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Figure 1. Typical heap-leaching operation for recovery of gold from crushed ore using dilute cyanide solutions. Heap leaching of crushed ore usually involves 30- to 60-day leach cycles and yields gold recoveries of 60 to 90 percent.

Gold and Silver Extraction: the Application of Heap-Leaching Cyanidation

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In the last decade, heap leaching has established itself as an efficient method of treating oxidized gold and silver ores. Also known as solution mining, heap leaching involves the extraction of soluble metals or salts from an ore by distributing solutions over an open ore heap piled on an impervious pad. For example, gold and silver can be separated from their ores by the application of a weak solution of cyanide and lime or caustic soda. Figure 1 shows a typical precious-metal heap-leaching operation. This processing technique is an extremely efficient way of extracting metals from small, shallow deposits, but is especially attractive for treating large, low-grade, disseminated deposits. Compared with conventional milling (crushing, grinding, and agitation leaching), recovery of gold and silver by heap leaching

offers several advantages: lower capital and operating costs, shorter start-up times, and fewer environmental risks. These advantages, however, are sometimes offset by lower metal extractions.

The first commercial application of heap leaching, by the Carlin Gold Mining Company in northern Nevada, occurred in the late 1960's. Since that time, advances in solution-mining technology and the continued high price of gold have sustained a strong interest in heap leaching. About 25 percent of the new gold and 10 percent of the new silver currently produced in the United States are obtained through heap leaching. Nevada is clearly the leader in precious-metal heap leaching with about 50 stable operations and another 50 that operate depending on the price of gold and silver (Carrillo, 1985). Two examples of large-scale heap-leaching operations, both of which are in Nevada, are the Smoky Valley operation, which mines 11,000 metric tons of ore per day (mtpd) and produces about 3,700 kilograms (kg) of gold and 2,200 kg of

silver annually; and the Candelaria plant, which is primarily a silver mine that processes 9,400 mtpd and produces about 90,000 kg of silver annually.

The locations of the major western U.S. gold-and-silver heap-leaching operations are shown in Figure 2. The newest of these are the Picacho mine of Chemgold, Inc. and the Mesquite mine of Goldfields Mining Corporation. Both plants are in California, approximately 25 miles outside Yuma, Arizona.

The purpose of this article is to review important factors related to cyanidation and heap-leaching practice. The article briefly summarizes the history of cyanidation and discusses the operational features of heap leaching using dilute cyanide solutions.

HISTORY OF CYANIDATION

The historical fabric of cyanidation is very colorful: it is woven with many threads of controversy and disagreement. Numerous patent disputes have been documented in technical journals. Cyanidation technology appears to be evolutionary, with advances progressing from prior work. Seven such advances provide a historical summary of cyanide leaching: early cyanide chemistry, the cyanide process, Merrill-Crowe (zinc-dust precipitation), carbon adsorption, carbon-in-pulp (CIP), Zadra (stripping and electro-winning), and heap leaching.

Early Cyanide Chemistry

As early as 1793, aqueous solutions of potassium cyanide were known to exhibit a solvent action on gold (Habashi, 1970). In 1843 Bagration produced the first scientific treatise on the subject. During his investigation, he observed the following:

- (1) Dissolution is more rapid when the gold is divided into very small particles.
- (2) Dissolution increases with heating.
- (3) Gold dissolved in cyanide will precipitate on metallic surfaces in the absence of an applied potential.
- (4) The presence of air decreases the time necessary for dissolution (McCann, 1912).



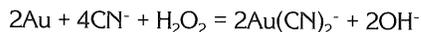
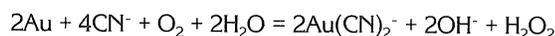
Figure 2. Major western U.S. gold-and-silver heap-leaching operations.

