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Recovery of Gold and Silver from Ores by Hydrometallurgical Processing

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ABSTRACT

The Bureau of Mines has played an important role in the revival of precious-metal mining in the Western United States. During the past 30 years, many techniques used by industry to recover gold and silver were pioneered and developed by the Bureau of Mines. In 1952, technology was developed to strip gold from granular activated carbon and allow the carbon to be reused. In 1969, the heap leaching concept was applied to low-grade gold and silver ores and mine wastes. Heap leaching in conjunction with carbon adsorption-desorption permits very low value material to be economically processed. In 1970, an oxidation treatment based on hypochlorite was developed to increase the recovery of gold from carbonaceous gold ores by cyanidation. In the early 1950's, attempts were made to employ carbon-in-pulp technology to recover gold from ores, but the fixed price of gold and increasing operational costs made cyanidation unprofitable. The Bureau of Mines and Homestake Mining Co. jointly operated a carbon-in-pulp pilot plant, and the technology was used in full-scale production at the Homestake Mine in 1972. In 1973, a pressure stripping method, which decreased the time needed for the stripping step, was developed to desorb gold and silver from carbon. An alcohol desorption method, developed in 1976, also decreased the carbon stripping time. In 1979, an agglomeration pretreatment was developed that permitted clayey precious metal ores to be heap-leached. Almost all precious-metal-mining companies use at least one of the above techniques in production facilities.

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INTRODUCTION

The introduction of cyanide leaching in the 1890's revolutionized the processing of gold and silver ores. Since that time the standard hydrometallurgical process to recover gold and silver from disseminated ores has become cyanide leaching in a countercurrent decantation (CCD) plant (1). The operation of a conventional CCD plant is shown schematically in fig. 1 and consists of the following steps: (1) The ore is crushed and ground. (2) During grinding, the ore is slurried with dilute basic cyanide solution typically containing 0.1% NaCN and enough CaO to maintain the pH at 10-11. (3) The slurry is agitated in a series of leaching tanks to give a total leaching time of 12 to 48 h, which depends on the characteristics of the ore. (4) The slurry is thickened and countercurrently washed in a series of thickeners. (5) The pregnant solution from the first thickener is clarified by filtration and deaerated by vacuum. (6) Zinc powder is added to precipitate the gold and/or silver. (7) The gold-silver-zinc sponge is filtered and refined to bullion. (8) The barren cyanide solution is returned to the washing-leaching circuit, and makeup cyanide and base are added.

Gold-silver recovery from pregnant solutions by zinc precipitation can present problems. Ideally, the pregnant solution should be clear before precipitation and must be deaerated. This can be difficult to achieve with many slimy ores. Precipitation is also an inefficient method for recovering gold from dilute solutions. Different forms of carbon, especially activated carbon, were known to be good adsorbers of gold and silver cyanide from solution. However, since the only known means to recover the gold and silver from the carbon was to burn it, carbon was not used extensively. In a few cases, where slimy ores were being treated, gold adsorption on carbon was the preferred method to recover the precious metal values because the clarification

