Chapter 8

Metal Extraction (Recovery Systems)

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8.1 INTRODUCTION

Several methods currently exist by which gold may be recovered from a pregnant leach liquor. Two of these methods are discussed in this chapter, the Merrill-Crowe (zinc cementation) process and the carbon adsorption process. These two methods represent the most frequently used techniques for gold extraction and are, in fact, used almost exclusively in U.S. heap leaching operations. Because of the efficiency and ease of use of these two methods, it is extremely likely they will continue to be quite prevalent within the gold mining industry in years to come.

The remainder of this chapter includes information on the history of the two processes, descriptions of the actual processes, criteria to consider in selecting a recovery process, and commercial design and construction considerations for both of the gold recovery methods. As with other chapters in this book, some fairly technical information is presented for the benefit of those readers needing a greater level of detail. However, the overall intent of the chapter is to provide an overview of the processes likely to be used in gold extraction, thus giving the reader a firm basis for more technical research into the topic, should this be needed.

8.1.1 History of Zinc Cementation

During the late 1890's, zinc cementation was introduced for the precipitation of gold and silver from cyanide solutions. This occurred at about the same time as the introduction of the cyanidation process, the history of which is recapped in Chapter 1.

The initial cementation process involved introduction of a gold-bearing cyanide solution onto a bed of zinc shavings. It proved to be quite inefficient because the reaction rate was very slow. The zinc quickly became "passive", inhibiting further gold deposition. Shortly after this first introduction, zinc precipitation was improved by adding a lead salt (usually lead nitrate) to the zinc. This allowed a zinc-lead couple to form on the surface of the shavings, eliminating passivation of zinc surfaces and thereby allowing continued deposition of gold.

Further improvements were shortly forthcoming. The first of these involved the use of zinc dust rather than zinc shavings. This provided a much

larger specific surface area for precipitation and greatly speeded the reaction kinetics. The deareation of gold-bearing solutions to an oxygen concentration of less than 1 ppm significantly reduced zinc consumption caused by oxidation, again resulting in a significant increase in process efficiency. The use of clarified, deareated leach liquors was a logical next step in this process which ultimately became known as the Merrill-Crowe precipitation process, named for the two men most responsible for its final evolution to a widely used process.

8.1.2 <u>History of Carbon Adsorption/Desorption/Electrowinning</u>

Activated carbon was used early-on in the development of gold extraction processes to adsorb gold values from leached pulps in which a solid-liquid separation (necessary for gold extraction by Merrill-Crowe process) was difficult. Once the activated carbon was loaded with gold, it was sent to a smelter and burned to recover the gold. The cost of using the carbon only once, in combination with the cost of smelting, rendered this process economically unattractive. However, the potential of the process was realized, thus triggering a period of intensive research by the U.S. Bureau of Mines aimed at the development of techniques for stripping and reusing the carbon. A method of desorption was quickly developed using a caustic sodium sulfide solution, followed by electrowinning of gold. This, however, proved ineffective in stripping silver from the carbon.

Following further modification, a process was developed (Zadra et al., 1952) to effectively strip both gold and silver. It employed a hot NaOH-NaCN solution to desorb the loaded precious metals. Electrowinning of the stripping solution to recover the metals was followed by reactivation of the carbon through heating in the absence of air. The process was used successfully on a small scale at the Getchell Mine, Nevada, and at the Golden Cycle Mine, Cripple Creek, CO, in the 1950's. The first major successful commercial use of this process occurred at Homestake's South Dakota operations in the early 1970's.

8.2 PROCESS DESCRIPTION

Chemistry of Process. The chemistry of zinc precipitation depends mainly on the fact that gold and silver metals are more noble than zinc. This means that they are more apt to reduce to their native states (i.e., Au^O and Ag^O) than remain in a gold or silver-cyanide complex. A generalized cementation reaction may be written as follows (Zadra et al., 1952):

$$2Au (CN)^{2-} + Zn = 2Au = Zn (CN)_4^{2-}$$

As the gold is precipitated, the zinc combines with the cyanide to form a zinc-cyanide complex. High pH (10.0+) is required to precipitate precious metals and to minimize precipitation of copper which is at times present in solution.

Detailed fundamental studies of the kinetics and mechanisms of gold precipitation were published by Nicol et al. (1979). Their paper is an excellent reference for information concerning precipitation of precious metals by zinc dust.