In 1844 Elsner discovered that gold dissolution in cyanide was due to the action of dissolved oxygen and not the decomposition of water, as previously believed (Wilson, 1896). The "Elsner Equation," stated in its original form, is as follows:



This early formula established the overall stoichiometry of gold cyanidation and recognized the presence of a gold-cyanide complex.

Bodlaender (1896) rapidly dissolved gold in an aerated cyanide solution and found that significant quantities of hydrogen peroxide (H_2O_2) were produced during the reaction. The formation of hydrogen peroxide as an intermediate product suggested a two-step reaction sequence:



The sum of these reactions is equivalent to the overall reaction as proposed by Elsner.

Barsky and others (1934) provided some of the first fundamental thermodynamic and kinetic data for the cyanidation of gold and silver. Their work confirmed the accuracy of the equations offered by Elsner and Bodlaender. They determined the values for the free energy of formation of the aurocyanide ion, $\text{Au}(\text{CN})_2^-$ and the argentocyanide ion, $\text{Ag}(\text{CN})_2^-$. They also investigated the effects of cyanide concentration and pH on the rate of gold and silver dissolution. The maximum rate of gold dissolution was obtained with a 1×10^{-2} M NaCN solution. The rate of gold dissolution was found to be insensitive to pH between about pH 10.5 and pH 12.5.

Boonstra (1943) was reportedly the first to recognize the similarity between gold dissolution in cyanide and metal corrosion processes. This observation established the importance of the electrochemical dissolution mechanism involving distinct anodic and cathodic steps.

The Cyanide Process

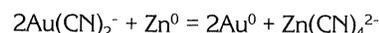
It was not until the pioneering work of MacArthur and the Forrest brothers (1887, 1889) that cyanidation became a commercial process. Their patents of 1887 and 1889 were milestones in the metallurgy of gold because they recognized a chemical process for treating gold

ores. Their contributions included two important advancements: (1) they used dilute cyanide solutions to produce a selective action on gold instead of using stronger lixiviants, which have a tendency to dissolve impurities; and (2) they proposed a method for recovering gold from cyanide solution by precipitation with zinc shavings.

Although cyanide had been used as early as 1870 to treat gold ores in the United States, the MacArthur-Forrest process was not officially introduced to domestic mining operations until 1892. The first cyanide gold mill in the United States was reportedly established at the Vulture mine near Wickenburg, Arizona (Young, 1967; Figure 3). Haynes (1892) reported the successful treatment of tailings and rebellious ores using cyanide by the Yavapai Gold and Silver Extraction Company in Prescott, Arizona. At about the same time, several plants near Tombstone, Arizona were using cyanide leaching to recover silver. By 1896, there were seven major cyanide plants in the United States, the largest of which was the Mercur mill in Utah. This plant had a capacity of 183 mtpd and achieved gold extractions ranging from 80 to 87 percent (Packard, 1896).

Merrill-Crowe

Early cyanide practice involved gold precipitation onto zinc shavings. Cementation of gold onto a metallic zinc surface is represented by the following reaction (Wilson, 1896):



The electrochemical cementation reaction shown above is relatively simple, involving the discharge of a noble metal ion (the gold-cyanide complex) at the expense of a more reactive metal (the zinc dust).

Zinc-dust precipitation, known as the Merrill system, was introduced in the United States in 1897 and is the basis of modern practice (Julian and others, 1921). Oxygen necessary for the oxidation of gold during cyanide leaching is detrimental to efficient zinc-dust precipitation. Merrill recognized this and designed a process to avoid air contact with the zinc during precipitation. Crowe (1919) improved the process by removing dissolved oxygen from the gold-bearing cyanide solution prior to addition of the precipitating agent. This approach improved the efficiency of gold precipitation and decreased zinc consumption. The Merrill-Crowe process consisting of solution clarification, deaeration, zinc-dust precipitation, and precipitate filtration continues to be an important precious-metal recovery method used by many modern plants.

