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Volume Author/Editor: Harold Barger and Sam H. Schurr

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Chapter Author: Harold Barger, Sam H. Schurr

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Chapter 7

The Purification of the Mineral Product

A REVIEW OF technological changes in mineral extraction would be incomplete without some account of developments in ore dressing and other types of mineral beneficiation and concentration. Many minerals, even some coal, copper and iron ore, are shipped to the consumer or smelter as they come from the mine. But most coal is sized, and much of it cleaned, in a surface preparation plant; and most metallic ores are ground, concentrated, and sometimes separated from each other, before they leave the vicinity of the mine.

Changes in the technology of ore dressing and other types of processing can be appraised most satisfactorily in the light of developments in mining proper. As we have noted, mining has evolved since the end of the nineteenth century in the direction of techniques which may best be labeled nonselective. Open cut operations in general, and block caving methods of underground copper mining in particular, illustrate extreme forms of this development. But regardless of the mining method in vogue, wherever drilling, blasting and loading have been mechanized the product is apt to stand in need of after treatment. This is because the mechanically mined mineral has more waste mixed with it than it would have if hand picked and hand loaded. The need to purify the product, and to do this as a separate operation prior to shipment, is therefore partly the result of the mechanization of the mining process. The responsibility for producing a waste-free product of a marketable grade has been transferred, in the mechanized mine, from the individual miner to a processing plant on the surface.

In the case of many metallic ores the need for processing prior to shipment is traceable also to a desire to mine a lower grade of material, a product which, as it comes from the mine, is too lean to be smelted. By using suitable processing equipment, a 2 percent copper ore can be shipped to the smelter as a concentrate containing 30 or 40 percent of the metal. Finally, many complex ores cannot conveniently be smelted unless separated into their constituents. For this reason, if a silver ore contains lead or zinc it may sell for a lower price on that account; with suitable milling equipment separate concentrates, containing only silver, lead and zinc respectively, can be produced and a higher combined value realized.

Specialization of function has proceeded farthest, and the most elaborate processing techniques have been perfected, in concentrating the ores of the nonferrous metals. Meanwhile the producers of iron ore, coal, crushed stone, and many of the minor nonmetals have also evolved methods for mechanically sizing, grading and purifying their products in surface preparation plants. After briefly noting the methods used for processing coal and iron ore, we shall devote the balance of this chapter to a review of modern techniques for concentrating nonferrous ores.

COAL[1]

Increased emphasis in recent years on the mechanical preparation of coal for market has resulted partly from the mechanization of loading, which prevents the miner from picking waste at the coal face, and partly from the growing interest of the consumer in grades of coal that have been cleaned as well as sized. Elementary forms of preparation have a long history, and in the case of anthracite date back almost to the beginning of mining. Partly because of initial difficulties in causing the coal to burn, partly because the character of the seams is such that a considerable admixture of refuse occurs, the producers of anthracite were faced with the problem of processing from the first. Crude sizing is known to have been practiced as early as 1830. A modern anthracite breaker screens the product, and may also crush it, into six or eight sizes, and includes an intricate array of jigs and picking tables for washing and cleaning the coal. The smaller sizes, particularly, are cleaned by hydraulic means. The jigs for this purpose make use of the fact that, while coal is only slightly heavier than water, rock and other impurities are usually much heavier. Coal is forced to the top of the jig by screens or by the upward flow of water, while the waste settles at the bottom. Such jigs recall those

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[1] This section is adapted from A. T. Shurick, *The Coal Industry* (Little, Brown, 1924), Chapter IV; and Willard E. Hotchkiss and others, *Bituminous-Coal Mining* (National Research Project, Philadelphia, 1939), pp. 31-42.

used for concentrating metallic ores (see below); in this respect the coal industry is said to have borrowed techniques from metal mining.

