To Float or Sink: A Brief History of Flotation Milling

By Dawn Bunyak

Each day metals play an important role in people's lives. Metals make the simple things in life possible. When you turned off the morning alarm, rolled out of bed, flipped on the light switch in the kitchen and turned on the electric coffee pot, you began your day with the assistance of metals in various products. The car that took you to work is chock full of metals. The information highway that aids you in your daily work is laden with base metals. The world is made up of metals and metals make up the world.

At the beginning of the twentieth century, the world's demand for minerals was minuscule compared to its requirements today. In 1866, a common electrical generator required five hundred pounds of copper strip and wire. A modern generator contains approximately fourteen *tons* for its internal components. The manufacturing industry requires inordinate amounts of metals to produce the luxuries that people have come to regard as staples in their day-to-day lives.

So where do metals come from? Mining the earth's bounty of minerals began with earliest man's production of tools. Today mining companies remove vast quantities of minerals from the earth's crust. However, extraction means reduction in the world's minerals supply. Minerals are not replenished as they are extracted. The majority of mines contain metals that are finely disseminated particles in a mountain of waste rock. For instance, the grade of copper in a ton of rock can be anywhere from 0.8 to four per cent grade. That means in order to smelt four million tons of copper, nearly 400 million tons of ore must be removed, milled, and smelted. If metals, like copper, are so intricately locked in vast amounts of waste, how is it isolated from that waste? In the twenty-first century, large companies with huge plants continuously work to separate metals through the process of flotation. The history of the flotation process began in the nineteenth century, but flotation is considered the most important development of the twentieth-century mining and milling industry.

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Flotation

Flotation is an innovative processing method for separating valuable minerals locked in waste rock. It abandons basic principles of ore treatment by gravity methods previously followed by early metallurgists. At the end of the nineteenth century, the world had almost exhausted its supply of high-grade ore. Mining engineers and inventors worked to create a concentration method to treat the world's abundant supply of low-grade and complex ores, which were often difficult to extract profitably from waste rock. In 1905, the world's first commercially successful flotation mill was established at Broken Hill, Australia. Soon, experimental plants in Australia, Great Britain, and the United States also spread the news of their success with flotation. Almost overnight, the mining industry shifted from exploiting diminishing high-grade ores to an abundant supply of low-grade ore. Without the development of the flotation process, metals (such as copper, lead, and zinc) would have become increasingly costly and difficult to produce causing a direct impact on the global economy.[1]

Industrialization and flotation propelled the mining industry into a new age. While earlier concentration methods, such as gravity followed by cyanidation, were effective in processing gold ore, flotation opened the minerals market. Metal production was increased to twenty-four metallic and nineteen non-metallic minerals by the mid-twentieth century. Flotation can be used in processing metallic ores (e.g., copper, lead, zinc, gold, silver) or non-metallic ores (e.g., clay, phosphate, coal). Flotation is the most widely used process in the world for extracting minerals. The process also recovers several metals from a single ore body into two or more concentrated products. The development of flotation solved an industry dilemma and allowed increased minerals production to meet twentieth-century industrial and manufacturing demands. Modern engineers and inventors assert that the evolution of the flotation process for the recovery of metals was the most important technological development of the century.[2]

Flotation Process

Flotation is a method for concentrating valuable metals from finely ground ores in a water bath, with either the ore pulp or water chemically altered with reagents and frothers to encourage separation of minerals. The term flotation has been loosely used for all concentration processes in which heavier mineral particles have been disengaged from lighter waste particles in water by "floating" the mineral away from waste. Today the term is generally used to describe *froth flotation*. Nevertheless it is important to understand that flotation evolved through three principal stages of development. These stages will be discussed in more detail later. The process of flotation involves:

1. reduction (crushing) of the ore to a size that will free the targeted minerals;
2. addition of water, reagents, and frothers, which encourage the minerals to adhere to air bubbles;
3. creation of a rising current of air bubbles in the ore pulp;
4. formation of a mineral-laden froth on the water surface;
5. skimming or floating off the mineral-laden froth; and
6. drying the resultant concentrate for shipment to the smelter.[3]

Flotation greatly differed from earlier mill methods that used variations of specific gravity. The most rudimentary form of metal recovery was gravity concentration. Gravity concentration used water and agitation to sort heavier metals, which settled to the bottom, from the waste that rose to the top.

Flotation isolates materials by taking advantage of the surface tension of liquids and the ability of minerals to attach to air bubbles in liquids.[4] Another innovation of the flotation process is its ability to alter the pulp chemically (in the water bath or ore pulp itself) allowing for an efficient separation of numerous minerals from waste without increasing the tonnage or grade of ore.[5] With minor adjustments in the chemicals added to the water bath, the process can be repeated as often as necessary to recover as many different types of metals or minerals from the ore pulp. Flotation, as developed in the twentieth century, has now become the most widely used process for extracting minerals from metallic ores.[6]

Development of Flotation

Nineteenth-century mill men acknowledged that current milling practices, i.e., crushing, gravity concentration, and smelting, were not efficiently and economically recovering all the mineral wealth from extracted ores. They anticipated that high-grade ores would soon be depleted. Earlier milling methods recovered one mineral or a mineral compound, e.g., lead, zinc, or lead-zinc. The dilemma was how to recover various minerals from low-grade ore into a high-grade concentrate.