Carbon Adsorption

Gross and Scott (1927) undertook the first rigorous study of the adsorption and desorption of gold and silver cyanide on carbon. They reviewed the early history of carbon adsorption, noting that charcoal

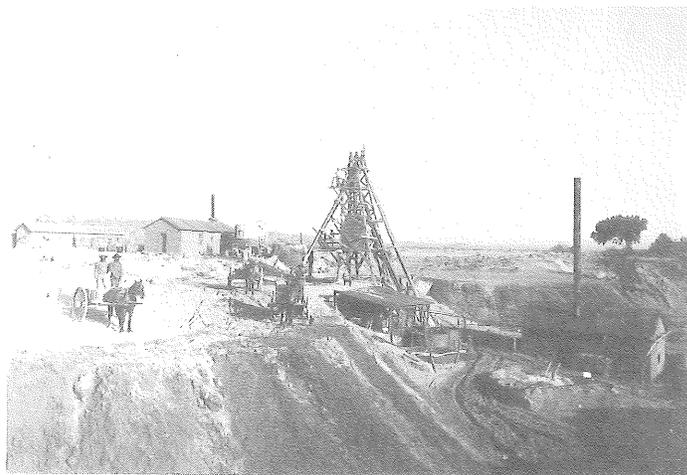


Figure 3. Reportedly the first U.S. cyanide plant, as seen in the early 1890's, at the Vulture mine, Wickenburg, Arizona. Photo courtesy of the Arizona Historical Society.

GOLD AND SILVER HEAP LEACHING

was first used in chlorination plants to recover gold. As cyanidation became more popular than chlorination, it was only natural that charcoal would be used to recover precious metals from cyanide solution. Charcoal was used at a number of locations by the turn of the century. As improvements in zinc-dust precipitation emerged, however, interest in the use of charcoal declined.

Early investigators believed that charcoal precipitated gold from solution (Green, 1913; Feldtman, 1915; Edmands, 1918). Actually, a reduction mechanism by which gold is deposited in the metallic state on the carbon surface does not explain the experimental evidence. Unfortunately, complete understanding of the adsorption mechanism is still lacking. High surface area (active sites) and pore diffusion are important aspects of the adsorption and desorption processes.

Carbon-In-Pulp

A major contribution to carbon-in-pulp (CIP) technology was made during the 1930's by Chapman (1939) of the Department of Metallurgy, University of Arizona. Chapman and his graduate students investigated dissolution of gold by cyanide and adsorption of dissolved gold onto activated charcoal in ore pulps. The general process used flotation to separate and recover the gold-bearing charcoal from the leached tailings. The flotation of powdered carbon proved to be highly selective, producing a charcoal concentrate that could be either smelted directly or ashed to recover the gold. A portion of the early research at the University of Arizona was devoted to the activation of carbon prior to adsorption of gold from cyanide solution (Rabb, 1939).

The lack of a convenient method for stripping adsorbed gold and silver from loaded carbon handicapped the development of CIP practice. Without stripping, it was impossible to recycle carbon in a closed-circuit system (adsorption, stripping, and reactivation). These techniques were pioneered by the U.S. Bureau of Mines (Zadra and others, 1952; Hussey and others, 1979) and have been improved and engineered for large-scale operations by MINTEK in South Africa (Laxen and others, 1979). Advantages of the CIP process include the ability to handle ores with poor settling and filtration characteristics by eliminating the need for costly liquid-solid separation systems; efficiency in the recovery of gold from dilute process streams; high capacities; and relatively simple design and operation.

Zadra

The next major contribution to the cyanide process was the recovery of gold by activated carbon, stripping the carbon with hot caustic cyanide solution, and electrowinning the gold and silver onto stainless-steel wool. This process was developed in the early 1950's by Zadra and others (1952). Stripping times ranged from 24 to 48 hours, as originally practiced. These times were quite long, consuming more chemicals and requiring more carbon in the circuit. In recent years, the U.S. Bureau of Mines and the Anglo-American Research Laboratory have developed pressure stripping of gold from carbon, which requires only 6 to 8 hours. Other improvements in the Zadra technique include the design of advanced electrowinning cells.

