where changes can be expected in the future.

Because of the high specific gravity of gold it has been collected in the past from placer-type deposits by gravity techniques, sometimes aided by amalgamation with mercury. Such processing techniques are relatively unimportant today. One hundred years ago, in 1887, John MacArthur and Robert and William Forrest registered a British patent on the use of KCN for the dissolution of gold from ores. This event radically changed the processing of gold although the action of cyanide on precious metals had been noted years earlier [1]. Of the 116×10^3 kg (3.733 million oz) of gold produced in the United States in 1986, only 2% came from placer deposits. Of the 111×10^3 kg (3.584 million oz) produced from lode deposits, 94% was processed by cyanidation.

Cyanide leaching was first used in New Zealand in 1889 and then in South Africa in 1890. The first cyanide plants in the United States were built in 1891. The first application of cyanide leaching was by percolation in vats. During the following decades the development of agitated tanks and classifiers for leaching and washing allowed development of the countercurrent decantation cyanide leach plant. Recovery of gold from cyanide solution was by zinc precipitation—originally patented by MacArthur and the Forrest brothers and later improved by Merrill and Crowe. Cyanidation continued in this mode with improvements in the mechanical and physical handling aspects of the process until about 1950. In the 1950s hydrocyclones started to replace mechanical classifiers in gold mills. Also, organic flocculants were developed that improved the thickening and washing of cyanide pulps, improving clarification of pregnant solutions for the zinc precipitation step.

Although it had been known since the late 1800s that activated carbon was a good adsorber of gold cyanide, it was usually a last resort when zinc precipitation could not be used. T. G. Chapman and his associates at the University of Arizona developed a method using fine carbon to adsorb gold and recover it by flotation [2]. In the late 1940s the Getchell Mine in Nevada used coarse activated carbon to adsorb gold cyanide from pulps because it was quite cheap as a surplus item from World War II gas masks. The carbon was recovered from the pulp by screening. The only known means to recover gold from carbon was to burn it; however, the loaded carbon produced at Getchell was not a salable product since the carbon did not completely oxidize in the smelter and hence there were high gold losses to the slag. At that time there was no known process to desorb gold or silver from the loaded carbon.

Around 1950, researchers at the U.S. Bureau of Mines began looking for ways to strip the precious metals from loaded carbon and enable the carbon to be used a number of times. A surplus of World War II activated carbon, which was manufactured from fruit pits, was available at bargain prices. A means for desorbing and recycling the carbon would make it a very economical process for the recovery of gold. First, an alkaline Na_2S stripping method that eluted the gold, but not the silver, from carbon was described [3]. Since most ores contain some silver, the sulfide stripping method was not satisfactory because the carbon would eventually be loaded with unstrippable silver. In 1952, Bureau researchers published a method for desorbing both gold and silver from loaded carbon by contacting the carbon with a boiling NaOH–NaCN solution [4]. Concurrently with stripping, the solution passed through an electrolytic cell where the gold and silver were deposited on the steel wool cathode. The hot NaOH–NaCN solution desorbed more than 90% of the gold and silver in 4–6 h. The carbon could be reused up to 10 times without thermal reactivation and without losing significant activity.

Carbon adsorption permitted gold and silver recovery from slimy ores by eliminating the requirement of a clarified solution. Carbon adsorption was also an efficient means for collecting gold from dilute solutions. This laid the foundation for two important developments in gold and silver ore processing: carbon-in-pulp (CIP) (including carbon-in-leach, CIL) cyanidation and heap leaching. The cylindrical electrolytic cell originally described is still used for electrowinning and is commonly referred to as a "Zadra" cell, even though many units in commercial use have been modified. Rectangular electrowinning cells are also used and make better use of floor space than cylindrical cells. Researchers at MINTEK in South Africa have been very productive in their studies of gold electrolysis from cyanide solutions [5]. With few exceptions, the NaOH–NaCN electrolyte and steel wool cathode remain common to the electrowinning cells.

