Gold – An Historical Introduction

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Chapter 1

Gold — An Historical Introduction

F. Habashi

Department of Mining, Metallurgical, and Materials Engineering, Laval University, Québec City, QC, Canada
e-mail: Fathi.Habashi@arul.ulaval.ca

1. GOLD IN ANCIENT EGYPT

From ancient times to the present day, gold has been valued by humans. Egypt was the principal gold-producing country in ancient times. Coptos, the present Quft on the eastern side of the River Nile, was the chief town of the Nomos of Harawi and was once politically important. In the eleventh dynasty (2133–1991 BC) it was overshadowed by Thebes, 50 km to the south, which became the capital of the Middle Kingdom (2133 BC) of ancient Egypt, the present-day Luxor (Figure 1.1).

Coptos was the world's first gold boom town. It was there in the Wadi Hammamat that alluvial gold had been washed down from the gold-bearing veins found later in the granite hills above. The world's oldest mine map (Figure 1.2), which is made on papyrus and held at the Turin Museum (Museo Egizio di Torino) in Italy, shows the huts of the Egyptian miners, the road to the gold mines, and the hills within which the gold veins occurred. The map is 0.4 × 2.8 m; it is believed that it
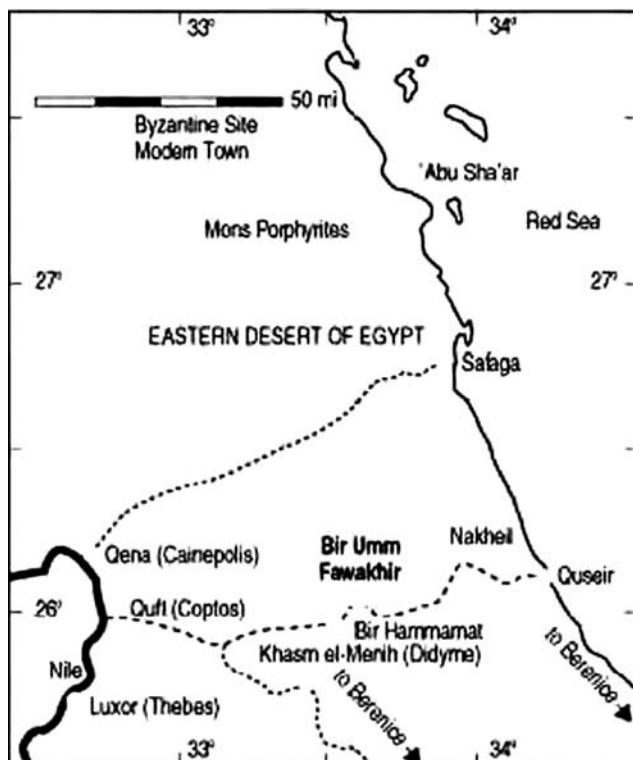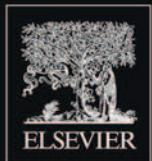

FIGURE 1.1   Location of Coptos in Upper Egypt, the most ancient gold-mining center.

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FIGURE 1.2 The world's oldest mine map.

was made during the reign of Ramses IV (1162−1156 BC). The scroll was found in a tomb near Thebes shortly before 1824 when it appeared in Turin. Ruins of these huts can be seen today at Fawakhir in the Eastern Desert.

In the old Egyptian language, the word *nubia* signifies "gold." By 1300 BC, underground mining of vein gold was well established in Nubia under Egyptian control. There were more than 100 mines in the area. A series of forts were built to protect the flow of Nubian gold along the rich trade routes. Egypt became the dominant power in the Middle East, having the greatest gold-filled treasury in the ancient world.

The ancient Egyptians did not have an important port on the Mediterranean and all their trade was through the Red Sea. Coptos was at the starting point of the two great routes leading to the coast of the Red Sea, one toward the port of Tââ ou (Myos Hormos) and the other more southerly, toward the port of Shashirit (Berenice). Under the pharaohs, the whole trade of southern Egypt with the Red Sea passed over these two roads. Under the Ptolemys, and in Roman and Byzantine times, merchants followed the same roads for purposes of barter with the coasts of Zanzibar, Southern Arabia, India, and the Far East. This place and the surrounding area were known for the richness of its gold mines and semiprecious stones. A temple was built there by Tahutmes III, who ruled from 1503 to 1450 BC and was co-regent with Queen Hatshepsut for 21 years. The area that it occupied was about twice as large as his temple at Madinet Habu in Luxor.

The Egyptians were the first to treat gold-bearing rocks. This is well documented on wall paintings, an example of which is given in Figure 1.3.

FIGURE 1.3 Ancient Egyptian wall painting dating from about 1450 BC in the tomb of Rekhmire, vizier to Thothmes III at Thebes, showing metal workers casting molten gold in the molds.

2. EARLY GOLD-MINING CENTERS

Herodotus (484−425 BC) refers to several great gold-mining centers in Asia Minor, and Strabo (63 BC) mentions gold mining in many different places. Pliny (23−79 AD) gives many details of ancient placer mining, which was extensive. The Romans had little of the metal in their own regions, but their military expeditions brought them major amounts in the form of booty. They also exploited the mineral wealth of the countries they had conquered, especially Spain, where up to 40,000 slaves were employed in mining. The state's accumulation of gold bars and coins was immense, but during the barbarian invasions and the collapse of the empire this gold was scattered, and gold mining languished in the Middle Ages.

Following the discovery of America at the end of the fifteenth century, the Spaniards transferred considerable amounts of gold from the New World to Europe. Although the conquistadors found a highly developed mining industry in Central America, their efforts to increase gold production were largely unsuccessful because most of the finds consisted of silver. Colombia's Muisca Indians, who dwelt in the highlands near present-day Bogota, installed their kings by dusting their naked bodies with gold and then washing them in nearby Lake. To the conquistadores, this wealthy chieftain became known as El Dorado — a Spanish word meaning "the Gilded Man" (Figure 1.4).

It was not until the discovery of deposits in Brazil, in 1691, that there was a noticeable increase in world gold production. Since about 1750, gold has been mined on a major scale on the eastern slopes of the Ural Mountains. In 1840, alluvial gold was discovered in Siberia and then at Coloma, California, in January 1848, a few days before the signing of a treaty between Mexico and the United States to end their hostilities. California was thus ceded by Mexico after a discovery that was apparently not known to either government. Coloma is about 50 km southeast of Sacramento on the slopes of the Sierra Nevada.

The discovery of gold in British Columbia was an epoch-making event. In the late 1850s, alluvial gold was found along the Thompson River, and in 1858 the famous Fraser River rush took place. Extraordinarily rich deposits were discovered in 1860 on Williams and Lightning creeks. For many years, British Columbia was the leading gold producer among the Canadian provinces and territories, but with the discovery of the Kirkland lake deposits in 1911, and the opening up of the Porcupine district in 1912, Ontario held first place ever since.