Heap Leaching

During the last decade, heap leaching of gold and silver ores has evolved into an extremely efficient method of treating small deposits once considered uneconomic; heap leaching as a mineral technology, however, has been practiced for centuries. As early as the mid-16th century, some mines in Hungary were recycling copper-bearing solution through waste heaps. By the 18th century, large-scale heap leaching was practiced by the Rio Tinto Company in Spain to recover copper from cupreous pyrites. By 1900 these leaching operations were employing such techniques as leach/rest cycles to maximize copper recovery (Taylor and Whelan, 1942).

As mentioned earlier, heap leaching of precious metals was commercially developed in the late 1960's. Improvements in heap-leaching performance and efficiency have continued to emerge in the areas of feed preparation (agglomeration), heap design and construction, solution distribution, and metal recovery.

To be amenable to heap leaching, a gold-bearing rock should be competent, porous, and relatively cyanide free and should contain clean, fine-grained gold particles (Potter and Salisbury, 1974). It is also essential that good aeration and uniform solution contact be maintained. These same factors influence the heap leaching of silver ores.

Since precious-metal ore bodies vary significantly in geology, mineralogy, and metallurgy, it is difficult to generalize about flow-sheet design. The layout of a typical heap-leaching operation is depicted in Figure 4. Like other solution-mining methods, heap leaching is sensitive to site-specific factors. These factors include topography and space, climatic conditions, availability of pad construction materials (i.e., clays), environmental restrictions, and water. Because of its intrinsic simplicity and flexibility, heap leaching is ideally suited to deal with these factors.

Leaching Methods

There are basically two variations of the heap-leaching method that are used on a commercial scale. The first approach is based on the leaching of run-of-mine ore. Long leaching cycles and low-grade ores are usually associated with this variation. The second approach, which involves the leaching of crushed ore, normally requires shorter leaching cycles. High-grade deposits generally justify the increased cost of crushing and are often expressly treated to maximize gold and silver recovery by increasing the exposure of gold and silver to the leaching solution.

Heap-leaching operations that use crushing typically leach ore crushed to 20 millimeters (mm), and sometimes as fine as 6 mm. The leach cycle for this type of operation usually takes a few weeks to several months. Most ores that do not contain excessive amounts of clay will exhibit good permeability down to ore sizes of approximately 10 mm. Feeds below this size or those that contain high proportions of clay can be treated by agglomerating techniques that stabilize fine clay particles. Run-of-mine feed sizes are those produced by the mining operation (blasting or ripping) and may typically contain 150-mm rocks, but may also include some boulders. The leach cycle for run-of-mine uncrushed ore frequently takes months or years.

The cycle commences when ore is delivered to specially prepared, impermeable drainage pads. The leach pad serves two important functions: to protect the environment and to collect and eliminate loss