What the breaker does for anthracite, the tipple does—usually with less elaboration—for bituminous coal. Most bituminous mines possess mechanical screening equipment, and most coal from them is sold in screened sizes. But price differentials based on size are less important for bituminous coal than for anthracite: in consequence sizing is rough, and much bituminous coal, even from mines with preparation plants, is still sold as run-of-the-mine. Plants for cleaning bituminous coal are a rather recent development: of the total output only about 5 percent was mechanically cleaned at the mine in 1915, about 12 percent in 1936. Where there is no cleaning plant, hand picking of impurities is often necessary at the time the coal is loaded onto railroad cars for shipment. As with anthracite, washing in some form of jig is the most common form of mechanical cleaning, although pneumatic devices also have been developed for the purpose.

IRON ORE[2]

As with coal, the processing of iron ore before shipment from the mine is a relatively simple matter. The purpose of such beneficiation, as it is called, may be to improve the physical structure of the ore by crushing or sintering, to concentrate the ore into smaller bulk through the removal of waste matter, or to do both of these things. Most ore is still shipped in the form in which it is mined, without beneficiation; but the need for such after treatment has increased rather steadily and is a function, in part at least, of the depletion of rich direct-shipping ores. Lean ores may be smelted directly, but an economy of fuel results if they are concentrated first. The proportion of all iron ore shipments consisting of concentrates rose from a negligible amount in the years before 1909 to a tenth in 1915, and nearly a fifth in 1935–37.[3]

The process, or combination of processes, used in a given bene-

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[2] This section is based on Nicholas Yaworski and others, *Iron Mining* (National Research Project, Philadelphia, 1940), Chapter VI.

[3] A rich iron ore may contain 50 percent, a lean ore 30 percent, of metal: the ratio of concentration (ore to concentrates produced from it) runs 1½ or 2 to 1. By contrast, a rich (direct smelting) copper ore may contain 5 percent, a lean (concentrating) ore 2 percent of metal: the ratio of concentration may be as high as 15 or 20 to 1.

ficiating plant depends mainly upon the characteristics of the ore to be treated. Some ores must be crushed and screened, i.e., broken to a uniform size. In other cases very fine ore is agglomerated through sintering into coarse porous lumps. The same treatment may be accorded finely ground concentrates. The operation is performed by heat, and when moisture and other volatile constituents are eliminated at the same time, sintering also yields some degree of concentration.

Washing is used extensively to concentrate Minnesota and Alabama ores in which the iron is found in coarser pieces mixed with finer particles of sand: after preliminary crushing, the sand is washed away. Jigging is a gravity concentration process applied to ores containing coarse particles of rock or other waste matter. When agitated under proper conditions, the lighter rock particles collect on the surface of a slowly moving mass of ore and are skimmed off. This operation, which resembles similar methods sometimes used in the cleaning of coal, is applied chiefly in Minnesota.

Magnetic methods have been used for many years to concentrate the magnetites of New York, New Jersey and Pennsylvania. These ores consist of oxides of iron having such pronounced magnetic characteristics that even large particles adhere to an ordinary horseshoe magnet, leaving the nonmagnetic waste material behind. The process cannot be employed to concentrate hematite ores, which are nonmagnetic; but methods are being developed to change hematite to magnetite. If these methods are successful, it may become possible to apply magnetic concentration indirectly to the hematites of Minnesota and Alabama. The improvement of concentration methods has received considerable attention in recent years. Vast reserves of lean ore susceptible of large scale open pit mining are known to exist, and the richer, direct-shipping, ores are steadily being depleted.

NONFERROUS ORES[4]

Like coal and iron ore, the ores of the nonferrous metals can be separated to some extent from waste material or gangue by such

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[4] See especially Y. S. Leong and others, *Copper Mining* (National Research Project, Philadelphia, 1940), Chapter V; A. B. Parsons, *The Porphyry Coppers* (American Institute of Mining and Metallurgical Engineers, 1933), Chapter XX; and T. A. Rickard, *History of American Mining* (McGraw-Hill, 1932), Chapter XVIII.