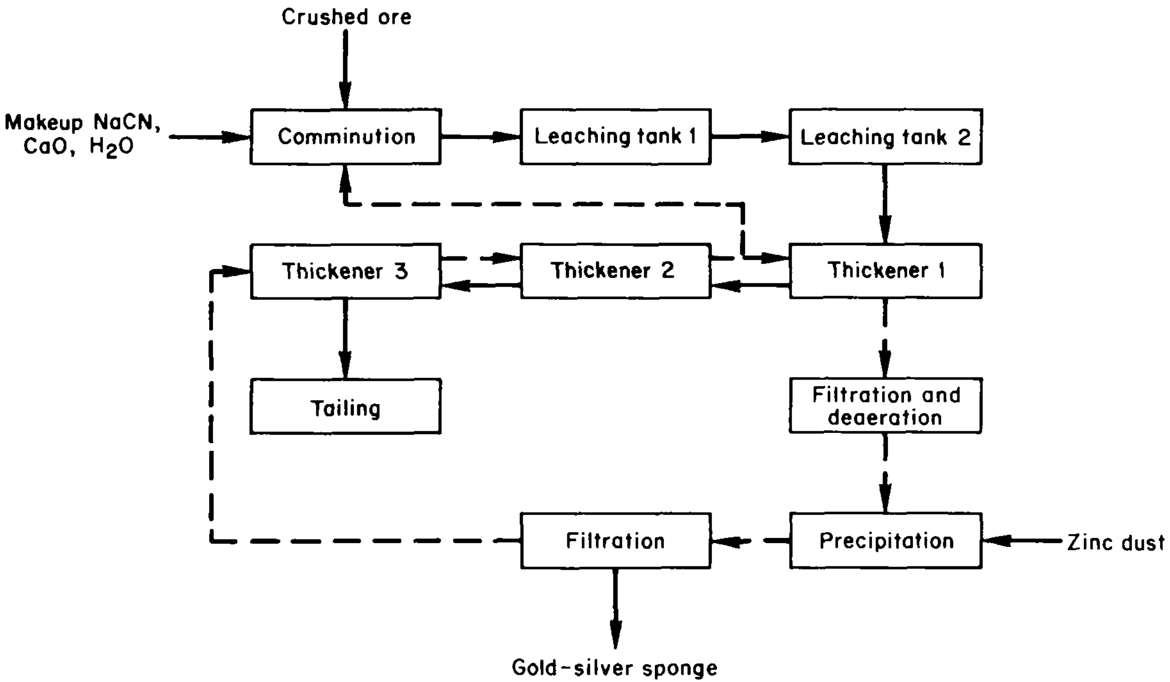

FIGURE 1. Flow diagram of countercurrent decantation cyanide leaching plant.

step was eliminated. The precious-metal-loaded carbon was recovered from the slurry by screening or flotation.

PRECIOUS METALS ADSORPTION-DESORPTION

In the late 1940's, Bureau of Mines researchers were 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 activated carbon from World War II, which was manufactured from fruit pits, was available at prices that made its use cheaper than using zinc. A means for desorbing and recycling the carbon would make it a very economical process for the recovery of gold. In 1950, an alkaline Na_2S stripping method which eluted the gold, but not the silver, from carbon was described (2). Since most ores contain some silver, and silver in some ores is the primary value, 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 gold and silver from loaded carbon (3). Precious metals were stripped by contacting the carbon with a boiling NaOH-NaCN solution. With each pass of the solution through the carbon bed, some of the gold and silver was removed. The solution entered an electrolysis cell where the gold and silver were deposited on the cathode. The barren solution was reheated and recycled through the carbon. A 1% NaOH-0.1% NaCN solution at its boiling point desorbed more than 90% of the gold and silver in 4 to 6 h. The carbon could be reused up to ten times without losing significant activity.

Carbon adsorption-desorption permitted gold-silver recovery from slimy ores, or the slimy portion of ores, by eliminating the requirement of a clarified solution. This became the foundation for two important developments in gold and silver ore processing: carbon-in-pulp (CIP) 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. The NaOH-NaCN electrolyte and steel wool cathode remain common to all the electrowinning cells. The Bureau's desorption-electrowinning process, known as the Zadra process, has been utilized in cyanide milling for more than 30 years.

Although gold and silver were eluted from the fruit pit carbon in 4 to 6 h in pilot-scale tests, this was not the general case. Commercial practice, which had adopted carbons made from coconut shells, showed that 24 to 48 h were required to desorb more than 90% of the precious metals with alkaline cyanide solution heated to boiling. Although this was better than not being able to strip the carbon, the long stripping time was undesirable. Bureau research was directed toward ways to decrease the stripping time. Two methods, pressure stripping and alkaline-alcohol stripping, were developed and greatly decreased the desorption time.

In 1973 Bureau researchers showed that by using a pressure vessel and increasing the temperature of the stripping solution, gold could be stripped from carbon in 2 to 6 h (4). The loaded carbon was conditioned with caustic cyanide solution at 90° C and eluted with water at 150° C. Another advantage was that consumption of cyanide and caustic was less with heated pressure stripping than with prolonged ambient pressure stripping. The stripping solution was cooled to 90° C and the gold recovered by electrowinning.