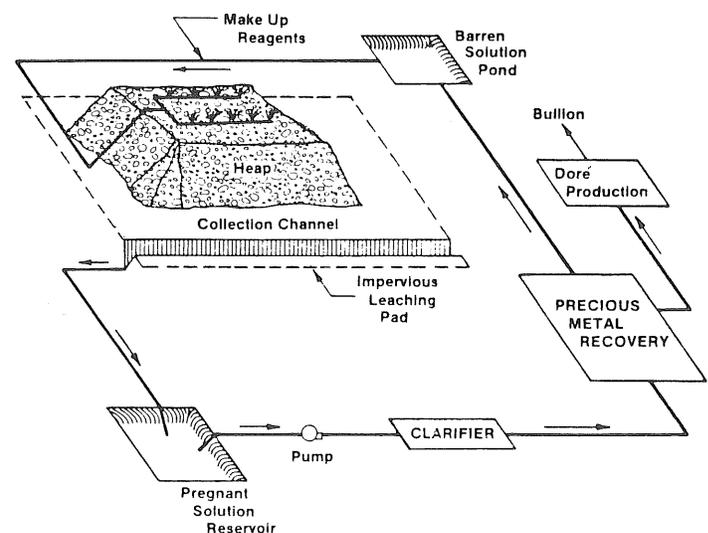


Figure 4. General layout of a heap-leaching operation. In addition to the main leaching circuit, which is described in the text, the figure shows the ancillary operations of doré production and reagent makeup. Doré production involves the smelting and refining of steel wool and zinc precipitates to produce bullion. Reagent makeup relates to the addition of chemicals to control cyanide concentration, pH, and scaling problems.

of pregnant solution, the solution that is saturated with the dissolved metal. Several types of materials are used to construct leach pads, including both natural and manmade materials such as synthetic membranes and geotextile fabrics. Van Zyl (1984) has listed the criteria that pad materials must satisfy: pad-permeability requirements (environmental restrictions), cost constraints, pad-construction considerations, and heap-construction factors. Single-use pads are often constructed from clay or plastic liners, whereas multiuse pads, which are used for more than one leaching cycle, are best made from asphalt or reinforced concrete. In all cases, pad construction must entail careful preparation of the base and subbase layers. In single-use pads, it is common to cover the pad area with a network of perforated pipes to aid drainage and to collect pregnant leach solution. These pipes are normally protected by a layer of coarse gravel.

There are several techniques for placing ore on the leaching pad. Chamberlin (1981) discussed heap-construction methods to maximize permeability and leaching efficiency. Some techniques used to build heaps include haulage trucks and dozers to spread the ore, front-end loaders, conveyor-stackers, and movable bridge-conveyor distribution units.

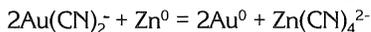
Solution distribution is of special importance in every heap-leaching operation. Leach solutions can be applied to the surface of heaps by a variety of methods such as ponding/flooding, trickle systems, multiple low-pressure sprinklers, single high-pressure sprinklers, and subsurface injection. The most popular systems used in gold-and-silver heap leaching are the impulse sprinkler and the wobbler-type sprinkler. These types of sprays provide uniform solution coverage of the heap surface. Solution application rate is also a critical factor in heap leaching. For typical heap-leaching operations, the maximum effective application rate that can be used without causing channeling and short circuiting of solution is about 4 cm/hr (1 gal/ft²/hr). Higher application rates restrict the movement of oxygen through the heap, dilute the pregnant-solution grade, and increase pumping costs. In general, solution-application rates for heap leaching range between 0.8 and 1.2 cm/hr (0.2 and 0.3 gal/ft²/hr).

Solutions migrate downward through the heap under free-flow conditions (gravity). The percolating solutions dissolve gold and silver as they contact the ore minerals. Gold and silver occur mainly along fracture surfaces in oxidized ores. Values exposed by crushing are readily accessible to the lixiviant and are recovered by simple surface flushing. Leaching solution can also penetrate particle fractures by capillary action; in this domain, long-range diffusion must occur. The pregnant leach solution is collected on the pad and drains to a collection system, which delivers it to a pregnant-solution reservoir. From this reservoir, the solution is pumped to a precious-metal recovery circuit.

Gold and Silver Recovery

There are two primary commercial methods of recovering gold and silver from alkaline cyanide heap-leach solutions: zinc-dust (Merrill-Crowe) precipitation and adsorption by activated carbon. The choice between carbon adsorption and zinc precipitation depends on several factors including solution concentration, solution volume, and solution clarity. Potter (1981) concluded that large volumes of low-grade solutions, mainly containing gold, are most economically treated by carbon adsorption, whereas small flows of relatively rich solutions or solutions containing large quantities of silver should be treated by zinc-dust precipitation. The feed solutions to a carbon-adsorption circuit do not have to be clarified. For optimal efficiency of zinc precipitations, however, it is essential that feed solutions be clarified.