Experimentation in flotation of complex ore concentrates began in England in 1860 with William Haynes. Haynes found, when mixing powdered ores, oil, and water, some minerals had a tendency to attach to certain oils.[7] By the end of the century, many others experimented with such variables as: 1) additives, such as oils, acids, or salts; 2) agitation; and 3) heat. Several individuals patented their findings in the late 1800s. American Carrie Everson's patents (1886 and 1891) included a two-step process thoroughly mixing pulverized ore, oil, and an acid or salt together into a pulp, then agitating the pulp (crushed ore and oil) on an irregular work surface. In earlier experiments, Everson had used a washboard as a work surface. The metals rose to the top and the waste settled in the recessed areas of the washboard. In her patent, Everson listed the minerals she successfully recovered.[8] The Wilfley table, developed in 1896, works on the same principal as Everson's irregular work surface.

By 1894, George Robson and Samuel Crowder working at a mine in Wales developed a mixture balance with oil. Their experiment resulted in the oil lifting mineral particles to the surface of the water bath. Their process was the forerunner of the Elmore bulk oil process.

Bulk Oil Flotation

The early development of bulk oil flotation was attributed to the Elmore brothers, Francis and Alexander, of England in 1898. The two men patented various modifications of a process involving equal parts of ore and oil in a drum. The contents were poured into a water trough, the concentrate rose to the surface, and the scum skimmed off the top.[9] Francis went to work for the English-based company, Minerals Separation Incorporated, where he continued his efforts to perfect the flotation process. In 1904, Elmore and Minerals Separation patented the introduction of bubbles, which subsequently led to another patent based upon those same mineral-clad bubbles rising to the surface under a vacuum.

Elmore's experimental plant led to the construction in 1905 of the first commercial flotation mill in Broken Hill, Australia. Soon after, the Elmore process could be found in mills in Australia, South Africa, Canada, England, and Wales.[10] Although all the Elmore process mills eventually failed, due to excessive amounts of oil that were used,[11] the process was found in limited use in Australia as late as 1938. Other experiments in bulk-oil flotation led to the use of gas bubbles and an altered chemical solution. In 1902, Italian Alcide Froment laid claim to the first patent to mention the use of gas for increasing buoyancy of metallic particles. A. E. Cattermole's patent in England in 1903 used less oil, introduced soap and alkali into the pulp stream, and agitated the pulp in a water bath through a continuous stream of gas bubbles. Although his process was a commercial failure, Cattermole's process is considered the forerunner to flotation methods used today.[12]

Skin Flotation

Another type of flotation used to remove minerals from waste, without the use of oils, was skin flotation. In June 1885, Hezekiah Bradford patented a process for separating sulfide ore based on the principle of surface tension on water.[13] (Sulfide ores can contain copper, lead, zinc, iron, molybdenum, cobalt, nickel, and arsenic.) The process, commonly called *skin flotation*, stipulated that dry ore be sprinkled, without agitation, onto the surface of a body of water. The heavier materials sank to the bottom, while the surface tension caused the lighter metals or minerals to float on the surface. Subsequent developments by de Bavay and Elmore in 1905 made this process commercially significant. Their process used a small amount of oil (fraction of 1 per cent) mixed with one ton of mineral pulp. The mixture was then poured onto a water bath and agitated to encourage frothing. The Macquisten tube mixed the ground ore with oil and gently pushed the pulp onto the surface of the water. The tubes were first commercially installed in 1906 in the Adelaide Mill at Golconda, Nevada. In 1911, the Morning Mine near Mullen, Idaho used the process on lead-zinc ores in its mill. Because the process was extremely fragile, its use was short-lived. The Idaho mill closed by 1920.[14]

Froth Flotation

The first successful commercial mill using froth flotation was built in 1905 at Broken Hill, Australia, today recognized as the "home of flotation." Independent experimentation, based on earlier patents, at Mineral Separation's Broken Hill mines and mills resulted in the froth flotation process and the Minerals Separation Machine. In 1905, Mineral Separation engineers, E. L. Sulman, H. F. K. Picard, and John Ballot, filed a patent for their process that distinguished froth flotation experiments from skin and bulk-oil flotation. Their froth flotation process (based on Froment's and Cattermole's earlier patents) used less oil in the ore pulp and added agitation by a rising stream of air bubbles. In another Minerals Separation mill, a new innovation was the use of a Minerals Separation Standard Machine, which was a spitz box invented by Theodore J. Hoover (brother of Herbert Hoover). The pulp passed over the spitz box causing the mineral-laden bubbles to rise to the surface. This in turn allowed the collection of mineral-laden froth from the water. The Minerals Separation Standard Machine consisted of a series of cells divided into agitation and frothing compartments. Although it was eventually superseded as improvements were made to the machine, Hoover's Separation Machine significantly advanced mechanization of the milling industry.