In the alkaline alcohol stripping method developed by Bureau researchers in 1976, ambient pressure was used, but the modified stripping solution contained 20% ethanol in addition to the alkaline cyanide (5). 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 (6). The separation of silver as a sulfide takes place after desorption from the carbon and results in a more pure gold bullion. For pregnant solutions containing considerable amounts of silver, the preferable sequence is to precipitate the silver before loading the carbon (7). A large carbon inventory is avoided by maintaining capacity for only gold adsorption. The Ag_2S precipitate can be smelted to a silver bullion. The gold in the filtrate from silver precipitation is adsorbed, desorbed, and electrowon.

Both pressure stripping and alkaline alcohol stripping are used by industry. The original ambient pressure stripping is also in use. The preference of the mill operator is the determining factor in choosing the stripping system.

HEAP LEACHING

In 1969, Bureau researchers proposed heap leaching as a low-cost means for recovering gold values from disseminated gold ores with porous gangue, mine stripping waste, and submarginal ores (8,9,10). Heap leaching was first used on oxide copper ores and uranium ores and had the advantage of very low capital cost, low operating costs, and operational flexibility (11). In heap leaching, the crushed material is piled in heaps on impervious pads. A dilute alkaline cyanide solution is distributed on top of the heap by a sprinkling system. The solution percolates through the heap and drains from the impervious pad. The pregnant gold solutions from the heaps contain typically 1 to 3 ppm Au. Precipitation of metal values with zinc may not be the most efficient recovery method for many operations, whereas carbon adsorption is very efficient for the recovery of metals from dilute solutions. The pregnant solution is passed through a series of columns containing activated carbon, and the gold is adsorbed. The resulting barren solution is fortified with reagents and recycled to the heap. The leaching continues until the gold extraction is completed. The gold-loaded carbon is stripped by one of the previously mentioned methods. Some pregnant solutions from silver heap leaching contain enough silver, typically 10 to 20 ppm Ag, so that zinc precipitation is used to recover the silver.

For heap leaching to be feasible, the ore must be porous and permeable to the leaching solution. Since the ore is not finely ground, the cyanide ions must diffuse through the host rock to dissolve a gold particle. The dissolved gold must diffuse outward. This gives leaching cycles varying from weeks to months, and may result in dissolved gold cyanide complexes which are not completely washed from the heap. Runoff from abandoned heaps is not discharged to surface or groundwater sources until the effluent from the spent heap is free of cyanide.

Heap leaching has been an important factor in precious metals recovery because it permits utilization of lean ores and wastes which are not economically processed by conventional agitation cyanidation. Fifteen years after its introduction, there are between 50 and 100 commercial gold and silver heap leaching operations, which range in size from 10 tons a week to 10,000 tons a day. A flow diagram of a typical heap leaching operation is shown in fig. 2.

CARBON-IN-PULP

Carbon-in-pulp techniques were proposed in the early 1950's (3,12), 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 use (Ref. 1, Vol II, p. 95; 13). Bureau of Mines researchers and the Homestake Mining Co. conducted pilot-scale tests in 1971 and published a description of development and operation of a CIP plant in 1974 (14,15,16). The impetus for implementing the process was the requirement by EPA environmental