simple expedients as washing and hand sorting. The pan used by the placer miner for treating gold-bearing gravel comes to mind in this connection. But the mining of nonferrous metals is for the most part distinguished by a high ratio of waste to mineral (many copper ores assay less than 2 percent of metal), and by the frequent presence, in intimate association, of more than one type of ore. These circumstances have prompted the development of increasingly elaborate techniques for processing nonferrous ores characterized by high ratios of concentration and small losses in recovery,[5] and for permitting the simultaneous separation of the ores of one metal from those of another. The ore itself undergoes no chemical change; it is merely separated from a large part of the waste in which it is embedded, so that actual extraction of the metal in smelting may be carried through with greater facility. Since ores may be dressed close to the mine, but are often smelted at a distance, an economy in freight charges also results. As already indicated, the successful concentration of the ore has frequently been a prior condition for the mechanization of mining itself. The elimination of the need for hand sorting at vein mines has facilitated the introduction of mechanical loading, while concentration of the ore has alone made possible the exploitation of the low grade porphyry coppers of the West.[6]

Ore dressing involves two steps, each of which has many variants, depending upon the particular type of ore to be processed. The first consists of breaking, crushing or grinding; the second involves the separation of particles containing metal from waste matter, and perhaps of particles containing one metal from those containing another.[7] In a modern concentration plant both steps are

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[5] The degree of concentration is measured by the ratio of ore treated to concentrates produced. The efficiency of recovery is indicated by the ratio of the metal content of concentrates to the metal content of ore from which they are derived. In any appraisal of the effectiveness of concentration techniques both ratios must be considered: see further discussion, with special reference to copper, in Appendix D.

[6] It is true that most nonferrous ores are first concentrated and then smelted. There are, however, many exceptional cases. Direct smelting copper ores (containing at least 3 to 4 percent of metal) may be smelted without prior concentration. Again, the precious metals are recovered from their ores largely by mechanical or chemical means which do not involve smelting. In addition, some copper is obtained from oxide ores by leaching with a solvent such as sulfuric acid, the copper being subsequently precipitated: however, copper ores that can profitably be leached are not very common.

[7] Why breaking the ore is an essential first step in the process of concentration is clear from the following explanation which, although it relates specifically to copper ore, is of general validity: "Essentially a copper ore is composed of minerals that

highly mechanized. In the first the ore passes through several different kinds of mill for successively finer grinding. In the second, water in combination with a variety of special reagents effects the desired separation.

Separation of the Precious Metals

These methods have a long development which stems from the original introduction of Mexican grinding mills (arrastres) on the Comstock lode in Nevada to extract silver in the 1860's,[8] and the researches prompted by the difficulty experienced in reducing the complex ores[9] of the Leadville district of Colorado in the 1870's. A partial solution was found, particularly for treating argentiferous and auriferous ores, in the stamp mill. In this device a heavy cylinder of metal is made to fall on a die upon which the ore has been placed, both the ore and the die being covered with water. The resulting pulp is then treated for recovery of the mineral content.[10] The stamp mill in use at the turn of the century was generally constructed of steel and powered by steam—a marked improvement over earlier wooden devices actuated by gravity or water power.

Until the introduction of the cyanide process in 1890 the stamp mill product was washed over tables coated with mercury which caught the gold particles and held them in alloy. This process known as amalgamation, was fairly successful in dealing with the

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contain copper . . . such as chalcocite . . . , and copper-free minerals such as quartz and pyrite, called gangue. If a typical piece or particle in a given ton of ore is 1/4 chalcocite and 3/4 gangue, no mechanical device can possibly effect a separation—can concentrate it. If, however, each piece or particle is broken into 4 smaller particles, one of which is clean chalcocite and the other 3 clean gangue, it is physically possible to make two products: 1/4 ton of chalcocite concentrate and 3/4 ton of waste or tailing." Parsons, *op. cit.*, pp. 431-32.