<u>Flowsheet.</u> Merrill-Crowe zinc precipitation is the most commonly used cementation process for gold recovery, and consists of four basic steps (Figure 8.1):

- Clarification of the leach liquor;
- Deareation:
- · Addition of zinc (and lead salts); and
- · Recovery of Zn/Au precipitate.

The precipitate is then smelted to recover the precious metals.

Solution Characteristics for Efficient Precipitation. Three types of solution constituents (or potential constituents) can have a major effect on the efficiency of the zinc precipitation process: suspended solids, dissolved oxygen, and interfering metallic ions.

<u>Suspended solids</u> can drastically reduce process efficiency, thus making clarification (i.e., the process of removing suspended material from a solution) important sinale factor the most in obtaining precipitation. Through long experience, pre-coat pressure clarification is provide the best operational results. When this clarification is followed, partial removal of dissolved oxygen has already been achieved when the solution enters the Crowe receiver (or vacuum tower), deoxygenation is completed. By clarifying and where the simultaneously, available vacuum is used more efficiently.

Efficient and complete precipitation of metals from cyanide leach liquors requires that the solution, after clarification, be further conditioned by the removal of <u>dissolved oxygen</u>. Even minute traces of dissolved oxygen have a deleterious effect on complete precipitation because of passivation of the zinc surface. Vacuum deareation removes dissolved oxygen from solution and appears to be the best process because it also removes carbon dioxide. Carbon dioxide can react to form calcium carbonate and blind precipitate filters.

When metallic zinc dissolves in alkaline cyanide solutions, hydrogen is formed. Provided the dissolved oxygen has been substantially removed (generally through vacuum dearation, as discussed above), the hydrogen will combine with and nullify the effect of any oxygen remaining in solution. Zinc and cyanide consumption then decreases and the formation of troublesome byproducts is minimized.

Several metallic ions are known to have varying degrees of detrimental (i.e., interfering) effects on zinc cementation. The most troublesome ions are those of antimony and arsenic (Finkelstein, 1972). Concentrations of these ions as low as 1 ppm can reduce the rate of cementation by 20 percent. High values of these ions may be reduced by treating the mill solution with sodium sulfide and filtering the resulting insoluble antimony and arsenic sulfides. However, all silver in the mill solution is lost when this process is used.

The presence of copper in cyanide solutions usually causes high cyanide consumption, and also decreases precipitation efficiency by passivation of the zinc, if allowed to accumulate beyond certain limits. However, with the use of powdered zinc, fresh surface is exposed on a continuous basis, and hence gold

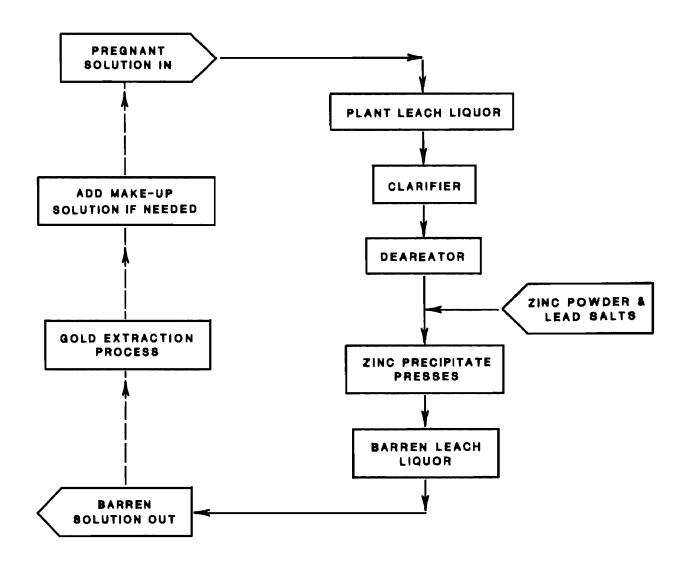


FIGURE 8.1

GENERALIZED FLOWSHEET OF A
MERRILL-CROWE PRECIPITATION PLANT

and silver precipitation is usually complete. Maintaining higher free cyanide concentration in the precipitation circuit normally keeps the copper from precipitating, thereby reducing passivation of the zinc surface.

The presence of small amounts of lead in solution has been found to be beneficial to precipitation. However, if lead concentrations are too high (i.e., greater tha 20 ppm), subsequent consumption of zinc is increased.

8.2.2 Carbon Adsorption

Adsorption Mechanism. Most types of charcoal will adsorb gold to some extent; however, the most effective charcoal is produced specifically for adsorption by charring coconut shells or peach pits at around 700 to 800 degrees Celsius in the presence of steam (Muir, 1982).