Gold deposits were also found in Eastern Australia (1851), Nevada (1859), Colorado (1875), Alaska (1886), New Zealand and Western Australia (1892), and Western Canada (1896). However, these deposits soon lost much of their importance. The strongest impetus was given to gold production through the discovery of the goldfields of the Witwatersrand in South Africa in 1885. South African gold soon occupied a commanding position in the world market. Production grew continuously except for a short interruption by the Boer War (1899−1902). Gold mining in Ghana (Gold Coast) began to play a modest role in the twentieth century, although the deposits were known in the Middle Age.

FIGURE 1.4   Eldorado.

3. GOLD AND ALCHEMY

To the medieval alchemists, gold has been regarded as a metal of perfection. They identified it with the sun by virtue of its bright yellow color, and it was given the symbol of a circle with a dot in the center. Gold was so precious that from earliest times man has left no stone unturned in searching for it in nature. It is not surprising, therefore, that humans should have sought to convert other metals into gold. The agent for transmuting base metals into gold was known as the *philosopher's stone*. In addition to its transmutatory power, the stone was believed to have the properties of a universal medicine for longevity and immortality. The attempts to transmute base metals into gold and to prolong life indefinitely contributed much to modern chemistry in the form of new chemical substances and laboratory techniques. Alchemical principles have also found their way into modern psychological ideas, notably by the Swiss psychiatrist Carl Jung (1875−1961).

Ancient Egypt is considered the birthplace of alchemy. Zosimos (ca. 350−420), who taught in Alexandria, is the earliest writer known to have practiced alchemy. Because of their lack of knowledge of the composition of common substances some alchemists viewed many ordinary chemical reactions as transmutations. For example, the deposition of copper on iron metal placed in a solution of blue vitriol (copper sulfate), a reaction known since Roman times, was assumed by some to be a transmutation of iron into copper until the late Renaissance. Similarly, the mineral galena [PbS], on heating, liberates sulfur dioxide and appears to be transformed into silver, which is often present as an impurity in galena.

Through the centuries, gold-making has been alternately encouraged and banned by monarchs and the Church. For example, Diocletian (AD 245−316), Emperor of Rome from 284 to 313, fearing that the Egyptians (Egypt was then under the domination of the Roman Empire) might become powerful through their knowledge of alchemy, ordered in AD 296 that all books and manuscripts "which treated the art of making gold and silver" to be burned. Consequently, only very few Egyptian alchemical works have been preserved. During medieval times, European kings and princes supported alchemists at their courts, hoping to acquire wealth through their work.

4. USES OF GOLD

Humans have valued gold for its lustrous color and its resistance to tarnishing, so it was used for special decorative ornaments and jewelry. The veneration reserved for gold by the ancients has led to its use for many centuries for religious artifacts. Gold was often cast in the form of idols or hammered into foil to make masks for the dead. Gold was used for barter and subsequently for coinage. By the eighth century BC, small, irregular bars of impure gold were being exchanged as currency in Asia Minor, and by the fifth century BC, gold coins were being used freely. Even today, the majority of the gold produced is turned into gold bars (i.e., bullion that acts as the standard for the world's monetary systems), and they are used in international trade and exchange.

Gold differs from most other metals in that the majority of the metal that has ever been mined is still in existence. The total amount of gold now in existence is estimated to amount to around 125,000 tons. If all of this gold could be collected together, it would produce a cube with an edge of about 18.6 m. Gold has always been a symbol of immortality, and this was also a common subject in mythology. For example, King Midas requested that everything that he touched be turned into gold. When this blessing had turned out to be a curse in disguise, Midas prayed to Bacchus to take back his gift. The myth of the Golden Fleece has been subject to various interpretations. The legend of El Dorado, the Indian ruler who plastered his body with gold dust in festivals, led to the rapid conquest of South America. In an ancient Sanskrit text, there is a reference to *Pipilika* gold (the Sanskrit word for "ants"), which refers to gold particles that are collected by ants and then presented to the king in a special ceremony. In *Thousand and One Nights*, there are numerous references to palaces being built using bricks made of gold.

Gold ornaments have been found in Egyptian tombs of the prehistoric Stone Age, and the Egyptian goldsmiths of the earliest dynasties were skillful artisans. Today, gold used in jewelry sums to about 2000 tons annually worldwide, which represents 75% of the total consumption. Gold in jewelry serves different purposes in different parts of the world. In the West, it has a primarily decorative role; it is not normally regarded as an investment and consequently the gold used for this purpose is less pure. In the East, exactly the reverse is true; gold has a strongly monetary role there, is typically high caratage (22 carat − 91.7% pure gold, or 24 carat − 100% gold), and is bought and stored as an investment. It is typically worn by women and so has an ornamental role as well; the presence of large amounts of gold ornaments in Oriental bazaars attests to this fact. The American Indians before the Spanish conquest used gold for ornaments but also as offerings in religious ceremonies, or to be buried with the deceased.

The extreme ductility of the metal is shown by the fact that 1 g can be pulled into a wire 3 km long. The gold threads that were used in embroidery and weaving were made in a variety of ways. Generally speaking, they consisted of metal

strips that were used either directly or, more often, in the production of composite threads, in which the metal strip was wound around a fibrous core of silk, linen, cotton, or other yarns. Wire was also used directly or for winding around such cores.

4.1 Gilding

Because of its occurrence in nature in minute amounts, gold was an expensive metal. It was not necessary to have articles made of solid gold since it was possible to prepare gold in thin foils and cover the object completely with them so that they appear as if they were made of gold. Gilding is the art of applying and permanently attaching gold leaf or gold dust to surfaces of wood, stone, and metals. Gold is the most malleable of metals and can be reduced to extremely thin leaves by hammering. Such leaves sometimes do not exceed 0.1 mm (1000 Å) in thickness, and they transmit green light. One gram of gold can be made to cover nearly 1 m^2 of surface. Many objects gilded by the Egyptians have survived to this day; the treasure of Tutankhamen's tomb is one example of their skill (Figure 1.5). The Egyptians appear to have been the earliest practitioners of the art of making thin gold foil, and the illustrations on tombs at Saqqara and Thebes show their goldbeaters working together with gold founders and goldsmiths (Figure 1.6).

FIGURE 1.5   Thin gold foil covering a wooden statue from an ancient Egyptian tomb.

FIGURE 1.6   An ancient Egyptian wall painting showing a worker pounding on gold to prepare a foil.

Gold foil was first used for gilding; when the technology was developed, the foil became thinner and thinner and was referred to as gold leaf. The invention of gold leaf was impossible before the perfection of methods for the purification of gold, as only pure gold or gold-rich alloys free from certain impurities can be beaten out to produce the thinnest leaf. Indeed, the methods of beating gold have not changed significantly since the days of the early Egyptians. The rounded stone has been replaced by a cast iron hammer with a wooden shaft and some machinery has been introduced to reduce the effort of beating by hand but, in essence, the process remains the same. The ability to make gold in very thin leaves made it more economical to use for gilding large objects such as statues, ceilings, columns, domes of churches, etc., with the minimum consumption of gold. Gold leaf is insufficiently strong to support its own mass and so new methods of attaching it to the substrate had to be developed. One obvious way was to use an adhesive, and this method is still used today for the gilding of wood and stone and for the decoration of leather book-binding.