New technology in crushing and separation of ground ore further advanced the development of flotation. While mechanical classifiers, separation machines, and the Wilfley table assisted in the separation phase of the flotation process, selective flotation required finely ground ore (sand or dust) to allow metals to be recovered on the froth of a water bath. Without improved grinding treatment in ball and rod mills, flotation would not have been possible.

Inventors Sulman, Picard, and Ballot continued to experiment with soluble frothing agents (commonly referred to as reagents) and patented several combinations used at the Broken Hill mills. Aware that many minerals react differently to reagents in the water bath, experimentation continued to create formulas necessary for the separation of various minerals. The isolation of desired metals would depend on the delicate balance of acid and alkaline agents in the flotation process. However, Minerals Separation's first froth flotation plant at Broken Hill was a success.

Flotation Circuits

Flotation plants operate through a series of flotation circuits. Finely crushed and ground ore is introduced into a water bath in the flotation circuit. In order to achieve separation, an optimum point has to be met. There are several variables that need to be considered: particle size, reagent additions, pulp density, flotation time, temperature of the pulp, type of circuit, and water. Next the ore itself must be considered: uniformity of the ore, settling and filtration data, corrosion and erosion, and finally, the mineralogy of the ore.[15] Once all these variables are tested in pilot plants, the concentrator flotation circuits are designed.

Generally, there are two types of separation circuits, the simple and the complex. Simple separation circuits are generally described as one-product separations. A single circuit divides the ore pulp into a concentrated product and tailing. In order to process more than one concentrate, the one circuit mill and its workings are periodically adjusted to recycle the ore pulp through the system. After chemically altering the bath or pulp, the process can be repeated as many times as necessary to float off all desired metals. (For a description of a single circuit refer to Figure 1.)

A complex flotation circuit rends several concentrates from the ore pulp. Valuable metals are floated together to form a bulk product. The bulk product continues its course through a series of flotation cells where metals are "selectively" separated into concentrates. The waste is sent to a tailing pond. The complex or selective flotation circuits are essentially several cells in a series. The first circuit of cells may remove lead and copper, the second zinc, and the third an iron reject. Yet, the flow of the pulp through the flotation circuit is continuous.

Additional operations in the mill include roasting, steaming, thickening, filtering, leaching, and regrinding of the ore pulp in the flotation circuit.[16] (For an example of a complex set of circuits, refer to Figure 2, for the flow sheet of the Shenandoah-Dives Mill in Silverton, Colorado.) Plants designed similarly to the Shenandoah-Dives did not necessarily produce the same concentrate, even on the same