Merrill-Crowe zinc-dust precipitation, as noted earlier, is a very mature and well-established technology. The basic process consists of solution clarification, deaeration, precious-metal precipitation, and precipitate filtration. As stated earlier, cementation of gold onto a metallic zinc surface is represented by the following reaction:



A similar reaction can be written to express the precipitation of silver. Based on the stoichiometry of this reaction, the theoretical zinc requirement for gold precipitation is equivalent to 0.17 grams of zinc

per gram of precipitated gold. Actual zinc consumption in practice is much higher than this, ranging from 10 to 30 grams of zinc per gram of precipitated gold for dilute heap-leach solutions. The difference between actual and theoretical ratios is attributed to the presence of impurities and dissolved oxygen.

Zinc precipitation is the preferred process for silver ores because of the high silver concentrations and poor silver-loading characteristics of carbon. Zinc-dust precipitation is especially attractive for small volumes of solution because they can be processed in modular Merrill-Crowe units.

A continuous multistage carbon-adsorption circuit is an efficient way of recovering gold and silver from high-volume, low-grade, heap-leach solutions. The standard design involves pumping pregnant leach solution countercurrently to activated carbon in a series of five or more columns. Carbon in the size range of 16 x 30 mesh is fluidized by the upward flow of solution and is advanced through the circuit to achieve loading in the range of 3,430 to 6,860 grams per metric ton (100 to 200 ounces per short ton). Carbon loadings in excess of this range are generally avoided because of gold losses to the barren solution. Loadings lower than these values would require advancing the carbon more frequently. This additional handling could result in a higher rate of carbon attrition and an attendant gold loss with fine carbon.

Loaded carbon is advanced from the first-stage adsorption circuit to stripping. The popular stripping methods involve variations of hot, atmospheric sodium hydroxide (NaOH) and sodium cyanide (NaCN), pressurized NaOH and NaCN, and alcohol stripping. Gold and silver are usually recovered from the rich strip solution by electrowinning onto steel-wool cathodes.

In time, surface sites on carbon are contaminated with organic materials and other impurities, and pores are blocked by precipitated salts (calcium carbonate). It is necessary to periodically reactivate the carbon to remove these contaminants and to restore the intrinsic chemical activity of the carbon. Reactivation requires a series of chemical and thermal treatments: acid washing to remove surface deposits, and calcining to 750°C by indirect means to activate the surface site. After screening to remove fines, the regenerated carbon is returned to the final stage of the adsorption circuit.

SUMMARY

The extractive metallurgy of gold and silver from ores is primarily based on cyanidation practice. Cyanidation has been practiced commercially for a century. The chemistry of leaching gold and silver in cyanide solutions is elegant and the process of metal recovery by this approach is very efficient. Unlike stronger lixivants, dilute cyanide solutions exhibit a high degree of selectivity in the dissolution of gold and silver from their ores. Another attractive feature of cyanide is that gold and silver can be conveniently recovered from solution by several methods.

Heap leaching using the principles of cyanidation has recently developed into an important alternative for treating gold and silver ores. Compared to other techniques, heap leaching is a simple process. Though it is especially appropriate for treating large, low-grade, disseminated deposits, heap leaching is also an expedient way of extracting precious-metal values from small, shallow deposits.

New leaching technologies are being developed in the United States and abroad. There is considerable interest in the development of ion-exchange resins for the recovery of gold from cyanide solutions. Resins have the potential of being more selective than carbon, and the design of resin-in-pulp circuits could eliminate such processes as pressure stripping and carbon reactivation. Other emerging technologies include solvent extraction and direct electrowinning from dilute solutions. Alternative lixivants for extracting gold and silver are also being developed; for example, thiourea and thiosulfate have been examined for various gold- and silver-bearing materials.