4.1.1 Gilding of Metals

When the gold leaf is applied on metal, the adhesion of the gold is enhanced by the application of heat to promote interdiffusion with the underlying metal. To cover a large metallic object such as the dome of a church or a statue standing in the street with a very thin layer of gold that would resist exposure to rain and wind, mercury use was made of as a sticking medium. Copper, not bronze or brass, was usually the metal of choice, although it is more difficult to cast than the alloys. The reason is that the alloying elements tin, zinc, and lead interfere with the gilding process because these metals have a high solubility in mercury and thus result in a defective layer. Although gilding with mercury was a rare and costly process in the first century AD, it had become the standard method of gilding by the third or fourth centuries and it remained unchallenged throughout history.

Two processes were developed to gild a copper substrate. In the cold process, mercury is rubbed on the clean copper surface until it has a mirror-like finish. Some copper dissolves in the mercury and forms a thin layer of copper amalgam. Any excess mercury is mechanically removed. Gold leaf is then pressed upon the surface. It bonds with the copper-amalgam very firmly. More than one layer of gold leaf is usually necessary to obtain the desired color. The hot process was developed at a later date to gild copper alloys and overcome the difficulty of casting unalloyed copper. In this method, gold leaf is dissolved in mercury; this takes place very rapidly. The amalgam is applied on the copper substrate to the desired thickness. The object is then heated to expel the mercury, leaving a tenacious gold layer. The poisonous fumes emitted during the process were a health hazard not only to the workers but also to those living in the neighborhood of a gilding workshop. St. Isaac's cathedral in St. Petersburg was constructed in the 40-year period 1818−1858 with a gilded dome 21.83 m in diameter (Figure 1.7).

4.1.2 Gilding of Glass and Porcelain

The gilding of glass, porcelain, and pottery, ranging from the simple edging on a plate to the elaborately decorated vase with richly gilt panels, has always been a prominent feature in industry. The Chinese applied gold leaf over a layer of

FIGURE 1.7 St. Isaac's cathedral in St. Petersburg was constructed in 1818−1858 with a gilded dome 21.83 m in diameter.

FIGURE 1.8   Museum pieces of glass colored with Purple of Cassius.

linseed oil and litharge [PbO], or with egg white or shellac; however, these gilded layers were not durable. Other workers used gold leaf ground up in honey, washed, dried, and applied with a flux; in these cases; however, the product was expensive because the gold layer was thick. The German chemist Johann Kunckel (1630–1703) discovered the precipitation of gold powder by the addition of a solution of ferrous sulfate to a solution of gold in *aqua regia*. This was published in his book *Laboratoria Chymica*, which appeared in 1716, 13 years after his death. The precipitate, separated by decantation and then dried, was thoroughly mixed with a finely ground lead-silicate flux and applied to the ware, then fixed by heating in a kiln. In 1827, a new gilding process was discovered in the Meissen factory near Leipzig by Heinrich Kühn. The process consisted of a solution of gold chloride in *balsam of sulfur*, an oily substance obtained by reacting sulfur with turpentine. This medium, which is of somewhat unknown chemical composition, had been known for many years. Kühn was thus able to produce a liquid preparation of an organo-gold compound that, on firing at a relatively low temperature, yielded a bright and shining gold that needed no polishing.

4.2 Gold in the Glass Industry

In the 1650s, the German chemist Andreas Cassius (1605–1673) discovered a purple pigment that can be used in coloring glass and porcelain, yielding an exceptionally beautiful purple color (Figure 1.8). The color was known as *Purple of Cassius*. It was prepared by adding a solution of stannous chloride to a dilute gold chloride solution and was applied in the most famous glass and porcelain factories of Europe in Meissen and Sèvre. The nature and constitution of *Purple of Cassius* presented scientists with a problem that was tackled throughout the whole of the nineteenth century by some of the most distinguished chemists of the time. Not until the turn of the century was the true nature of this pigment elucidated. Richard Zsigmondy (1865–1929), a Viennese chemist who had spent some years studying gold colors and had joined the Schott Glassworks in Jena in 1897, developed the ultramicroscope for the examination of colloids. He showed conclusively that the *Purple of Cassius* consisted of very finely divided gold with stannic oxide. For this investigation, he was awarded the Nobel Prize in Chemistry in 1925.

In modern times, gold films deposited on glass via thermal evaporation are superior to other metals for reflectivity in the infrared wavelength range. Such films applied to glass windows for offices permit good vision by substantially reducing the transmission of infrared energy by reflection rather than by absorption. The cost of production is very low, and the economy in energy saving due to cutting down on heating in winter or air conditioning in summer is appreciable. Many modern office buildings are now constructed using glass windows with a gold coating about 0.01 mm thick. In the deposition process, gold is heated to about 1390 °C and at a low pressure. The vaporized gold atoms move in nearly straight lines from the source to the surface to be coated.

4.3 Gold Masks

From ancient times, funeral gold masks were used to cover faces of the dead (Figures 1.9–1.11).

5. OCCURRENCE OF GOLD

Most gold occurs as native metal, nearly all alloyed with various amounts of silver as the mineral electrum, but not with copper. Certain minerals are characteristically associated with gold, and the most important are pyrite [FeS$_2$], galena [PbS],
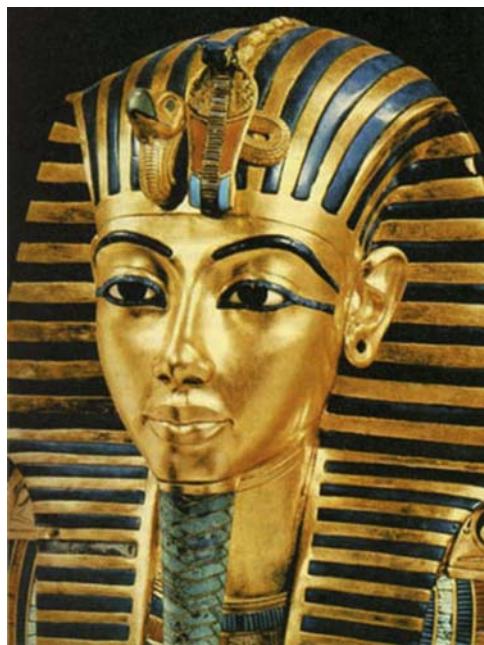
FIGURE 1.9 Ancient Egyptian gold mask.