During the last decade, a number of investigations aimed at understanding the mechanism of adsorption onto carbon have been undertaken. Although there is much confusion and little agreement among the various researchers, all seem to agree on the following postulate:

The adsorption of gold cyanide into a porous charcoal particle involves the simultaneous phenomena of pore diffusion and adsorption onto "active sites" or areas of the carbon having an affinity for gold and silver (Davidson, 1982; Ha Cho, 1979a and 1979b; McDougall, 1981).

Investigations on the adsorption process usually employ a pore diffusion model which is the adsorption isotherms to Freundlich isotherms. Study of carbon adsorption kinetics reveals that the activation energy for diffusion demonstrates that the limiting step in the rate of adsorption is diffusion. Without benefit of further theoretical development, suffice it to say that all the references listed above are excellent sources for more complete coverage of the subject matter.

<u>Carbon Specification</u>. Commercially available carbon which is used in gold extraction from leach liquors usually comes in two sizes (i.e., minus 6 plus 16 mesh or minus 12 - plus 30 mesh). These products are available from several suppliers. The following is a typical specification list for activated carbon:

Surface area, m ² /gm	1050 - 1150
Apparent density, g/cc	0.48
1b/ft ³	30.0
Particle density, g/cc	0.85
Voids in densely packed column, %	40

Typically, the product is available in 55-gallon drums.

Unit Operation. The carbon adsorption process for recovery of gold and silver can be separated into three major steps:

 Loading - Gold and silver is adsorbed from the leach liquor onto carbon particles;

- <u>Elution and reactivation</u> Gold and silver are desorbed from the carbon into a concentrated solution with the stripped carbon being regenerated and returned to step 1; and
- Recovery Gold and silver are recovered from the concentrated solution by electrowinning or precipitation on zinc dust; the resulting barren solution is returned to the elution and reactivation, and the recovered precious metals are fire-refined to dore bullion.

Figure 8.2 (from Jha, 1979) illustrates a typical flowsheet for recovery of gold and silver using carbon adsorption. This figure highlights the loading, elution, and recovery steps of the process.

Commercial or mine-site laboratory units can use several carbon adsorption methods to perform the three steps identified above. The paragraphs which follow deal primarily with the loading step and the various techniques available to effect the actual adsorption onto carbon particles. Chapter 9 discusses in some detail the elution and reactivation step as well as the actual recovery step.

Three methods of loading are commonly used and are referred to as: 1) carbon-in-column loading (CIC); 2) carbon-in-pulp loading (CIP); and carbon-in-leach loading (CIL).

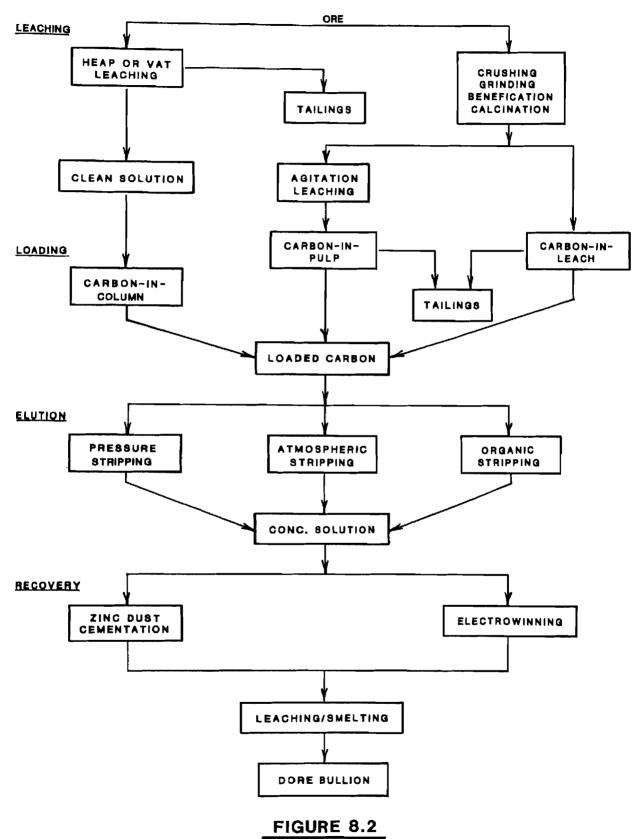
- CIC loading results when leach liquor is contacted with carbon via a carbon-packed column. The liquor is passed through the carbon in an upward direction, causing the carbon column to expand vertically. As a result of this vertical expansion, the term "expanded carbon bed" is also used to describe the process.
- CIP loading involves the introduction of leach liquor or ore pulp into an agitation tank having counter-current action (i.e., the carbon flows in one direction, while the liquor or pulp flows in another).
- CIL loading is actually a leach circuit variant that serves to enhance simultaneous dissolution and adsorption.