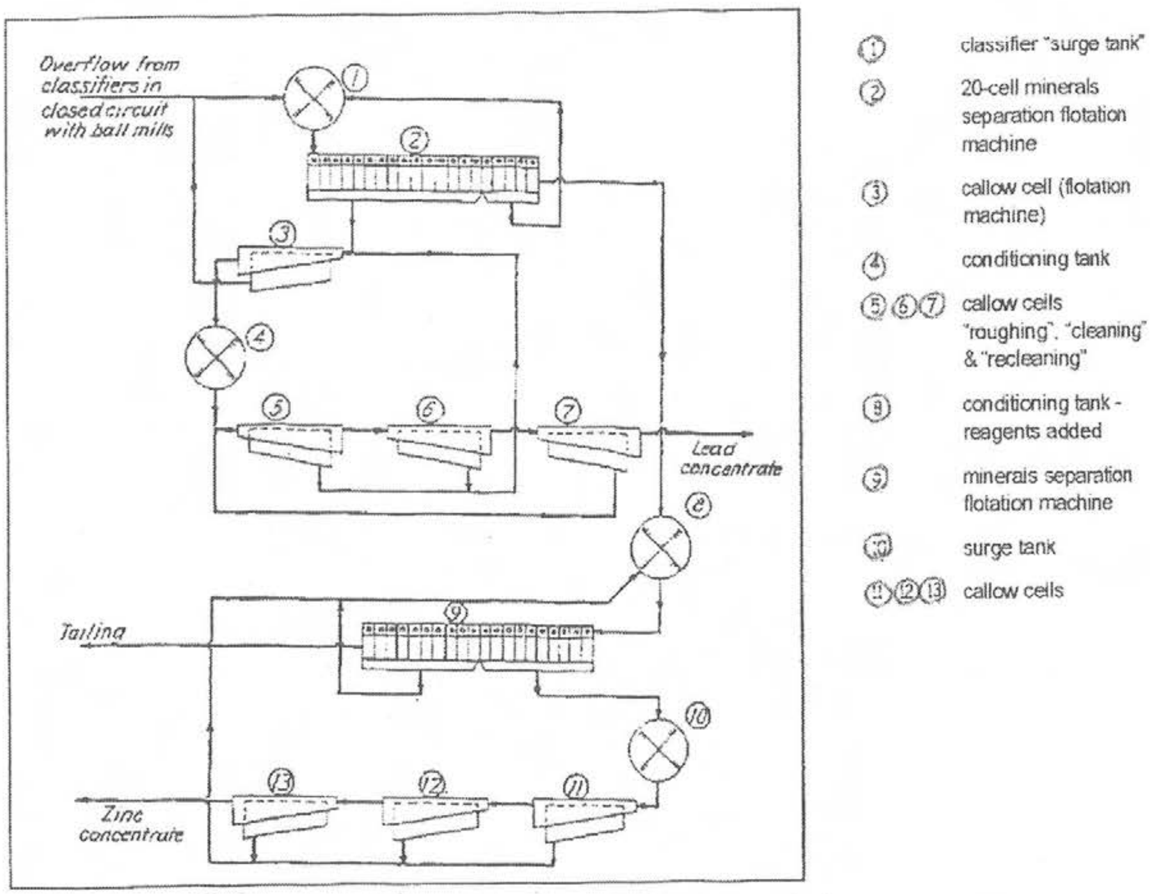


Fig. 1--Flotation Division, Timber Butte Mill
(A.M. Gaudin, Flotation, (NY: McGraw-Hill Book Co., 1932), 31.)

ore. Adjustments were made during the process to allow concentration of different grades of ore. Testing of ore was an on-going process. A circuit can remove zinc one day and be adjusted to separate copper the next day, depending on the needs of the mill and the mineralogy of the ore it was processing. Flexibility of the concentrator (mill) to simultaneously treat various grades of ore improved the mill's ability to stay viable in fluctuating markets.

Equipment found in a complex circuit may include: roughers, flotation cells (in many sizes), launders, thickener tanks, regrinders, reagent or frother machines, tubes for roasting or heating pulps, pumps, samplers, settling boxes, filters, and concentrate bins.

Commercial Milling

In the early decades of the twentieth century, new patent applications for innovative milling processes were filed almost yearly, in some years even monthly. From 1910 into the 1920s, litigation, generally contesting whose idea came first or concerning wording in patents, tied up courts for years.

Nevertheless, experimentation in flotation continued to take place in small plants around the world. Sulman, Picard, and Ballot perfected their froth flotation process in a pilot plant in Broken Hill, Australia. American engineer James Hyde traveled to Australia in 1911 to study the Broken Hill mills and found four different milling methods in

1942 Flow Sheet:

1. 1,200-ton ore bin
2. Pan conveyor, 24"
3. Symons short-head cone crusher
4. No. 86 Marcy grate ball mill
5. Dorr quadruplex classifier 12'x26'
6. No. 64 Stearns-Roger ball mill
7. Bucket elevator 35'x22'
8. Trash trommel, 9-mesh, 2-1/2'x6'
9. Belt elevator 24"
10. Three No. 6 Wilfley tables
11. 20-cell No. 21 M.S. flotation
12. 20-cell No. 21 M.S. flotation
13. Liberty Bell type sampler
14. Hydroseal pump, "B" frame size
15. Wilfley pump, 2"
16. Wilfley pump, 2"
17. Wilfley pump, 2"
18. Wilfley pump, 2"
19. Dorr thickener, 35'x10'
20. Stearns-Roger ball mill, 4'x10'
21. Esperanza-type classifier, 6'x16'
22. Wilfley pump, 3"
23. Wilfley pump, 3"
24. 8-cell No. 18 Denver flotation
25. Denver conditioner, 3-1/2'x5'
26. Wilfley pump, 2"
27. 6-cell No. 18 Denver flotation
28. Liberty Bell type sampler
29. Denver 1" concentrate pump
30. Dorr thickener, 35'x10'
31. Settling box, 3'x6'x2'
32. Dorr filter 2-1/2'x6'
33. Dorr filter 5'x10'
34. Table concentrate bin
35. Zn concentrate bin
36. Pb-Cu concentrate bin