FIGURE 1.10 Ancient Greek gold mask.

zincblende [ZnS], arsenopyrite [FeAsS], stibnite [Sb_2S_3], pyrrhotite [$Fe_{(1-x)}S$], and chalcopyrite [$CuFeS_2$]. Various selenium minerals and magnetite [Fe_3O_4] may also be present. In Witwatersrand, South Africa, uraninite [UO_2] and, to a lesser extent, thucholite [a varying mixture of hydrocarbons, uraninite, and sulfides] are associated with the gold ore; uranium was recovered as a byproduct of gold milling. Carbonaceous matter is associated with some gold ores. Gold has affinity for tellurium, and it forms two main telluride minerals: calaverite [$AuTe_2$] and sylvanite [$(Ag,Au)Te_2$]. It was in these minerals that tellurium was first discovered. On the other hand, it occurs with palladium as porpezite (Au containing 5−10% Pd) and with rhodium as resinrhodite [Au, Rh]. In placer deposits, it may be present as minute particles or large nuggets. In certain ores known as *refractory* ores, gold is associated with sulfide minerals in an extremely finely divided state.
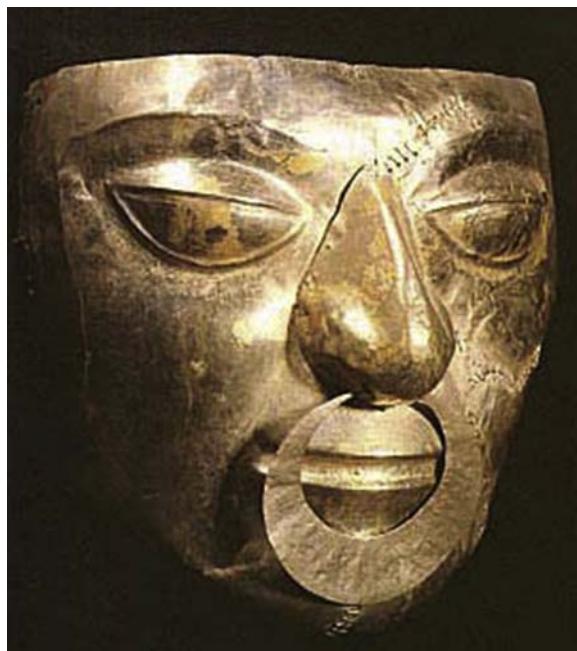
FIGURE 1.11 Inca gold mask.

Ouro Preto, or black gold, is the name of an old town in Brazil about 400 km north of Rio de Janeiro. It was near there that gold was first discovered in Brazil in 1691 and resulted in the Brazilian gold rush. The Brazilian gold was black in color, hence the name *ouro preto*. In these deposits, gold occurred as fine particles covered with a thin black coating. In 1876, the Brazilian emperor Dom Pedro II (1825−1891) inaugurated the first School of Mines in Brazil in Ouro Preto.

6. PROCESSING OF GOLD ORES

6.1 Gold Panning

Gold played a central role in the development of metallurgy. At one time, however, there was no need for any chemical or metallurgical knowledge to recover gold; it occurred in nature in the native state and simple panning was enough to collect the glittering particles and sometimes nuggets. Because gold has such a high density (19.3 g/cm^3), panning can be used to easily separate it from the sand and gravel with which it is associated. In this method, the material is mixed with water in a shallow pan, and by careful swirling the impurities can be washed away, leaving the gold behind. However, this requires great patience and hard work. Gold collected by panning or from rich veins was melted to recover it as relatively pure metal. With earlier primitive methods, only the easily accessible, pure gold was obtained. As machinery was developed and extraction processes perfected, mining was extended to less-rich deposits. For low-grade deposits, other methods were developed.

6.2 Amalgamation

Although mercury was known to the ancient Chinese and Hindus and has been found in Egyptian tombs dating back to 1600 BC, it was extracted and used only in the Roman times. Mercury ores occur in abundance in Italy and Spain. The Roman writer Dioscorides mentioned its preparation from cinnabar. Pliny gave a method of purifying mercury by squeezing it through leather. He described the amalgamation process and introduced the term *amalgam*, from *malagma* (meaning "I soften," because mercury softens gold). An alchemical representation of the amalgamation of gold is shown in Figure 1.12.

Although the Romans were acquainted with the fact that mercury dissolves gold and silver, it does not appear that they applied this knowledge to the extraction of these metals from their ores. Vanoccio Biringuccio mentioned the amalgamation of ores in his book *De la Pirotechnia*, published in 1540, as does Georgius Agricola in his book *De Re Metallica*,

FIGURE 1.12 Alchemical representation of the amalgamation of gold: mercury conquers gold, the king of metals.

published in 1556. Mercury dissolves gold rapidly at ambient temperatures; an amalgam containing 10% gold is liquid, that containing 12.5% gold is pasty, and that containing 15% gold is solid.

Stamp mills (Figure 1.13) were closely associated with the amalgamation process. A stamp mill is a grinding machine where the grinding action takes place by falling weights. The ore from the crushers varying in size from 10 to 60 mm is fed with water in the stamp mill. A stamp is a heavy iron pestle 3−5 m long and about 7 cm in diameter carrying a weight 200−400 kg. The stamp is raised by a cam that is keyed on to a horizontal revolving shaft and allowed to fall by its own weight. Mortars are made of cast iron about 1.2 m long, 1.2 m high and 0.3 m wide. The height of the drop of the stamp varies between 30 and 50 cm and the number of drops per minute varies from 30 to 100. Five stamps are usually present in one mortar.
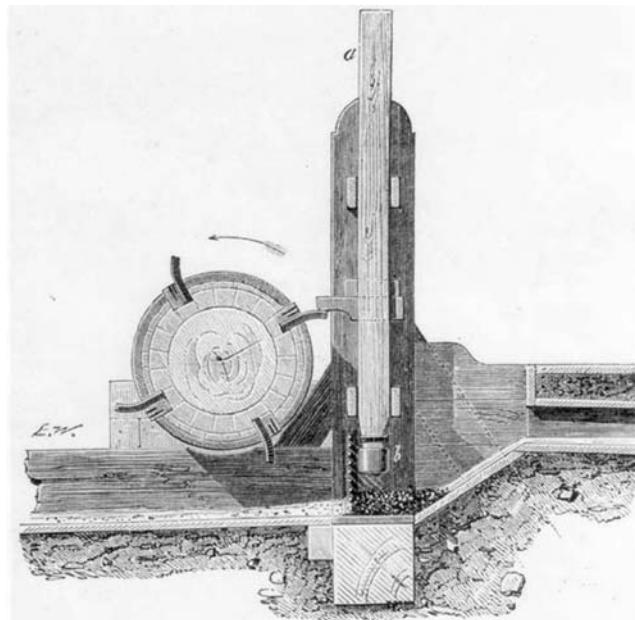

FIGURE 1.13 Stamp mill used for crushing gold ores before amalgamation.
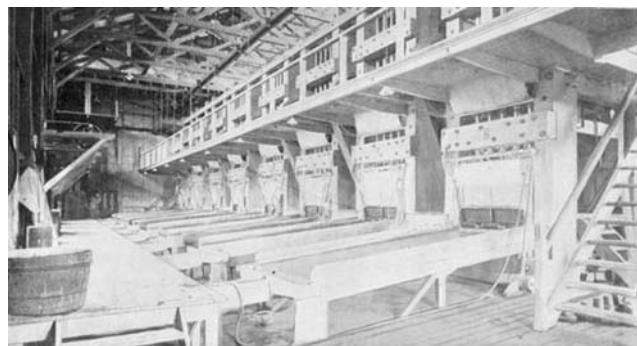
FIGURE 1.14 Amalgamation table.