[8] The arrastre or arrastra was still employed to some extent in 1902. In its simplest form the "arrastra . . . consists of a circular bed of rock from 6 to 10 feet in diameter, with walls of vertical planks, having an upright pivoted post in the center, from which extend 2 or 4 horizontal arms. Stone drags, weighing usually from 200 to 1,000 pounds each, are attached by ropes or chains to the extremities of the arms, and are slowly drawn around by the rotation of the latter. The depth is usually between 18 and 30 inches. The pavement and drags are of the hardest rock conveniently obtainable." (U. S. Bureau of the Census, *Special Reports,* "Mines and Quarries, 1902," pp. 575-76.)

[9] Complex ores contain more than one metal.

[10] "Mines and Quarries, 1902," p. 576. By 1900 arrastres had largely passed from the picture, but at the time the Census of 1880 was taken they outnumbered stamp mills.

so-called free milling ores in which gold occurs in metallic form, but it was entirely unable to cope with the much more plentiful refractory ores in which the gold occurs in intimate association with other minerals. The latter type of ore had to be smelted or treated by costly chemical processes. As a result, large bodies of low grade ore were rejected until cyanidation was discovered. Indeed, the adoption of the cyanide process led to the reopening of many abandoned gold mines containing large quantities of ore previously considered unworkable, as well as the reworking of gold-bearing tailings accumulated at stamp mills. These tailings resulted from the inability of amalgamation to capture very fine particles of gold even in free milling ore. The cyanide process, on the other hand, is applied to finely ground ore from which the gold is taken up by the sodium or potassium cyanide dissolved in water. This process, which still remains the chief method for the extraction of gold and silver from their ores, was one of the forces that served to foster the abandonment of selective mining.[11]

Improvements in the design of gravity concentration devices during the nineteenth century culminated in the shaking riffled tables introduced around 1875. Particles of ore were carried over several tables on a stream of water. The tables shook up, down and sideways, thereby causing the heavier metallic particles to sink lower than the lighter waste. The waste flowed off, and the metal was caught against the ridges of the table.[12] These tables effected such a satisfactory separation of sulfide minerals at so low a cost that they became an important factor—even before the development of modern methods for concentrating the base metals —in the shift to nonselective mining.[13] As the result of such improvements in the technique of ore dressing in the closing decades of the nineteenth century a decided fall occurred in the grade of gold and silver ores that could be treated economically.[14] Again,

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[11] *Ibid.*, pp. 594-95; C. E. Julihn, "Copper: An Example of Advancing Technology and the Utilization of Low-Grade Ores," in *Mineral Economics*, ed. by F. G. Tryon and E. C. Eckel (McGraw-Hill, 1932), p. 126.

[12] James H. Collins, "Mining Copper and the Nobler Metals" in Waldemar Kaempffert (ed.), *A Popular History of American Invention* (Scribner's, 1924), Vol. II, pp. 71-76.

[13] Julihn, *op. cit.*, p. 126.

[14] Figures presented by Isaac Hourwich in the 1902 Census are of interest in this respect: "By the old amalgamation process not more than 70 percent, and usually not more than 60 percent, of the gold contents of the ore was saved. With the aid of modern processes [i.e. cyaniding and shaking riffled tables] more than 90 percent of the assay contents can be recovered" ("Mines and Quarries, 1902," p. 577). When

many complex ores, in which gold is found in union with silver, copper, iron, pyrites and other minerals, could not have been handled at all without the combination of improved concentration and cyanidation.

Thus methods for extracting the precious metals from their ores, principally by direct recovery (i.e. without the necessity of smelting), had already reached an advanced stage of development by the end of the nineteenth century. Judged by present day standards, techniques for concentrating and separating copper, lead-zinc, and complex ores had not, by 1900, made nearly so much progress. In the treatment of these ores in order to separate mineral from gangue, the various devices in use at the opening of the period we are studying relied upon a difference in specific gravity between the components of crushed ore. It was known that if particles of nearly equal size are agitated in water, the heavier metallic particles tend to sink to the bottom, while the waste material can be skimmed from the surface. In fact this technique —basic to all processes then employed—had already reached a high state of practicability more than a century earlier in the Harz jig, named for the German Harz mountains where it had been developed.[15] Since then no basic improvement had occurred. The cyanide process had proved a sort of philosopher's stone which "transmuted" waste material into gold: what this process had done for auriferous minerals, flotation techniques were to do for ores containing copper, lead and zinc.