Although gold and silver were eluted from the fruit pit carbon in 4–6 h when the eluate was simultaneously put through an electrolytic cell, commercial practice had adopted coarser carbons made from coconut shells and electrowinning was not done simultaneously with elution and resulted in much longer elution times. Twenty-four to 48 h were required to desorb more than 90% of the precious metals with boiling alkaline cyanide solution. Although this was better than not being able to strip the carbon at all, a shorter stripping time was needed. Two methods, pressure stripping and alkaline–alcohol stripping, were developed by the Bureau of Mines and greatly decreased the desorption time.

In 1973 it was shown that by using a pressure vessel and increasing the temperature of the caustic cyanide stripping solution to 150°C, gold was removed from the carbon in about 2 h [6].

In the alkaline alcohol stripping method developed a few years later ambient pressure was used, but the modified stripping solution contained 20% ethanol in addition to the alkaline cyanide [7]. At 80°C, gold and silver were desorbed in 6 h. A concurrent development was the separation of gold from silver by precipitating silver as a sulfide [8]. For pregnant solutions containing large amounts of silver, the silver is precipitated before loading the carbon [9]. A large carbon inventory is avoided by maintaining capacity for only gold adsorption.

Pressure stripping, alkaline alcohol stripping, and ambient pressure stripping are all in use. A stripping technique described in the original U.S. Bureau of Mines publication, that of conditioning the carbon in hot alkaline cyanide solution followed by hot water washes, has found application in South Africa. The use of organic solvents to elute gold from activated carbon has been proposed in Australia [10].

A problem that plagued operators of some gold cyanide mills was the occurrence of active-type carbon in ores. Many carbonaceous ores cannot be treated by cyanidation because, even if the gold is dissolved by cyanide, the carbonaceous component partially adsorbs the gold cyanide complex. If even a small amount of "preg-robbing" carbonaceous ore enters the milling circuit, the recovery of gold can be severely affected.

In 1968, researchers at the U.S. Bureau of Mines pioneered the use of an oxidizing system based on hypochlorite to oxidize the carbonaceous component of ores and render it inactive before conventional cyanidation [11]. A process was developed that could use either chemical oxidation by the addition of NaOCl or chlorine gas, or electrical oxidation by electrolysis of a NaCl solution. Pilot plant studies were conducted at the Carlin gold mine, Nevada. Oxidation pretreatment of carbonaceous ores increased the gold recovery from about 30 to 90%. The chlorine oxidation process for carbonaceous ore has been in use since the early 1970s [12, 13].

The rise in the price of gold and discoveries of numerous large, low-grade, disseminated gold deposits in the Western United States spurred interest in cheaper recovery methods. In 1969, Bureau of Mines researchers proposed heap leaching as a low-cost means for recovering gold values from low-grade material containing micron-size particles of gold [14–16]. Heap leaching had been used on oxide copper ores and uranium ores and had the advantage of very low capital and operating costs. The pregnant gold solutions from the heaps contain typically 1 to 3 ppm Au. Precipitation of metal values with zinc from such dilute solutions is not an efficient recovery method, whereas carbon adsorption is ideally suited to the recovery of metals from dilute, unclarified solutions. Some pregnant solutions from silver heap leaching contain enough silver, typically 10–20 ppm Ag, so that zinc precipitation is the preferred method to recover the silver.

Application of the cyanide solution to the heaps is usually through a sprinkler system. The technique of utilizing a drip irrigation method is now being tried. This would have the advantage of much lower evaporative water losses.

Heap leaching has been an important factor in precious metals recovery because it permits utilization of lean ores and wastes that are not economically processed by conventional agitation cyanidation.

It was estimated in 1986 that less than 20 yr after the introduction of the heap leaching, 30% of the gold recovered by cyanidation was produced by that method. These gold and silver heap leaching operations range in size from 10×10^3 kg (10 tons) of ore a week to more than 10×10^6 kg (10,000 tons) a day.