Fine powdered ore slurry containing native gold and silver is then passed over copper plates amalgamated with a thin layer of mercury onto which the noble metals adhere (Figure 1.14). Depending on the gold content of the ore, the amalgam is scraped once or twice a day and a fresh mercury surface is exposed. About 3–10 t of ore per square meter of mercury surface is usually used (i.e., a mercury consumption of about 30–50 g/t ore). The amalgam is washed with water to remove any attached gangue particles, then pressed to remove excess mercury. An amalgam containing 40–50% gold can be obtained. It is charged on trays and heated in a horizontal retort to distil the mercury. A gold sponge is obtained, which is then melted with fluxes and then cast as a bullion. Gold bullion contains some silver, copper, and other metals, which are separated at mints or private refineries.

The amalgamation process was used extensively for the recovery of gold and silver from their ores. In many countries, it is now illegal to use this process because of the toxicity of mercury. Despite this, the process is used on a large scale by numerous small illegal operators in several parts of Africa and by the so-called *garimpos* in the Amazon basin in Brazil. This practice has resulted in the mercury pollution of soil, rivers, and the atmosphere, because the final step of gold recovery is usually done by heating with an oxygen flame in the open air to remove the mercury, a hazardous procedure.

6.3 Chlorination

Gold, the most noble of all metals, was insoluble in all acids and alkalis known at that time. The discovery of *aqua regia* by the Arab alchemist Jabir Ibn Hayyan (720–813 AD) and its ability to dissolve gold introduced a new technology for the extraction of gold from its ores. *Aqua regia*, or royal water (the water that dissolves the king of metals), is a mixture of hydrochloric and nitric acids, neither of which alone can attack gold. An alchemical symbolization of this process is shown in Figure 1.15. In modern terms the action of the mixture is due to chlorine and nitrosyl chloride.

Chlorine was discovered and isolated by the Swedish chemist Carl Wilhelm Scheele (1742–1786) by the action of hydrochloric acid on manganese dioxide in 1774; Scheele also noted that it attacked all known metals. This knowledge was first applied to the recovery of gold from its ores in 1851 by Karl Friedrich Plattner (1800–1858) (Figure 1.16) of Freiberg using aqueous solutions of the gas. Although the concept of the transmutation of metals was abandoned by the chemists of the nineteenth century, metallic iron was used to displace gold from the chloride leach solution. A variation of this technology was the barrel chlorination process, in which chlorine gas was generated by means of bleaching powder and sulfuric acid inside a rotating barrel. In 1863, Plattner's method of chlorination was introduced in gold mines in the United States and shortly afterward in Australia.

6.4 Cyanidation

The cyanide process was based on the fact that dilute cyanide solutions will dissolve gold from its ores and that when the solution is brought into contact with zinc, gold will be precipitated. The cyanide process has been a great help in the extraction of gold at the Witwatersrand deposit because gold occurred in such fine particles that extraction of only 55–65% could be obtained by amalgamation and chlorination. Today about 1 billion tons of ore are treated annually worldwide using cyanide solution to recover gold, representing the largest tonnage of any mineral raw material that is treated chemically.

To understand the factors that led to the discovery of the cyanidation process, it is essential to refer to the activities of chemists during the eighteenth century. Extensive research was under way in the emerging chemistry of the so-called *blue*

FIGURE 1.15 Alchemical depiction of *aqua regia* − the lion eating the sun (gold).

FIGURE 1.16 Karl Friedrich Plattner (1800−1858).

acid and its compounds. Chemists at that time were occupied with a number of blue-colored compounds obtained by heating dried blood with potash [K_2CO_3] and then treating the aqueous extract with iron vitriol [$FeSO_4$]. The precipitate obtained thereby yielded an intense blue pigment. Its accidental discovery was made in Berlin in 1704, by the German alchemist Johann Conrad Dippel (1673−1734) and therefore the pigment became known as *Berlin blue*. In English

literature, it became known as *Prussian blue* to refer to Prussia, the former state of northern Germany. This new blue pigment immediately displaced the naturally occurring ultramarine blue pigment because it was much cheaper. It was the first artificially manufactured pigment, and its discovery opened up a new field of chemistry, the chemistry of cyanogen compounds.

The French chemist Pierre Joseph Macquer (1718−1784) discovered in 1752 that when Berlin blue was boiled with alkali, iron oxide separated out and the remaining solution when concentrated by evaporation yielded yellow crystals, now known as potassium ferrocyanide. In 1782, Scheele heated the blue pigment with dilute sulfuric acid and obtained an inflammable gas that dissolved in water and reacted acidic with litmus paper; he called it *Berlin blue acid* or simply the *blue acid* (*blausäure*), which was also used in Germany during World War II in gas chambers. In 1811, the French chemist Joseph Louis Gay-Lussac (1778−1850) liquefied the gas (boiling point 261 °C) and determined that its composition was HCN. When Berlin blue was heated with nitric acid, a red/violet compound was obtained, which became known as *prussiate* in reference to Prussia. In 1822, Leopold Gmelin (1788−1853) in Germany prepared potassium ferricyanide in the form of deep red prisms, by passing chlorine into a solution of potassium ferrocyanide.

As we know today, blood contains the red pigment hemin, which is an iron chelate containing a porphyrin structure. The building units of this structure are alkylated pyrrol nuclei. On heating with potash, potassium ferrocyanide is formed; this is extracted by water and reacted with iron salt to form ferri-ferrocyanide. When numerous new compounds of the blue acid became known, Greek terminology was introduced to name them. *Kyanos* in Greek means *blue*; hence, the modern term "cyanide" was used for compounds derived from the blue acid. Potassium ferrocyanide became a commercial product around 1825. Production of potassium cyanide followed a few years later. The dissolving action of cyanide solution on metallic gold was known as early as 1783 by Scheele, who experimented with the hydrogen cyanide gas he discovered. The solution obtained by dissolving gold in cyanide solution was used by George Elkington (1801−1865) and his cousin Henry Elkington (1810−1852) in England in 1836 to prepare the bath necessary for electroplating gold.

In 1835, the formation of HCN in blast furnaces became known, and in 1843, the existence of cyanogen compounds in coal gas was discovered (in the 1950s, cyanides were also identified in different forms and at different locations throughout a petrochemical complex). Coal gas was produced in large amounts for heating and illuminating purposes; it was the equivalent of today's electricity. Because of their poisoning action, it was necessary to remove cyanogens; this was accomplished by absorption, using a mixture of ferrous and ferric hydroxides. Many other processes were developed that contributed considerably to an understanding of the chemistry of cyanides, cyanogens, thiocyanates, cyanates, cyanamides, amides, nitrites, guanidines, and other related compounds.