Concentration by Flotation

As with the ores of the precious metals, modern methods of treating copper, lead and zinc ores consist of two principal stages: first, milling, and second, concentration. In many cases, and especially in the treatment of the low grade porphyry ores of copper, crushing and grinding must produce particles no larger than a few thousandths of an inch in diameter: so intimately are

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translated into monetary terms, the importance of the change is more easily grasped. In California in the early 1880's only gold ores yielding at least $100 to $200 per ton could be treated, and dumps were covered with large quantities of tailings ranging in content from $40 to $60 per ton. In 1900, with the improvement in recovery techniques, the rejected ore was considered exceptionally rich.

[15] Julihn, *op. cit.*, pp. 118-19. The jig consisted essentially of a set of inclined screens moving up and down in boxes of water. The ore passed over the screens, and the heavier metallic particles gathered at the bottom of the box.

mineral and waste material associated that any coarser treatment would fail to render separation possible. The ore to be crushed, if it comes from an underground mine, is sometimes a foot in diameter; from an open pit mine it may be even larger. No single milling device is adequate. The coarser operations are performed by jaw or gyratory crushers,[16] which reduce the lumps of ore to an inch or two in size. These are then ground in ball or tube mills, which utilize the abrasive action of steel balls or flint pebbles in a revolving tube.[17]

Some of the simpler base metal ores can be successfully treated by gravity methods, and jigs and shaking tables, familiar in the technology of the precious metals, were the earliest devices used for concentrating copper, lead and zinc ores. But today concentration, especially of low grade copper ores, depends heavily upon flotation methods. The flotation process, introduced in 1912, may be said to turn gravity concentration upside down. The metallic content of the ore is made to float while the waste material sinks to the bottom. This apparent interchange of physical properties is accomplished by the addition of a minute quantity of oil to a pulp consisting of water and ore. When the pulp is then agitated —by the introduction of air from a blower at the bottom of the flotation cell—the mineral particles attach themselves to the air bubbles thus formed and may be scraped from the surface.[18] The gangue particles, on the other hand, remain below. Parsons has supplied a simplified explanation of the mechanics of the process in the following passage: "A mutual attraction exists between a bubble of air and a particle of mineral (either sulphide or gangue) that is coated with a minute film of grease or oil. However, in the presence of water, oil has a stronger tendency to film a particle of sulphide . . . than a particle of gangue." [19]

In its tremendous impact on the copper, lead and zinc mining industries, the flotation process matched the earlier changes

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[16] As its name implies, the jaw crusher relies chiefly on compression. Gyratory crushers consist usually of an eccentric cone revolving in a cylinder, and produce both compression and abrasion.

[17] John Gross, "Crushing and Grinding," *Bulletin 402* (U. S. Bureau of Mines, 1938). The fine-grinding techniques used today in milling metallic ores were originally developed in the cement industry (Frederick Laist, "Developments in the Metallurgy of Copper, 1880–1940," unpublished manuscript).

[18] Parsons, *op. cit.*, p. 442; also Laist, *op. cit.*

[19] *Op. cit.*, p. 443.

wrought by cyanidation in the mining of the precious metals. As in the case of amalgamation and cyanidation, the new process could profit by the very conditions that had affected the older method adversely. The chief difficulty of gravity concentration lies in its inability to effect a separation of metal from gangue when the material has been slimed (too finely ground). Yet with most ores of copper, lead and zinc, fine grinding is essential to liberate the metal from the gangue. For this reason, as much as 30 to 40 percent of the copper in porphyry ores[20] was wasted with gravity concentration, mostly in slimes which could not be concentrated.[21] This problem was solved by the flotation process, which in fact works best with finely ground ore. With such ores flotation not only achieves a higher recovery than gravity concentration, but also produces a cleaner concentrate, precisely because finer grinding liberates a higher percentage of the mineral from the gangue.[22]