8.3 SELECTING A SOLUTION RECOVERY SYSTEM

This section outlines considerations and guidelines for use in the selection of an appropriate metal recovery system. As with the other parts of this chapter, the discussion focuses on two processes - zinc precipitation and carbon adsorption. Table 8.1 presents a summary comparison of the two processes.

8.3.1 When to Use Zinc Precipitation

Zinc dust cementation, or Merrill-Cowe precipitation is the most widely used method for gold and silver recovery. Because of its simple and efficient operation, the Merrill-Crowe process is currently used at the 10 largest gold producing mines in the free world, all of which are in South Africa. This process is attractive for use at new mines where the ore exhibits a high silver to gold ratio (ranging from 5:1 to 20:1). Ores with high silver values



FLOWSHEET FOR RECOVERY OF GOLD AND SILVER USING CARBON ADSORPTION

TABLE 8.1 - SUMMARY OF ADVANTAGES AND DISADVANTAGES OF CARBON ADSORPTION AND MERRILL-CROWE PRECIPITATION

MERRILL-CROWE

ADVANTAGE

Low labor costs for operation and maintenance;

- Low capital cost; and
- Can handle large silver to gold ratios in the pregnant liquor.

DISADVANTAGES

- Pregnant solution needs pretreatment prior to precipitation.
- Process is sensitive to interfering ions; and
 - Low precious metal concentration in solution increases the quantity of zinc required to precipitate an ounce of metal.

CARBON SYSTEMS

ADVANTAGES

- No pre-treatment of pregnant liquor required;
- Process handles slimy and carbonaceous ores; and
- Very efficient recoveries, irrespective of incoming precious metal concentration.

DISADVANTAGES

- High silver grade in pregnantliquor results in high carbon movement;
- Carbon is susceptible to fouling by calcium and magnesium salts;
- Carbon regeneration and stripping is labor intensive; and
- Adsorption processes have a higher capital cost than zinc cementation operations.

present significant problems to carbon adsorption circuits because the silver causes high carbon stripping requirements which may be economically prohibitive. Several of the existing operations using Merrill-Crowe precipitation actually experience higher silver recoveries than gold.

One other advantage to the zinc cementation system is that once dyamic equilibrium (steady state) is reached in the process plants, relatively few people are required for operation and maintainence (i.e., only simple valve operation and meter reading tasks are required).

The process does, however, have some disadvantages. The leach liquor must be treated (i.e., clarified and deareated) prior to precipitation. Indeed, as noted in a preceding section, inefficient pretreatment is detrimental to successful precipitation. Other disadvantages stem from the process being quite dependent on and sensitive to the pregnant liquor composition. Lower gold concentrations in the feed solution result in higher zinc consumption. This is because the zinc is mostly used to precipitate all of the other metals in solution before gold and silver are recovered. Also, interfering ions such as arsenic and antimony can be problematic, leading, in some cases, to the consideration of other recovery methods.

8.3.2 When to Choose Carbon Adsorption

Activated carbon recovery systems have gained a wide acceptance in the gold industry within the last 10 years. As alluded to earlier, one of the major advantages of this process is related to the fact that leach liquor does not have to be treated prior to recovery. In the CIC process (which is commonly used in conjunction with heap leaching) the pregnant liquor is run through a bed of carbon without pretreatment.

Slimy and carbonaceous ores present few problems to carbon adsorption systems, unlike the Merrill-Crowe system which is sensitive to these. The CIP or CIL processes eliminate the need for complicated solid-liquid separation. Carbon systems seem to operate at a maximum efficiency, irrespective of feed solution grade. Thus, recoveries may be better with carbon systems if none of the complicating factors discussed below or listed on Table 8.1 are involved. However, the carbon can easily be fouled by dissolved salts, in particular calcium or magnesium carbonates. Carbon can also be fouled by organic compounds like oils and flotation reagents.