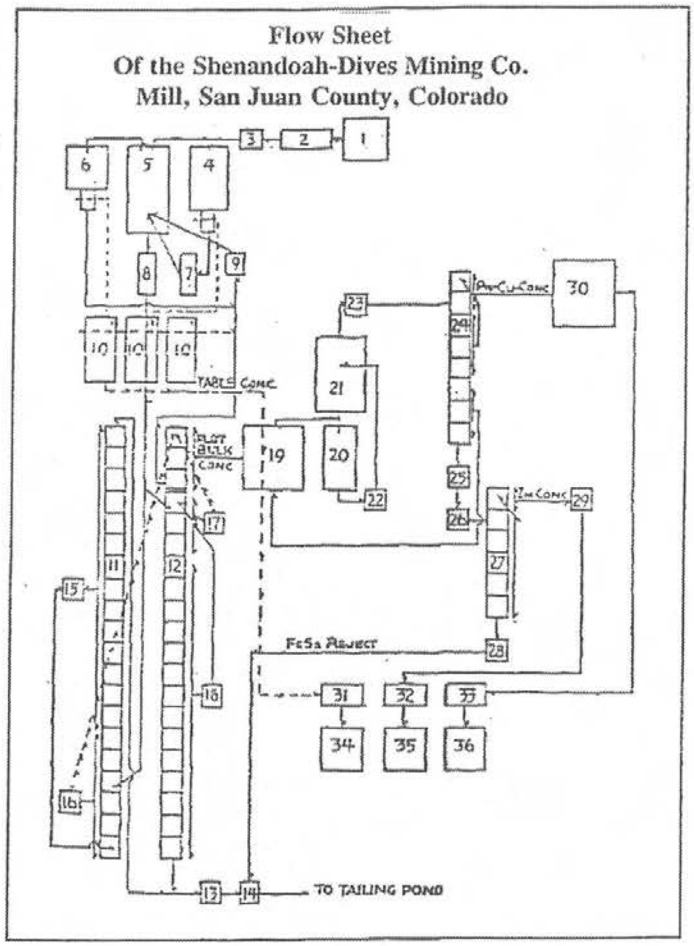


Fig. 2—Flotation Division, Shenandoah-Dives (Mayflower) Mill (Mining World June 1942: 12)

use.[17] Mills used either froth flotation, a wet-film process, agitation-froth flotation, or the Elmore vacuum.[18] Eventually, only froth flotation remained economically viable.

In August 1911, James Hyde experimented with froth flotation in the Basin Reduction Company Mill in Basin, Montana. Butte and Superior Copper Company for Hyde's experiments leased the Basin Mill. When the lease expired in 1912, Butte and Superior designed and built a mill at the Black Rock Mine in Butte, Montana. This mill was recognized as the first commercial froth-flotation plant in the United States. The facility used gravity concentration in the first three stages and froth flotation in its final stage.[19]

By 1914, there were forty-two American mining companies using froth flotation in their mills.[20] Skin and bulk-oil flotation soon became obsolete. The first mill to use only the flotation process was the Engels Mine and Mill in Plumas County, California in 1914.[21] In 1914, J. M. Callow at Miami Copper Company in Arizona developed and marketed his own version of pneumatic flotation cells, similar to the Minerals Separation Standard machine.[22] Metallurgists continued to experiment with reagent use on a variety of ores in the froth flotation process. Chemical agents, acid or alkaline, in the flotation process affected metal recovery in various ore bodies. The Sunnyside Mill at Eureka, San Juan County, Colorado was credited in 1918 with perfecting the flotation of two minerals (lead-zinc) from a complex ore.[23] C. H. Keller introduced xanthates (water-soluble froth collectors) into water baths in flotation circuits in 1925.[24] In 1932, G. K. Williams introduced the first continuous refining process.[25] However, the fundamentals of flotation had already been established by the end of the 1920s.

The development of flotation had a major impact on the mining world. In concentration, flotation replaced several of the earlier methods: gravity concentration, amalgamation, and leaching. In his 1932 text, *Flotation*, A. M. Gaudin attributed major changes in mining and milling metals to the development of flotation concentration. Flotation, in fact, had increased recovery and grade of concentrates and, at the same time, had decreased the cost of metal production and the price of metals in the market place. More importantly, Gaudin asserted, flotation increased the manufacturing use of metals in American industries.[26]