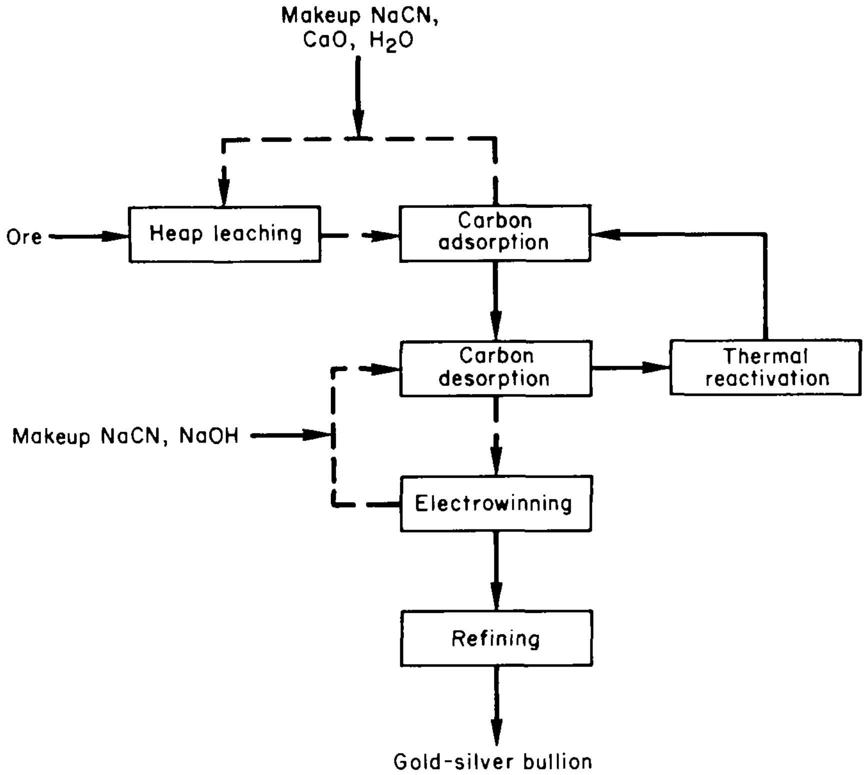

FIGURE 2. Flow diagram of heap leaching.

regulations to discontinue amalgamation for recovering gold from the fine-grinding circuit at the Homestake plant in South Dakota. The original plant was designed to grind the ore to a nominal 200 mesh. The ground ore was split into a sand and a slime fraction which were leached separately with dilute cyanide solution. The gold, which was formerly amalgamated during grinding, was treated in the slime plant. Because of the short leaching time (4-1/2 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 very 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 which have a high clay content, or generate large amounts of slimes during grinding. In CIP processing the ore is ground to less than 65 mesh and leached with alkaline cyanide solution. A coarse, hard coconut shell carbon, 20 mesh or larger, is added to the slurry after leaching is completed, and the slurry is agitated for several hours. The carbon is passed countercurrently through several tanks to achieve gold loading of several hundred ounces per ton of carbon and is separated from the slurry by screens. The loaded carbon is washed to remove adhering slurry and is stripped by the previously described methods. With CIP no solid-liquid separation is needed and the barren slurry is discarded in the tailing pond. After settling, some of the 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. 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 (17,18).

Carbon-in-pulp, heap leaching, and conventional countercurrent decantation methods are the major hydrometallurgical processes for treating gold and silver ores. Carbon-in-pulp processing was the topic of a panel discussion at the 1981 annual AIME meeting, where advantages and disadvantages of modern carbon-in-pulp plant practice were discussed (19). A flow diagram for typical CIP processing is shown in fig. 3.

AGGLOMERATION-HEAP LEACHING

Although the application of the heap leaching technique to gold and silver ores permitted many low-grade and/or small prop-