The dissolution reaction was studied by noted chemists of the time, e.g., Prince Bagration in Russia (1844), Franz Elsner in Germany (1846), and Micheal Faraday in England (1857). It remained, however, for John Stewart MacArthur (1856−1920) (Figure 1.17) in Glasgow in 1887 to apply this knowledge to gold ores. When the process was applied industrially, research was initiated in many universities. The most important was that by the German chemist Guido Bodländer (1855−1904) at the University of Breslau (now Wroclaw in Poland) in 1896, whose contribution was twofold:

FIGURE 1.17   John Stewart MacArthur (1856−1920).

he confirmed that oxygen was necessary for the dissolution as claimed by Elsner and Faraday and doubted by MacArthur and he discovered that hydrogen peroxide was formed as an intermediate product during the dissolution of gold. The action of cyanide solution on gold remained a mystery for a long time for three reasons:

- It was difficult to understand why gold, the most noble of all metals, which could not be attacked by any strong acid except hot concentrated *aqua regia*, could be dissolved at room temperature by a very dilute solution (0.01−0.1%) of NaCN or KCN.
- A strong solution of NaCN was found to be no better than a dilute solution, whereas in the case of other metals dissolving in an acid; for example, the more concentrated the acid, the faster the metal is dissolved.
- It was not obvious why oxygen was necessary even though, alone, it has no action on gold.

The mystery was resolved about 60 years after the discovery of the process when it was realized that the dissolution of gold in cyanide solution is an electrochemical process (i.e., similar to a galvanic cell). This has been demonstrated by embedding a small gold sphere in a KCN gel to which air was introduced from one direction. It was found that the gold corroded at the surface far away from the air flow (i.e., an oxygen concentration cell was formed around the sphere); the surface less exposed to oxygen acted as anode while the surface in direct contact with oxygen acted as cathode. Thus, oxygen picks up electrons from the gold surface while gold ions enter the solution and are rapidly complexed by the cyanide ions.

By analogy with the "transmutation" of iron into copper, MacArthur used zinc shavings to precipitate gold from the cyanide solution. The process became more efficient when zinc dust was introduced by Charles W. Merrill (1869−1956) (Figure 1.18) in 1904 and further improved when Thomas B. Crowe removed air from the solution by passing it through a vacuum tank before introducing the zinc. This new technique, developed in the United States, later became known as the Merrill−Crowe process.

Activated charcoal was first applied in metallurgy for the recovery of gold by the chlorination process. When this process was displaced by cyanidation, charcoal was also used for the new process because large stockpiles of activated charcoal from gas masks were available after World War I when poisonous gas was used in combat and the charcoal in the masks no longer needed. In both cases gold was recovered from the gold-laden carbon by burning the carbon to ashes and melting to bullion, which was a wasteful process. This disadvantage, coupled with the major advances that were made in the technology of gold recovery by precipitation with zinc dust at that time, led to abandoning the process using activated carbon.

In the early 1950s, however, interest in the metallurgical application of activated carbon was revived when a procedure was developed by John B. Zadra (1898−1967) (Figure 1.19) at US Bureau of Mines for the elution and electrowinning of gold and silver adsorbed on carbon granules, which allowed re-use of the carbon, and the utilization of the process as a concentration purification step. Practical developments in the 1980s led to a widespread application of the carbon-in-pulp

FIGURE 1.18 Charles W. Merrill (1869−1956).

FIGURE 1.19 John B. Zadra (1898−1967).

technology. The adsorption capacity of activated carbon for metal ions is small compared with that of ion exchange resins; however, activated carbon is a much cheaper material to manufacture and is more selective. The process also has the advantage of eliminating an expensive filtration operation.

6.5 Refining of Gold

There are three methods for the refining of gold. The hydrometallurgical process is the oldest and depends on the gold content and the type of impurities present. While silver is soluble in both nitric and sulfuric acids and gold is insoluble, these acids cannot be used to dissolve silver away from an alloy containing more than 25% Au. For high-gold alloys, *aqua regia* is therefore used. In such alloys, gold is leached, while silver forms an insoluble residue. Further, gold is soluble in *aqua regia*, but a gold−silver alloy containing more than 85% Ag cannot be attacked due to the formation of an insoluble layer of AgCl, which stops the attack. Therefore, the *aqua regia* leaching process is used only for refining high-gold bullions, where the silver content does not amount to more than 8%, or to cases where the bullion contains enough copper to open it up to attack despite the silver present.

The chlorination process was first applied at the Sydney Mint in Australia in 1867 by F. B. Miller. It is based on the fact that chlorine readily combines with silver and the base metals present, forming chlorides, before it starts to attack gold. The electrolytic process was invented by Emil Wohlwill (1835−1912) (Figure 1.20) in 1874 at the Norddeutsche Affinerie in Hamburg.

6.6 Some Recent Trends in Gold Ore Processing

The cyanidation process has remained practically unchanged since its discovery, but tremendous engineering developments have occurred, making it very efficient. The developments include the introduction of heap leaching, the application to the so-called refractory ores, the improved use of activated carbon technology, and the increased attention paid to the abatement of pollution. The increased price of gold in the 1970s made possible the leaching of old tailings containing as little as 1 g/t Au thanks in part to the newly developed heap-leaching technology that was developed for the leaching of low-grade copper and uranium ores, with agglomeration where necessary.

Refractory ores were often treated by roasting followed by leaching, but this could be an expensive proposition, as well as creating potential environmental issues. A hydrometallurgical approach proved to be a successful solution for this type of ores, for example, that now in operation at Goldstrike, using horizontal autoclaves operating at 160−180 °C and 2000 kPa. Gold ores containing carbonaceous material are also known as refractory ores and are difficult to treat, not only because part of the gold is tied up with the organic matter but also because dissolved gold is adsorbed on the carbon present in the ore and therefore reports in the tailings. This problem was solved by aqueous oxidation using chlorine. Some of the
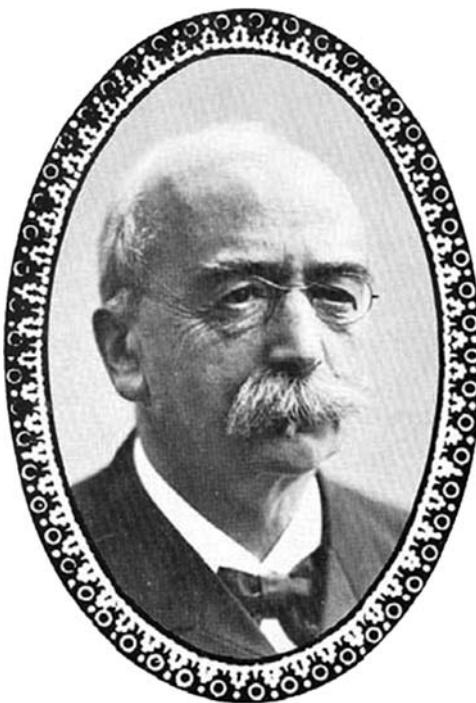
FIGURE 1.20 Emil Wohlwill (1835−1912).

gold may be solubilized by the chlorine water but the major function of the controlled chlorination is to oxidize organic matter before cyanidation. A plant at Carlin, Nevada, used this technology. Another solution to this problem was found by using the carbon-in-leach process as described in Chapter 30.

Cyanidation under high oxygen pressure has recently been used commercially at the Consolidated Murchison Mine near Gravellote in South Africa. The process has been developed by Lurgi in Germany using tube autoclaves 1.5 km long and with a 5-cm inner diameter. Leaching is conducted at ambient temperature but at about 5 MPa oxygen pressure. As a result, residence time is only 15 min at 85% recovery. It should be noted that at high oxygen pressure, a high cyanide concentration must be used to achieve high reaction rates. In practice, the leach solution is 0.2−0.5% NaCN. Although cyanide solutions are susceptible to oxidation, the short residence time renders this drawback negligible.