The flotation process was originally developed in Australia about the year 1910 and was first applied in the United States in 1912 at a zinc concentrator.[23] Its use in copper concentrating dates from the period 1913–16, when it served merely as an accessory to gravity concentration. Usually it treated the slimed portion of the ground ore, to which gravity methods could not be applied. As grinding became increasingly fine, flotation gradually became the chief process, and the period 1923–27 witnessed the adoption of "all-flotation" methods at copper concentrators.[24]

The spread of flotation during this period was accelerated by a major refinement in the process. Although flotation recovered a higher percentage of the mineral in the ore than was possible with gravity methods, it could not distinguish adequately among the several minerals that might be found in the ore. If, for example, a copper ore included pyrite (iron sulfide) with the copper sulfide, the flotation concentrate was likely also to include the pyrite. Since the presence of pyrite meant greater difficulties in smelting and therefore served to augment costs, it was desirable to find a method that would eliminate pyrite from the concentrate. Such

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[20] Porphyry ores are characterized by the fact that the mineral occurs in small particles finely disseminated through the rock, rather than in veins.

[21] Parsons, *op. cit.*, p. 441.

[22] Laist, *op. cit.*

[23] Parsons, *op. cit.*, p. 445; Rickard, *History of American Mining*, pp. 404-05.

[24] Thomas G. Chapman, "Concentration of Copper Ores in North America," *Bulletin 392* (U. S. Bureau of Mines, 1936), p. 5.

a technique, which came to be known as selective or differential flotation, was introduced around 1923.[25]

In selective flotation new reagents known as "collectors" and "depressants" are added to the mineral pulp. "These reagents are not oils but are chemical compounds. They do not take the place of oils, which still have to be used, but modify the surfaces of the sulphide particles in such a way that they become more receptive or less receptive to oiling, as the case may be." Thus, "the addition of a few ounces of sodium xanthate per ton of ore greatly accelerates the floatability of the minerals" and "a similar amount of sodium cyanide tends to keep iron pyrite from floating." [26] In this case the pyrite may be either removed with the gangue or recovered as a separate concentrate suitable for further processing.

Thus among the advantages of selective flotation is the fact that it facilitates the recovery of byproducts. For example, by earlier methods of concentration a lead-zinc ore would yield a lead concentrate containing some zinc (which not only interfered with smelting but was lost in the process) and a zinc concentrate containing enough lead to make smelting difficult (but not enough to be recovered). Moreover, both concentrates were often so lean that smelting became an expensive undertaking. The use of selective flotation now produces a lead concentrate practically free of zinc, and a zinc concentrate practically free of lead, both rich enough to be cheaply smelted.[27]

Since the introduction of selective flotation there has been no major change in concentration practice, although a number of modifications of the basic technique have increased recovery of metal and improved the grade of concentrate produced. Important among these changes has been the development of new chemical reagents which permit increasingly broader selective action in flotation.

The record of beneficiating plants—especially those working metallic ores—is impressive. In the face of a declining grade of material they have been able to recover ever higher percentages of the metal contained in the ore. Figures on percentage of recovery —the least ambiguous measure of increasing mill efficiency available to us—tell a story of remarkable achievement. In a sample of

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[25] Parsons, *op. cit.*, pp. 456-57.

[26] Laist, *op. cit.*

[27] We are indebted to Professor Read for elucidating this example.

several of the leading copper concentrating plants, recovery rose from about 70 percent of the assay content in 1911 to about 90 percent in 1930.[28] These increased recoveries were accompanied by a marked improvement in the grade of concentrates produced. A smelter today need not treat as large a tonnage of concentrate to obtain a given amount of metal as was necessary some thirty years ago. In addition, the enhanced selective action of the flotation process has resulted in the elimination of many impurities that formerly rendered smelting difficult if not impossible.

The net result of all these changes has been not only an increase in the product obtainable from a given volume of raw material, but a greatly expanded scope of the methods of mass exploitation, which have been the distinctive contribution of the last five decades to mining technology.

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[28] For source of data see below, Appendix D.