Heap-leaching technology is continuing to advance. In-situ leaching, however, is another option for extracting gold and silver from their ores. The possibility of in-situ leaching opens up an area of technology with many challenges as well as the potential for considerable rewards.

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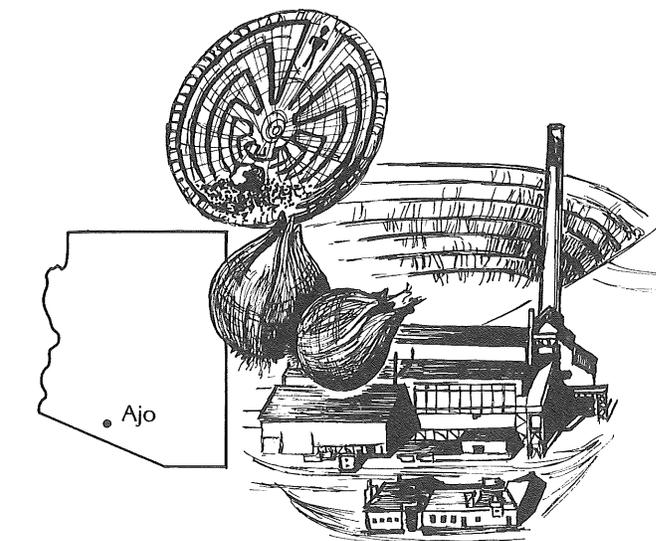
GEOLOGIC PLACE NAMES: AJO

Ajo, Pima County, Arizona. Population 5,650. Pronounced ä'hō. Derived from the Papago word *au'auho*, which means "paint."

A similarity between the sound of the Papago word for this locality and the Spanish word *ajo* for many years led to misapprehension concerning the origin of the name of present-day Ajo. The Papago Indians used *au'auho* in connection with the mines at Ajo because the ores were a source of red paint which the Papagos used to decorate themselves. This was so noted by one of the earliest American travelers in the region. Nevertheless, the fact that the Mexican miners pronounced the word without the double pronunciation of the *au* of the Papago resulted in a word that sounded much like *ajo*. This, added to the fact that the Ajo lily (the root of which looks and tastes much like a spring onion) grows abundantly in this area, led to the belief that the locality was named Ajo because of the wild lilies.

The first American citizen to notice the mining possibilities in the region was Capt. Peter R. Brady, who was with the surveying party for the Thirty-Second Parallel railroad in 1853. When the party broke up in San Francisco, Brady was influential in organizing a group of men to explore mining possibilities at Ajo. This group soon had shipped out all the rich, easily smelted ores from Ajo's mines. Despite the fact that the remaining ores were unquestionably rich, there was no satisfactory way to reduce them economically, and for many years the treasure in copper at the Ajo mines remained relatively untouched. The hills with their rich exposed ores were a speculator's paradise.

In 1910 the population—including Mexicans, Indians, and American citizens—was fifty people. The main business among these people was grazing cattle. Lack of water was a serious problem and poverty [was] rampant. In February 1911, there were only four Americans at what later came to be known as Old Ajo. However, Ajo was on the verge of becoming a boom town. With the



discovery of a leaching process which made it possible to work the ores efficiently and inexpensively, Ajo entered into a prosperous period. The New Cornelia Copper Company was organized, a smelter built, and wells dug. From three to five thousand people were employed by the mines.

The battle between the few old timers in Old Ajo and the powerful mining company was soon joined. The old town of Ajo was far too close to huge deposits of low grade ore which the copper company wanted to develop. The company located its own town a mile to the north, which it proposed to call Cornelia. However, nearly all of Old Ajo burned down, and the name Ajo became attached to the new town.

—Excerpted from Granger, B. H., 1960, Will C. Barnes' Arizona place names: University of Arizona Press, p. 257-258.