The carbon-in-leach process is another variation that was developed to circumvent problems faced when leaching gold ores containing carbonaceous material, that is low recovery because of the adsorption of the gold cyanide complex on the organic matter, which then reports to the tailings. In this process, the carbon granules are added during leaching of the ore so that any gold dissolved is immediately retained by the carbon and not by the carbonaceous matter in the ore.

7. GOLD STANDARDS AND ASSAYING

Gold is too soft in the pure state for the purposes to which it is generally applied. For practical application it is alloyed with copper or silver. The former renders the gold more red and the latter metals paler than their true colors. The proportion of gold contained in an alloy is expressed in *degrees of fineness* or as *carats*. *Fineness* is expressed in parts per 1000, for example 916.6, or decimally 0.9166. The *carat* is expressed in parts of 24, pure gold being 24 carats fine. Thus, 9-carat gold contains 9 parts of pure gold and 15 parts of some alloy of copper and silver. For several 1000 years, weighing seems to have been restricted to determining the mass of gold.

Georgius Agricola (1490−1555) described the use of the touchstone and touch needles for examining bullion, coins, and jewelry (Figure 1.21). *Touching* involves rubbing the alloy under investigation onto the surface of a piece of smooth, fine-grained, slightly abrasive black stone and comparing the color of the streak produced with those obtained from standard alloys. The method was already known to the ancient people. Theophrastos (371−288 BC) gave a detailed description of touchstone in his book on stones. The touchstone method of assay was also discussed in Sanskrit texts (third century BC) describing the manufacture of touch needles (standard alloys) in which the ratio of gold to copper is varied in steps. By the Renaissance, the sets of touch needles had grown to include ternary alloys of gold, silver, and copper.

The gold content of ores and rocks is commonly determined by means of a *fire assay*, a method known to metalworkers for 3000 years. A weighed sample of pulverized rock is melted in a mixture of flour, lead oxide, soda, borax, and silica
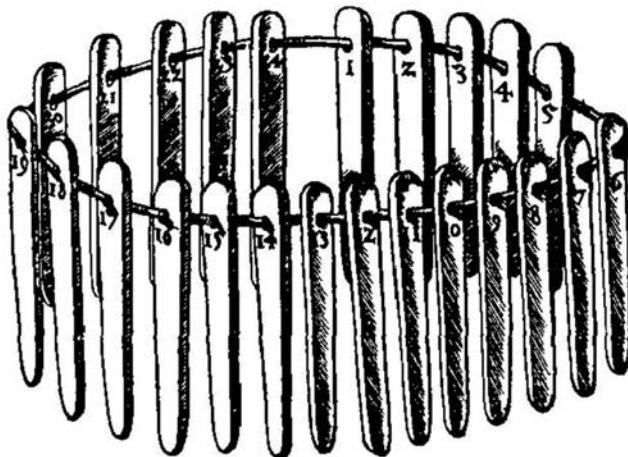
FIGURE 1.21   Touchstone and touch needles for examining bullion, coins, and jewelry.

within a furnace at temperatures that range from 900 to 1,000 °C. The lead oxide is reduced easily to the metal, which collects the gold, and this lead−gold melt separates to cool as a button. The button is then remelted in a bone-ash cupel, which absorbs the lead oxide formed but leaves behind a bead of gold that is weighed to obtain the ratio of gold to rock. The basic unit of weight used in dealing with gold is the *troy ounce*, so named after Troyes, a town south of Paris on the Seine that is famous for its medieval fairs and where the pound of Troyes (∼12 oz) was in use. One troy ounce is equivalent to 20 troy pennyweights. In the jewelry industry, the common unit of measure is the pennyweight (dwt), which is equivalent to 1.555 g. The *avoirdupois pound* was also developed in France and was based on 16 oz (*avoir-du-poid* in Old French, meaning *goods weight*).

Incidentally, gold has almost exactly the same density as tungsten, 19.3. In the 1970s, a person deposited gold-plated tungsten bricks in a bank in lieu of true gold. The fraud was discovered later, and since then all gold bullion deposits are now routinely examined by banks by neutron diffraction to confirm their identity.

8. GOLD IN CURRENCY

Gold has been used as a medium of exchange and as a form of savings from the earliest times to the present day. For many civilizations, gold and money have been, and still are, regarded as one and the same thing. The first use of gold coins is attributed to the Chinese. In the West, the first gold coins were minted by the Lydians in Asia Minor from around the sixth century BC. It was only in the fifth century BC, however, that techniques were developed to produce pure gold coins by removing the naturally occurring silver content. Thereafter, coins became more important and were widely produced by the Romans in a variety of metals, besides gold. Metals other than gold were commonly used for coinage for much of history. The scarcity of gold precluded its widespread use as a means of payment. It was only with the major gold discoveries of the nineteenth century that gold became widely used as a form of currency.

The East Slovak Museum in Košice has one of the largest collections of gold coins in the world, dating back to the eighteenth century (Figure 1.22). The collection, comprising 2500 pieces, was discovered in a box buried under a building during construction. It is believed that the owner had to flee in a hurry during a revolution.

9. BANKS

There is a close historical relationship between the growth of banks and the use of gold as money. At one time, people would leave their gold at goldsmiths, who had safe places to store the gold. Carrying gold around as a means of exchange was inconvenient because of its weight and great value. To facilitate trade, goldsmiths began to issue certificates of deposits of gold, which were handed over as payment. These were equivalent to today's cheques.

The second step, which completed the transformation from being a goldsmith to being a bank, was the realization by goldsmiths that the majority of the gold sitting in their vaults was rarely withdrawn at the same time. This meant that the goldsmiths could lend out a portion of the gold in their vaults. They could charge interest for the loan and so make a return. If they lent gold prudently, they could still retain enough gold in their vaults to honor the daily demands for withdrawals from their depositors.

FIGURE 1.22   Gold coins of the eighteenth century in the East Slovak Museum in Košice.

As a result of the goldsmith/bank's activity there was a net increase in the amount of money in circulation. In 1717, Sir Isaac Newton, then Master of the Mint in London, fixed the value of the British pound in terms of its value in gold, since the price of an ounce of gold was set at 4 pounds 17 shillings and 10½ pence. In the early nineteenth century, discoveries of gold in California and elsewhere greatly increased the world stocks of gold. For the first time, there was sufficient gold to act as the sole basis for monetary systems. Starting with the United Kingdom in 1816 and culminating with the United States in 1900, the majority of the world's trading nations adopted the gold standard. This meant that gold was minted into coins and circulated as currency. These coins were not token money, since they provided full value.

Because of gold's bulk, bank notes were issued in a number of countries. The gold backing to this paper currency meant that the notes could be taken to the bank at any time and cashed in for the prescribed amount of gold. During the financial crisis caused by World War I, most countries suspended the convertibility of their currencies into gold. The warring nations decided to conserve their reserves to finance the war effort. They would otherwise have been in danger of losing their gold reserves as the gold standard moved to correct the balance of payments deficits they found it necessary to run.