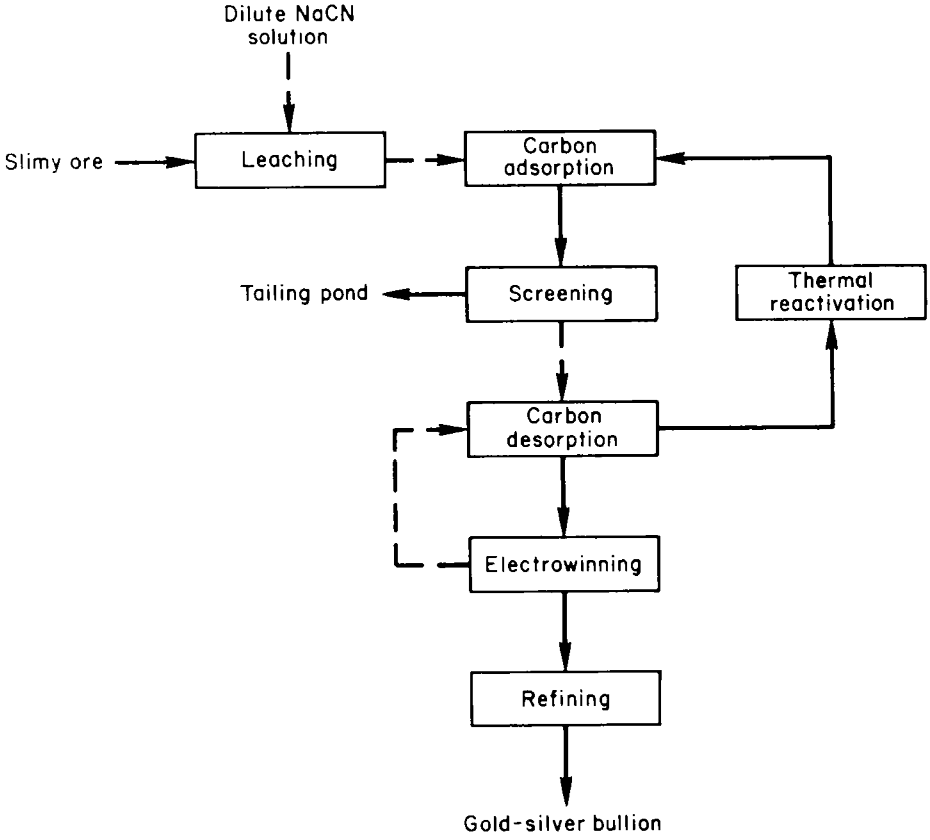

FIGURE 3. Flow diagram for carbon-in-pulp processing.

erties, which would not have been exploitable, to be developed, some ores were untreatable by heap leaching. This was due to two conditions: (1) the ore contained clay which swelled on contact with leaching solution, blocked the voids in the heap, and prevented solution flow, and (2) the ore after crushing to the liberation size for gold-silver extraction generated an unusually large amount of fines (minus 200 mesh) which were washed into the voids by the percolating leaching solution and caused channeling and partial leaching of the gold and silver from the heap material. In 1979, Bureau researchers published a report describing an agglomeration method that was successful in overcoming these problems (20,21). 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, which can contain cyanide to start leaching before the heap is built, and mechanical tumbling of the mixture so that the fine particles adhere to the larger particles. Several hours of aging are needed for the cement to bond to the particles. When stable bonds are formed, the pellets are very durable and resistant to degradation. This simple pretreatment has increased the flow through columns of some ores as much as 6,000-fold and, in actual heaps, has decreased the leaching cycle to days instead of weeks. It is estimated that one out of two heap leaching operations use some type of agglomeration pretreatment.

CARBONACEOUS ORES

A problem which plagued operators of some gold cyanide mills was the occurrence of activated-type carbon in sedimentary ores. Many carbonaceous ores cannot be treated by cyanidation because, even if the gold is dissolved by cyanide, the carbonaceous component acts as activated carbon and adsorbs the gold cyanide complex. If small amounts of carbonaceous ore enter the milling circuit, adsorption of the dissolved gold on the carbon will occur and the gold will be lost in the tailings.

In 1968, Bureau researchers reported on the use of oxidizing agents, such as hypochlorite or chlorine, to oxidize the carbonaceous material before conventional cyanidation (22). A process which could use either chemical oxidation by the addition of NaOCl or chlorine gas, or electrical oxidation by electrolysis of a NaCl solution, was developed. The carbonaceous component of ores was rendered inactive by oxidation. Pilot plant studies were conducted at the Carlin gold mine, Nevada. The chlorine oxidation process for carbonaceous ore has been in use since the early 1970's (23,24,25,26). In the process, ore is ground to liberation size, which is between 65 and 200 mesh. For chemical oxidation, lime is added to the slurry to maintain a high pH, and metered amounts of NaOCl solution or Cl_2 gas are added to the slurry. Sufficient time is allowed for the hypochlorite to react because any residual hypochlorite is deleterious in the cyanide circuit. If electrooxidation is used, the ground ore is slurried in a 10%-NaCl solution and the slurry is electrolyzed with a graphite electrode system. In either case, the oxidized slurry is mixed with slurry from oxide ore and treated by conventional cyanidation methods. Oxidation pretreatment of carbonaceous ores increased the gold recovery from about 30 to 90%.

SUMMARY

The Bureau of Mines contribution to gold and silver hydrometallurgy during the past 30 years has been significant. There are very few leaching operations which do not use at least one of the Bureau of Mines-developed techniques. Of the 12 large operating gold mines listed in a recent report, all but one use one or more of the techniques described in this paper (27).

The extensive application of cyanidation/carbon adsorption process can be attributed to the Bureau of Mines research and development of processes for desorbing gold and silver from granular activated carbon that permitted reuse of the carbon. Heap leaching has made possible the development of numerous gold and silver properties, and agglomeration heap leaching has added to that number. A technique to destroy the carbonaceous content of ores has resulted in the commercial exploitation of carbonaceous gold ores. The Bureau's research and improved economics have significantly rejuvenated the domestic gold and silver mining industry.

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