Carbon systems tend to be more labor intensive, often requiring frequent acid washing or reactivation. The elution and regeneration steps are the most expensive parts of the flowsheet. Pressure stripping appears to be the most popular method in current use, although work is continuing on development of several organic stripping methods. Following carbon stripping, a process such as zinc cementation or electrowinning must be used to treat the concentrated liquor; each of these supplementary processes presents its own operational complications.

With both Merrill-Crowe and carbon systems, it is prudent to investigate the existence and effect of mercury in the pregnant solution. Increasingly, operations are having to deal with operational difficulties associated with the existence of mercury. Mercury tends to be detrimental to the operation, causing an increase in the consumption of zinc on the one hand, and decreasing

the ultimate loading of gold onto the carbon, on the other. Mercury passifies the zinc in the Merrill-Crowe process, and occupies valuable active surface space in carbon adsorption.

8.3.3 Economic Considerations

Several economic comparisons have been made between carbon systems and Merrill-Crowe systems. One of these, a systematic comparison completed by DeMent and King (1982) is summarized below.

Five separate conventional mills involving both Merrill-Crowe and the CIP processes were compared from an economic viewpoint. The gold concentration on the feed leach liquor ranged from 0.428 to 0.054 oz of gold per ton (14.6 to 1.8 g/mt) of solution.

Capital costs at the front end of a CIP plant are based on incoming flow rate, and are not a function of the gold grade. However, the capital costs of carbon stripping recovery portions do vary, as they are dependent on the grade of gold in the solution. Carbon regeneration is also dependent on the amount of carbon processed. On the other hand, with a Merrill-Crowe process, the total capital cost is solely a function of the initial flow rate.

Operating costs vary in the CIP plant according to the grade of gold in the leach liquor. This cost does not vary with the Merrill-Crowe except in the case of zinc usage which increases with higher input concentrations.

Gold losses in conventional CIP plants result from pregnant values which are not adsorbed onto carbon and are therefore discarded to tails. Another gold loss occurs whenever gold is loaded onto very fine carbon particles. This fine carbon passes all screens and also ends up in tailings. The main gold loss in a Merrill-Crowe circuit has a much different source (i.e., it results from incomplete washing of the filter cake on the precipitate presses).

DeMent and King's results are based on estimated costs of a CIP and Merrill-Crowe plant, bearing in mind that costs are dependent on the particular characteristics of each ore. However, it seems pertinent to point out that within one operation using Merrill-Crowe precipitation, the author's personal experience showed that for a lower grade leach liquor, Merrill-Crowe was selected. In the plant in question, the decision was made to use zinc precipitation based on the varying grade of pregnant liquor (from 0.075 ounces per ton to 0.010 ounces per ton (2.6 to 0.3 g/mt) gold). As operating costs were negligibly affected by this variation, the design decision proved profitable.

It is worth noting that operations do exist which combine carbon adsorption with zinc precipitation. Usually a zinc precipitation plant is followed by a CIC set up. This is done to enchance the removal of gold from barren solution coming from the zinc circuit. Very frequently, if no clear distinction is evident as to whether zinc or carbon is the best choice, the final decision is based on the particular experience of the project personnel who will be operating the proposed plant.

8.4 COMMERCIAL DESIGN & CONSTRUCTION

8.4.1 Zinc Precipitation

Portable Units/Shelf Units. Depending on the expected flow rate and the size of operation, Merrill-Crowe zinc precipitation units can come in a variety of sizes. These range from 20 gallons per minute $(1.3\ l/sec)$ in small self-contained units to 4,000 - 5,000 gpm $(250\ to\ 315\ l/sec)$ throughput in custom plants.

Smaller skid-mounted units are available from several suppliers. Each unit comes equipped with all the necessary pumps and piping. All the user must provide is a feed line to the unit, an effluent (barren) line out, and electrical supply. These units are very useful for ranges of flows from 50 to 250 gpm (3 to 16 l/sec). They are easily assembled or dismantled and often are mounted on trailers for easy transportation. However, beyond a certain point, it becomes apparent that the filtration supplied with these units is insufficient for optimum operation. The operator may spend more time cleaning the clarifier filters than actually treating solution. It is for this reason that operations are custom designed for handling large daily volumes of pregnant solution.

<u>Custom Designed Units</u>. Here the choice of size and volume throughput is not limited. Typically, the designs are based on an expected volume of requirements, with a built-in over-design included. Stationary pressure filters, or the leaf-vacuum type, are incorporated as well as vacuum deareators. Plate and frame presses are often a standard. Larger throughputs of these plants justify instrumentation such as turbidimeters or continuous flow (in-line) oxygen probe detectors to facilitate the operation and improve efficiency.