After World War I, bank notes were made legally acceptable at their face value, and the requirement for a complete gold covering for the money supply was removed. This gave governments the power to control the supply of money in circulation according to the needs of the economy. Gold did, however, retain its key functions as a measure of value and as a central bank reserve asset, although no longer exclusively but now in conjunction with foreign exchange. Consequently, currencies were still defined in terms of a specific amount of gold, but there was no obligation to deliver gold on demand and the value of money in terms of gold could be changed. This system was eventually ratified after World War II. Because currencies were still denominated in terms of gold, there were still semifixed exchange rates between nations. The United States fixed its currency at $35 per ounce, although US citizens were banned from holding gold. As a result, the dollar took on the role of the official monetary price of gold. Many countries began to denominate their currencies relative to the dollar, which came to be regarded as "as good as gold."

By the late 1960s, the US balance of payments had slipped so far into deficit that the dollar was perceived to be overvalued relative to gold. Many gold mines were shut down because the cost of production was higher than the value of gold recovered as fixed by the government. The United States revoked its undertaking to pay dollars in exchange for gold in August 1971. Eventually the gold price was left to find its own level. Consequently, gold rose progressively through the 1970s, rising to its high of $850/oz on January 21, 1980.

A large part of the gold stocks of the United States is stored in the vault of the Fort Knox Bullion Depository located about 50 km southeast of Louisville in Kentucky. Gold in the depository consists of bars about the size of ordinary building bricks (18 × 9.2 × 4.4 cm) that weigh about 12.5 kg each, stored without wrappings in the vault compartment.

FIGURE 1.23 Brazilian Gold Museum in the former palace of the Portuguese governor of the Province of Mina Gerais in Sabara, a suburb of Belo Horizonte.

Today gold is borrowed and lent in just the same way as money. Gold's interest rate is low in comparison with most currencies, which probably reflects the lower long-term risk of inflation in holding gold compared to currency. Interest rates vary within a range of 1−2%. Low interest rates make it attractive for companies in the gold business to finance themselves in gold rather than currency. From the mid-1980s mining companies wishing to raise money to develop new gold mines have commonly borrowed gold. The gold is then sold for cash to start development. When the time comes for repayment, the mine repays its debt in ounces of gold, from the new mine. So their financing is completely safeguarded against movements in the gold price, whereas if they had borrowed in dollars they would have been exposed to movements in the dollar price of gold. Gold has served the human race well as a dependable form of money from the earliest of times right up to the modern day.

10. GOLD MUSEUMS

The historical importance of gold to our civilization is attested by the number of museums devoted exclusively to this metal. There are four gold museums in South America and one in Central America, preserving gold artifacts from Inca and other ancient civilizations. They are located in Bogota (Columbia), Lima (Peru), La Paz (Bolivia), Sabara (Brazil), and San José (Costa Rica). The Brazilian museum is located in the former palace of the Portuguese governor of the Province of Mina Gerais in a suburb of Belo Horizonte and shows the history of gold in Brazil (Figure 1.23).

A number of gold museums can be found in the other major gold-producing countries, for example, the Ballerat Gold Museum in Australia and the Gold of Africa museum in South Africa.

SUGGESTED READING

Dube, R.K., 1991. Gold powder: its preparation and application as described in ancient Sanskrit texts. Gold Bull. 24 (3), 95−102.

Habashi, F., 1987. One hundred years of cyanidation. CIM Bull. 80 (905), 108−114.

Habashi, F., 1995. Gold through the ages. Bull. Can. Inst. Min. Met. 88 (990), 60−69.

Habashi, F., 1999. History of gold on postage stamps. Bull. Can. Inst. Min. Met. 92 (1034), 77−78.

Habashi, F., 2008. Gold in American Indian empires. De. Re Met. 10/11, 91−98.

Habashi, F., 2009a. Gold in the ancient African kingdoms. De. Re Met. 12, 65−69.

Habashi, F., 2009b. Gold rush in Tierra del Fuego. CIM Mag. 4 (4), 76.

Habashi, F., 2009c. Gold. History, Metallurgy, Culture. Métallurgie Extractive Québec, Québec City, Canada. Available from: Laval University Bookstore "Zone". http://www.zone.ul.ca.

Habashi, F., 2011. Gold in Siberia. A historical essay. CIM Mag. 6 (6), 109−111.

Habashi, F., 2012. Gold museums. Metall. 66 (6), 271−273.

Habashi, F., 2014. Gold in Egypt. A historical introduction. De Re Met. [Madrid] 23, 85−92.

Healy, J.F., 1979. The processing of gold ores in the ancient world. CIM Bull. 78 (874), 84−88 (Also in J. Met. 31 (8), 11−16 (1985)).

Hunt, L.B., 1973. Gold in the pottery industry. Gold Bull. 6 (1), 116−127.

Jaro, M., 1990. Gold embroidery and fabrics in Europe: XI−XIV centuries. Gold Bull. 23 (2), 40−57.

Kauffman, G.B., 1985. The role of gold in alchemy. Gold Bull. 18 (1), 31−44, 18 (2), 69−78; 18 (3), 109−119.

Murphy, R., 1992. The monetary role of gold. Interdiscip. Sci. Rev. 17 (3), 234−238.

Oddy, A., 1983. Assaying in antiquity. Gold Bull. 16 (2), 52−59.

Ogden, J., 1992. Gold in antiquity. Interdiscip. Sci. Rev. 17 (3), 261−270.

Rapson, W.S., 1992. Mining, extraction, and refining of gold. Interdiscip. Sci. Rev. 17 (3), 203−212.

Scheel, B., 1989. Egyptian Metalworking and Tools. Shire Publications, Aylesbury, UK.

Sinclair, P.J.N., 1992. The economics of gold. Interdisc. Sci. Rev. 17 (3), 229−233.

Vittori, O., 1979. Pliny the Elder on gilding. Gold Bull. 12 (1), 35−39.

Wise, E.M. (Ed.), 1964. Gold: Recovery, Properties, and Applications. Van Nostrand, Princeton.

Fathi Habashi, Professor Emeritus of Extractive Metallurgy at Laval University in Quebec City. He was born in Minia, Egypt, on October 9, 1928. He holds a BSc degree in Chemical Engineering from the University of Cairo (1949), a Dr. Techn. degree in Inorganic Chemical Technology from the University of Technology in Vienna (1959), and honorary degrees from the Technical University of Oruro in Bolivia (1986), the Saint Petersburg Mining University in Russia (1993), the National Technical University in Lima, Peru (2010), and San Marcos University also in Lima (2014).

He held the Canadian Government Scholarship in Ottawa (1960−1962), taught at Montana College of Mineral Science & Technology (1964−1967), then worked at the Extractive Metallurgical Research Department of Anaconda Company in Tucson, Arizona before joining Laval in 1970. He was elected a Fellow of the Canadian Institute of Mining, Metallurgy, and Petroleum (1998) and holds its Silver Medal. His research interests are inspired by a desire to develop an integrated understanding of extractive metallurgical processes and to put them into a systematic order within a historical background. He was a guest professor at a number of universities and authored a number of books on extractive metallurgy.