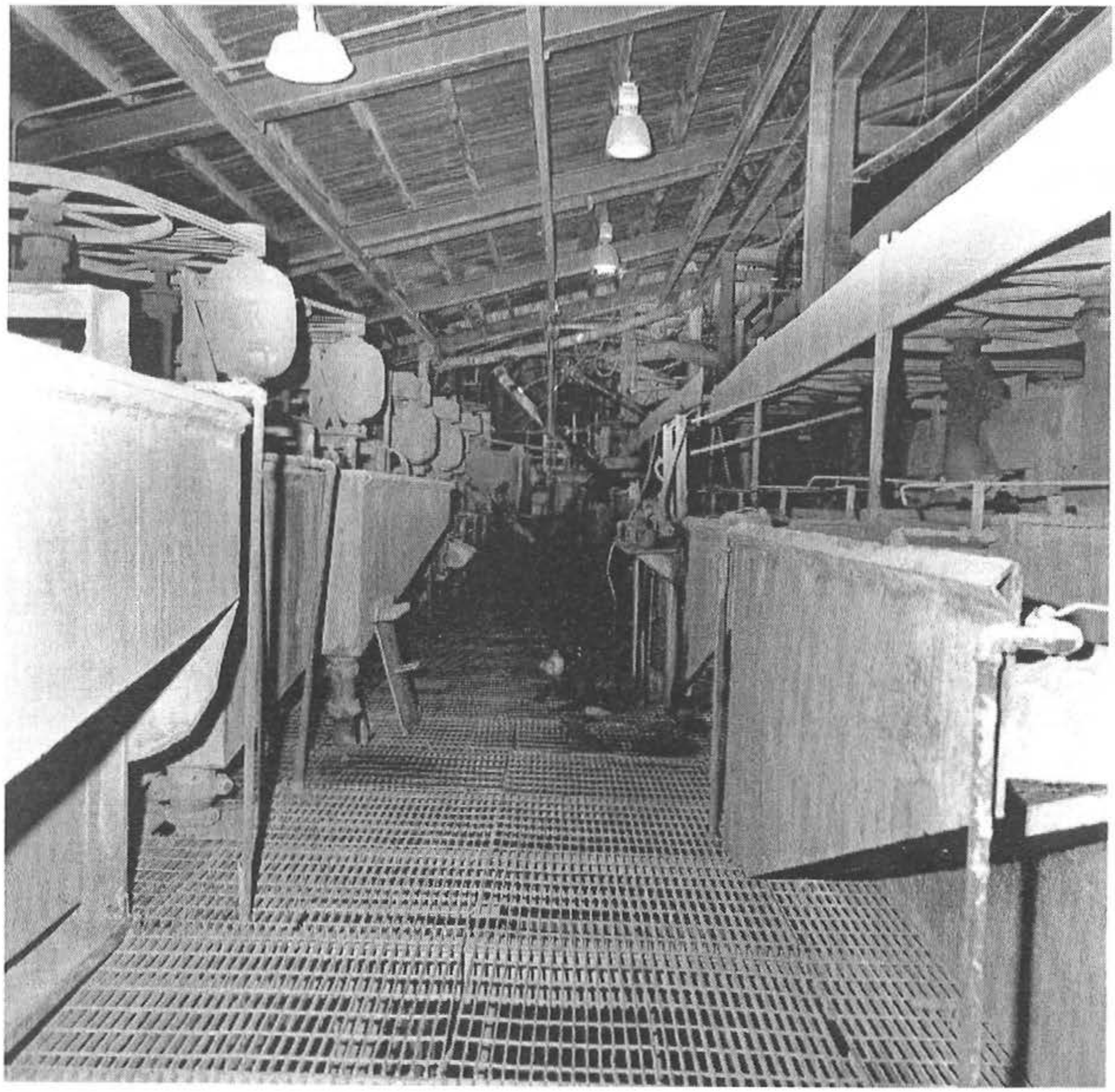
By the 1930s, froth flotation allowed mining and milling companies to recover low-grade ore and by-products once considered waste for profit. Construction of poly-metallic mills allowed the separation of more than one metal in a series of flotation circuits. Single circuit plants continued to be useful in many regions. New poly-metallic mills were larger in size, generally processing 750 to 2,000 tons per day to accommodate multiple circuits and ore bins. Financially strong companies in the industry made a move to consolidate mineral patents. Mills and their equipment also expanded in size and processing capability. By the 1940s, mining companies also increased their use of open-pit mines, which greatly increased the amount of ore extracted. As a result of increased ore extraction, the size of mills grew exponentially to accommodate ore delivered to the mills. New mills had multiple buildings in complexes that

Shenandoah-Dives (Mayflower) Mill, Silverton, San Juan County, Colorado, San Juan County Historical Society, Silverton, Colorado.