Disadvantages are inherent with the size of the plants. They are usually permanent installations and are expensive to relocate.

8.4.2 Carbon Adsorption

<u>Small Commercial Operations</u>. As with zinc cementation units, a large variety of sizes of carbon adsorption units are available. Although only a few shelf units are available, columns are designed for specific leach liquor flow rates.

Smaller units are designed typically with four or five columns in series. The pregnant liquor flows through a bed of activated carbon. The solution is then routed from the top of the first column, through another bed of carbon in the bottom of column 2, in the following fashion (Figure 8.3). The carbon is educted counter currently from the flow of the leach liquor. Thus, in the Figure 8.3 example, the carbon flows from the last column (#3) to the second, and then to column #1. Fresh carbon is introduced to column #3 and fully loaded carbon is removed from column #1.

 $^{^{1}}$ Eduction refers to the transportation of carbon in a slurry.

Large Commercial Operations. Larger plants incorporate larger columns to handle the larger volume throughputs. Most plants operate with a carbon bed expansion approaching 60 to 70 percent. Therefore, the bottom 1/3 of the column is loaded with carbon, such that after expansion the carbon column depth amounts to roughly two-thirds of the tank depth; one-third of the depth is available for free-board.

SOLUTION FLOW

COLUMN

+2

COLUMN

+3

BED OF CARBON

FIGURE 8.3 TYPICAL CONFIGURATION OF A CARBON-IN-COLUMN PLANT

Generally, the solution flow rate required to maintain fluidization in a bed of carbon containing minus 6 - plus 16 mesh particles is about 25 gpm/ft² (17 $1/s/m^2$) of cross-sectional area of the column, whereas for the minus 12 - plus 30 mesh carbon, the required flow is 15 gpm/ft² (10 $1/s/m^2$). Under these conditions, the carbon bed expands about 60 percent.

As can be seen, the column diameter requirements are dependent on the flow rate requirements. Whereas smaller operations might stockpile their loaded carbon and treat it elsewhere in bulk, larger operations would have elution -regeneration - recovery unit operations on site.

8.5 REFERENCES

- Davidson, R.J., W.D. Douglas, and J.A. Tumility (1982). The selection of granular activated carbon for use in a carbon-in-pulp operation, in Carbon-in-pulp technology for the extraction of gold, Austr. Inst. Min. Met., Parkville, Australia, pp. 199-218.
- DeMent, E.R., and N.D. King (1982). Merrill-Crowe/carbon-in-pulp, an economic evaluation, The Aust. Perth and Kalgoorlie Branches and Murdock University, July.
- Finkelstein, N.P. (1972). The chemistry of the extraction of gold from its ores, in Gold metallurgy in South Africa, ed. R.J. Adamson, Chamber of Mines of South Africa, Johannesburg, pp. 284-351.
- Ha Cho, E., and C.H. Pitt (1979a). The adsorption of silver cyanide on activated charcoal, The Metallurgical Society of AIME.
- Ha Cho, E., and C.H. Pitt (1979b). Kinetics and thermodynamics of silver cyanide adsorption on activated charcoal, The Metallurgical Society of AIME, June.
- Heinen, H.J., D.G. Peterson, and R.E. Lindstrom (1976). Gold desorption for activated carbon with alkaline alcohol solutions, Chapter 33 in World mining and metals technology, ed. A. Weiss, AIME, New York, pp. 551-563.
- Jha, M.C. (1979). Recovery of gold and silver from cyanide solutions: a comparative study of various processes, AMAX Extractive Research and Development, Inc., August.
- McDougall, G.J., and R.D. Hancock (1981). Gold complexes and activated carbon, J. South African Inst. Min. Met., pp. 138-152, April.
- Muir, D.M. (1982). Recovery of gold from cyanide solutions using activated carbon: a review, in Carbon-in-pulp technology for the extraction of gold, Austr. Inst. Min. Met., Parkville, Australia, pp. 7-22.
- Nicol, M.J., E. Schalch, P. Balestra, and H. Hegedus (1979). A modern study of the kinetics and mechanism of the cementation of gold, J. South African Inst. Min. Met., pp. 191-198, February.
- Zadra, J.B., A.L. Engel, and H.J. Heinen (1952). Process for recovering gold and silver from activated carbon by leaching and electrolysis, Report of Investigation 4843, United States Bureau of Mines.