Although the application of heap leaching permitted the development of many low-grade and/or small properties, which would not otherwise have been exploitable, some ores were untreatable by heap leaching. This was primarily due to two conditions: (1) the ore contained clay that swelled on contact with leaching solution and prevented solution flow, and (2) crushing the ore to the liberation size for gold–silver extraction generated large amounts of fines that were washed into the voids by the percolating leaching solution, caused channeling, and resulted in partial leaching of the gold and silver from the heap material. In the late 1970s, Bureau researchers developed an agglomeration method that successfully overcame these problems [17, 18]. Agglomeration as a pretreatment for heap leaching consists of mixing the crushed ore with Portland cement, which acts as a binding agent, and lime to provide alkalinity, wetting the mixture evenly with solution, and mechanically tumbling the mixture so that the fine particles adhere to the larger particles. After aging for several hours stable bonds are formed and the pellets are very durable and porous. This simple pretreatment has increased the flow of solution through some ores several thousandfold and decreased the leaching cycle to days instead of weeks or weeks instead of months. The key to successful agglomeration heap leaching is to use the requisite amount of Portland cement. Too little cement does not form stable pellets and too much produces impervious golf balls. It is estimated that one out of two heap leaching operations uses some type of agglomeration pretreatment.

CARBON-IN-PULP

Carbon-in-pulp techniques were proposed in the early 1950s, and used by a few mills, which burned the screened carbon to recover gold, until the low price of gold and escalating costs curtailed their used [19, 20]. Around 1970 the idea was revived and the Bureau of Mines together with the Homestake Mining Co. conducted pilot-scale tests and published a description of the development and operation of a CIP plant in 1974 [21–23]. The impetus for implementing the process was the requirement by EPA regulations to discontinue amalgamation for recovering gold from the fine-grinding circuit at the Homestake plant in South Dakota. The plant split ground ore into sand and slime fractions that were leached separately. The gold, which was formerly amalgamated during grinding, was now treated in the slime plant. Because of the short leaching time (4.5 h) and the coarser size of the gold particles, dissolution was not complete and gold recovery decreased. A technique was needed that would provide a longer contact time with the cyanide solution, and would not require an increase in the capacity of the expensive filter presses used to separate the pregnant solutions from the slime. Carbon-in-pulp solved this problem and has proven very useful in treating ores that have a high clay content, or generate large amounts of slimes during grinding. With CIP no solid–liquid separation is needed and the barren slurry is discarded in the tailing pond. After settling, solution from the tailing pond is recovered for use in the mill circuit. A disadvantage of the system is that some of the cyanide in solution is not recovered for reuse. With increasingly stringent discharge requirements, the impoundment and control of cyanide in the tailings may become a greater problem. However, with very slimy ores, CIP may always be the preferred method of processing because of the high cost and difficulty of separating slimes from solution. CIP has also been successfully used on silver ores [24, 25].

Conventional countercurrent decantation or filtration, carbon-in-pulp (including carbon-in-leach), with or without oxidation pretreatment, and heap leaching are the major hydrometallurgical processes for treating gold ores.

What are some areas where problems still exist and what new technologies are being worked out that will be put into practice in the coming years?

One area where there is no simple answer is the treatment of refractory gold ores containing large amounts of sulfides. Although chlorine oxidation is very effective in destroying carbonaceous materials or making them innocuous, it is of limited value in treating sulfides. When gold ores contain large quantities of base metal or arsenic sulfides, the preferred treatment is to make a high-value flotation concentrate that can be sent directly to a smelter or that can be roasted prior to treatment. If it is not possible to pre-concentrate the ore effectively, or if roasting is not permitted, other approaches have to be considered. The approach developed by Sherritt–Gordon is to pressure oxidize the ore in autoclaves before cyanidation [26, 27]. Another approach, taken by Johannesburg Consolidated, is to use low-alkalinity presssure cyanidation [28]. Lakefield Research has used pressure oxidation in autoclaves followed by acidic thiourea leaching [29]. The approach taken by Equity Silver Mines was to leach the sulfides with hot caustic sodium sulfide solution before sending the concentrate to a smelter [30]. An ambient pressure oxidation with peroxysulfuric acid prior to cyanidation has been proposed by Ontario Research Foundation [31]. Sherritt–Gordon used an ammoniacal thiosulfate solution to leach gold from copper sulfides [32]. An interesting approach proposed by the National Research Council of Canada was to concentrate the sulfides by agglomerating them in a heavy oil phase [33].