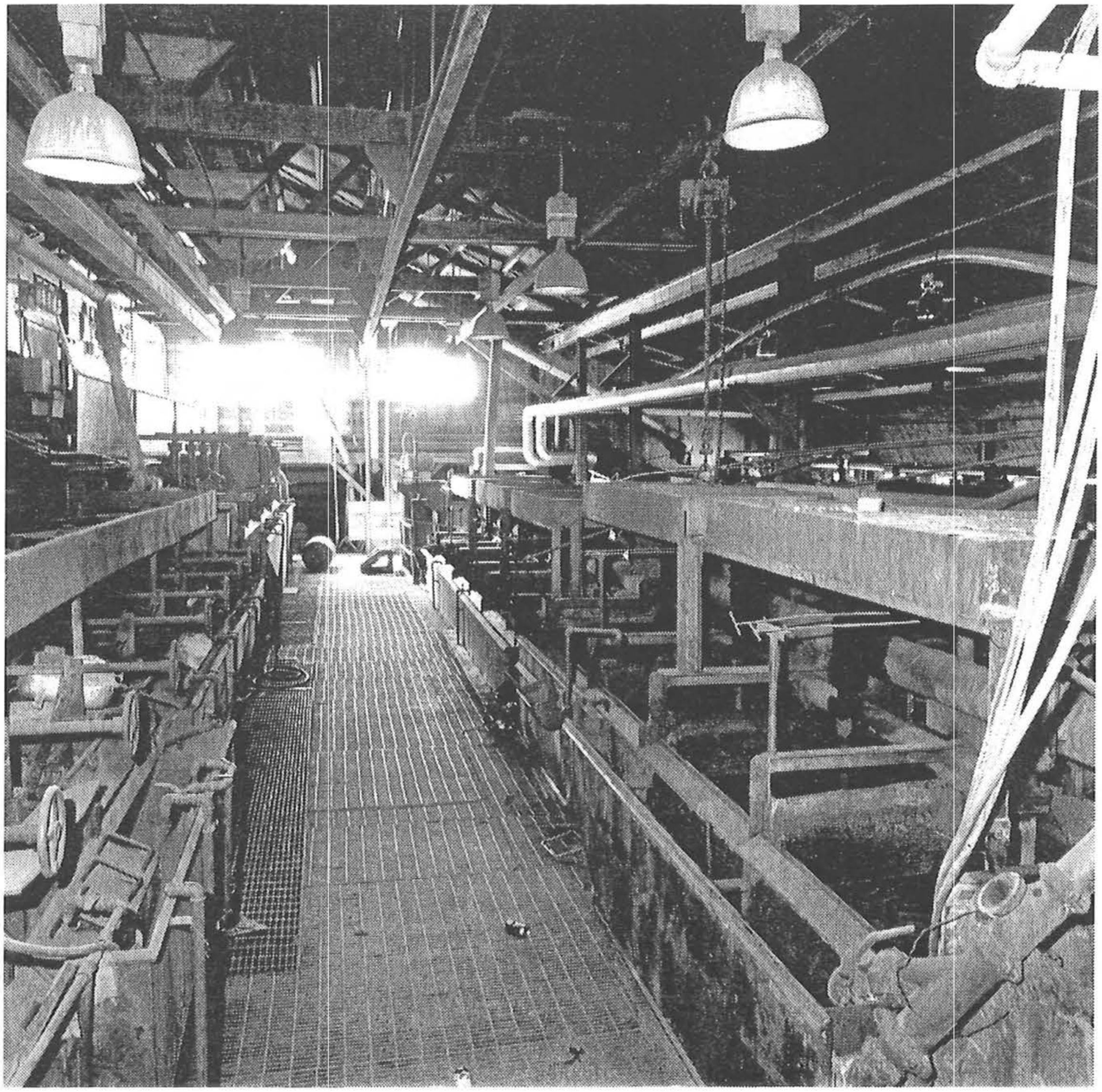
covered acres of land.

Mill expansion resulted in the replacement of obsolete or exhausted operations. By the 1960s, engineers designed larger electric generators, which allowed for variable speed drives in mills. Even larger sizes of mill equipment could be built and operated with this increased horsepower. New equipment allowed for the addition of automatic controls and instrumentation. When small mills could not be adequately developed, new and larger plants were constructed on those sites.

In 1960, 202 flotation plants were operating in the United States. These mills processed metallic minerals, nonmetallic minerals, bituminous coal, anthracite, waste paper, and miscellaneous materials. Of the metallic-mineral mills, 30 per cent processed copper, lead and zinc. An additional 26 per cent processed lead-zinc.[27] In addition, industries altered the flotation process to fit their particular needs, whether it was non-metallic minerals, coal or paper industries.



No. 18 Denver Flotation Cells. Interior of Shenandoah -Dives Mill, Silverton, Colorado San Juan County Historical Society, Silverton, Colorado.



20-Cell No. 21 Minerals Separation Flotation. Interior of Shenandoah -Dives Mill, Silverton, San Juan County, Colorado, San Juan County Historical Society, Silverton, Colorado

Conclusion

Flotation had a profound affect on the mines and minerals industry, as well as industry as a whole, by providing all the needed metals at a lower price than otherwise would have been possible. Principally, flotation shifted the focus of the mining industry from extraction of high-grade ores to one featuring complex and low-grade ores. Without flotation the mining industry would have collapsed by the 1950s.

Flotation essentially reorganized the industry. It allowed *non-selective* mining and *selective* milling practices. Miners extracted vast quantities of metals from underground mines, while the mill men worked to separate valuable metals in the mill on the surface. The mining industry extracted ores that had minimal quantities of valuable metals, often difficult to extract, locked in tons of waste rock. In the flotation process, the mill men were able to selectively isolate metals, which were profitable or desirable, from the waste. Flotation also increased the recovery and grade of concentrates without increasing the tonnage or the grade of the ore. In 1962, mining engineers Charles Merrill and James Pennington wrote an essay on new resources available in U.S. flotation mills, which was included in *Froth Flotation, 50th Anniversary*. They found that flotation increased production with twenty-four metallic and nineteen non-metallic ores since the commercial success of flotation in 1905. Many modern engineers believe that flotation was the most important twentieth-century development in the recovery of metals.