An area where there is intense activity by a number of workers is in the use of biological systems for precious metal recovery. This includes the use of bacteria to oxidize sulfides prior to gold recovery by cyanidation or thiourea leaching [34–37], and the use of biomass to recover gold from solution [38, 39]. Some of these applications are in the pilot plant stage and should be implemented in plants in the next decade.

Another area where there has been a lot of interest in the past few years is noncyanide leachants. For the most part this means thiourea leaching, although as mentioned earlier, thiosulfate has been looked at and the halogens are being reexamined for gold extraction. Many articles have appeared since 1980 reporting the use of thiourea to solubilize gold in acidic media [40–46]. However, commercial application in the minerals industry remains limited. There are reportedly one plant in France and one in Belgium using thiourea to extract gold from mineral industry products. The only documented commercial use is from Australia where thiourea is used to leach gold from an antimony concentrate [47]. This is a specialized case where the solubilized gold is recovered by adsorbing it on activated carbon and burning the carbon, a practice that is too costly for most applications. The challenge for thiourea leaching is to develop and demonstrate solution recovery systems. Until data are available to evaluate the steps needed to produce gold metal, with concurrent regeneration of the leachant, commercial use will not occur. Many loose ends need to be tied down to develop an integrated process.

There has been much interest in developing systems other than carbon adsorption to recover gold from cyanide solutions. Ion exchange resins have been examined, but have the problem of either requiring solution pH adjustment to an undesirably low level to obtain adsorption (weak base resins), or that it is difficult to strip gold from the loaded resin (strong base resin) [48, 49]. The concept of using a resin-in-pulp process, analogous to carbon-in-pulp except an ion exchange resin is used in place of activated carbon, has been extensively studied by MINTEK in South Africa [50–52]. The main difficulty in implementation is the problem mentioned for the resins: either a low pH adjustment is required or it is difficult to elute the resin. There is the additional uncertainty of how well the resins will resist attrition in abrasive pulps for long term use.

Solvent extraction has been examined as a means to recover gold from dilute cyanide solutions [53, 54]. Although solvent extraction is a good technique to selectively remove low levels of metal ions from solution, it suffers the disadvantages of considerable solvent loss. It also requires clarified solutions to avoid "crud" formation in continuous operation.

A problem that is becoming apparent as heap leaching is extended to a wider range of ores is coleaching of undesired metals that adsorb on carbon and stripped with gold. the most troublesome of these metals are mercury and copper. Although control of these elements is possible to some extent in a plant setting [55], there is currently no method to control them in the dilute effluents from heaps. Heap leaching would benefit if techniques were developed to either remove the metals from pregnant solutions, prevent their adsorption, or selectively remove them from the carbon. The possibility of preventing their codeposition during electrowinning should be investigated. Another option would be to take a bleed stream from solutions that have become badly contaminated and perform a cyanide regeneration step. Cyanide regeneration was practiced in the early days of cyanidation, and there is renewed interest, which could be beneficial both economically and environmentally [56].

Another problem arises with heap leaching in cold climates, the freezing of solutions on the heaps. Development of a system that would lower the freezing point of leaching solutions and allow year-around operation would be very advantageous. The drip irrigation system mentioned earlier may allow operation in sub-freeezing temperatures if it is buried inside the heap below the freeze zone.

The area in which extensive work has to be carried out is the chemistry of the degradation of cyanide and its complexes, specifically of dilute cyanide solutions in contact with ore bodies [57, 58]. Several techniques are available to destroy cyanide if it becomes necessary to discharge plant or heap leaching solutions. These include alkaline chlorination, Inco's SO_2-air process, and Homestake's biological degradation treatment [59, 60]. However, little is known about the fate of the cyanide complexes in solution, when left alone for extended periods, as in abandoned heaps or in tailing ponds.

For any producing gold operation this knowledge is of great importance. Future requirements will be rigorous and the mill operators will be accountable for the protection of the environment. Unless a thorough understanding of the life cycle of cyanide complexes can be provided, attempts to destroy certain species may cause potential long-term problems. Time and effort spent on studies of "problems", which in fact are not real problems, could be avoided.

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