Notes

1. Jeremy Mouat, "The Development of the Flotation Process: Technological Change and the Genesis of Modern Mining, 1898-1911," *Australian Economic History Review* 36, no. 1 (March 1996): 4.
2. "The Trend of Flotation," Colorado School of Mines Magazine (January 1930): 20; Mouat, "Development of Flotation," 4; author's phone interview with Richard Graeme on 10 July 1997 concerning developments in twentieth-century mining; and Charles White Merrill and James W. Pennington, "The Magnitude and Significance of Flotation in the Mineral Industries of the United States," in *Froth Flotation 50th Anniversary* (New York: American Institutes of Mining, Metallurgical and Petroleum Engineering Inc., 1962), 56-57.
3. *Flotation Fundamentals and Mining Chemicals* (Midland, MI: Dow Chemical Co., 1968), 8.
4. Mouat, "Development of Flotation," 6 and *Flotation Fundamentals*, 11.
5. Thomas Rickard, *Concentration by Flotation* (New York: John Wiley and Sons, Inc., 1921), 408.
6. E. H. Crabtree and J. D. Vincent, "Historical Outline of Major Flotation Developments," in *Froth Flotation 50th Anniversary Volume*, D. W. Fuerstenau, editor (New York: The American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., 1962), 39.
7. Robert Richards, *Textbook of Ore Dressing* (New York & London: McGraw-Hill Book Co., Inc., 1932), 233, and Crabtree and Vincent, "Historical Outline," 39.
8. Rickard, a leading engineer in twentieth-century mining, disputed Carrie Everson's stature as an innovator in the milling world. He did not disclaim her findings, but was distressed that the findings were attributed to Carrie Everson. Rickard wrote several articles discussing the topic including an article called, "Everson Myth" in the January 15, 1916 issue of the *Mining and Scientific Press*. Rickard was editor of the journal.
9. Crabtree and Vincent, *Froth Flotation*, 40.
10. Rickard, *Concentration*, 8.
11. C. Terry Durell, "Universal Flotation Theory," *Colorado School of Mines Magazine* 6 (February 1916): 27.
12. Durell, *Colorado School of Mines Magazine*, 28; and Crabtree and Vincent, *Froth Flotation*, 42.
13. Theodore J. Hoover, *Concentrating Ores by Flotation* (San Francisco: Mining and Scientific Press, 1914), 20.
14. Crabtree and Vincent, *Froth Flotation*, 40.
15. Adrian C. Dorenfeld, "Flotation Circuit Design," in *Froth Flotation 50th Anniversary*, 365.
16. Dorenfeld, "Flotation Circuit Design," 370-1.
17. Durell, "Universal Flotation Theory," 29-30.
18. Durell, "Universal Flotation Theory," 29-30; and Crabtree and Vincent, *Froth Flotation*, 42-43. For more details on Hyde's familiarity with Minerals Separation's process refer to Pierre Hines and J. D. Vincent=s essay, "The Early Days of Froth Flotation," in *Froth Flotation 50th Anniversary Volume*.
19. Richard O. Burt and Chris Mills, *Gravity Concentration Techniques* (Amsterdam, Oxford, New York: Elsevier, 1984), 17 and Hines and Vincent, "Early Days of Froth Flotation," 12-14.
20. Hines and Vincent, "Early Days of Froth Flotation," 29, citing G. A. Roush, *The Mineral Industry, 1914* (McGraw-Hill Book Co., New York, 1915).
21. Hines and Vincent, "Early Days of Froth Flotation," 28.
22. Richards, *Textbook of Ore Dressing*, 234.
23. Hines and Vincent, "Early Days of Froth Flotation," citing Editorial, *Engineering and Mining Journal* 125 (Feb. 4, 1928): 195.
24. Crabtree and Vincent, "Historical Outline," 45.
25. Cedric E. Gregory, *A Concise History of Mining* (New York: Pergamon Press, 1980), 140.
26. A. M. Gaudin, *Flotation* (New York: McGraw-Hill Book Co., Inc., 1932), 534.
27. Merrill and Pennington, "The Magnitude and Significance of Flotation," 56-57.
28. Flotation is used in the processing of copper, copper-molybdenum, copper-lead-zinc, copper-zinc-iron-sulfur, gold-silver, lead-zinc, barite, bastnaesite, calcite, garnet, kyanite, and talc. Clay, feldspar, mica, quartz, spodumene, waste paper are processed by flotation. Flotation concentrates fluorspar, glass sand, ilmenite, magnesite, iron oxide, manganese, tungsten, phosphate, anthracite, bituminous coal, chicle, naphthalene and oil.