# STATE OF TENNESSEE DEPARTMENT OF CONSERVATION DIVISION OF GEOLOGY

INFORMATION CIRCULAR No. 14

# THE COPPER-SULFURIC ACID INDUSTRY IN TENNESSEE

By STUART W. MAHER



NASHVILLE, TENNESSEE

1966

# STATE OF TENNESSEE

FRANK G. CLEMENT, Governor

# DEPARTMENT OF CONSERVATION DONALD M. McSWEEN, Commissioner

DIVISION OF GEOLOGY
WILLIAM D. HARDEMAN, State Geologist

# PREFACE AND ACKNOWLEDGEMENTS

This report was prepared to acquaint the reader with one of Tennessee's most important mineral industries. Tennessee produces a diversity of mineral products in all three Grand Divisions. These industries now yield more than \$170 million of new wealth annually. The mining, milling, and treatment of copper ores and related minerals are large contributors to this wealth and are of national as well as local importance.

Mining in the Copper Basin, Polk County, dates from shortly after the removal of the Cherokees to the West in 1838 and has continued with varying success and periods of inactivity until the present. As the following pages will demonstrate, the enormous and diversified operations now in the Basin are a tribute to American technical skill and applied industrial research. This history also emphasizes how materials once regarded as waste or of too low quality become, through improved technology and changes in the economy, major sources of income.

This report was prepared under the supervision of W. D. Hardeman, State Geologist, whose able assistance is gratefully acknowledged. Robert J. Floyd of the Division of Geology was of great help in editing the manuscript.

The writer gratefully acknowledges the valuable information furnished and the courteous cooperation extended by the Tennessee Copper Company. Special thanks are due the Company for writing the section on Milling and for reviewing the entire report.

# CONTENTS

| P   | age                                     |  |  |
|---|---|--|--|
| Preface and acknowledgements                                  | . iii                                   |  |  |
| History and production  |   |  |  |
| Early industry  | . 1                                     |  |  |
| Modern industry   |   |  |  |
| Present mines and mills                                       |   |  |  |
| Geology   |   |  |  |
| General   |   |  |  |
| Tennessee   | 1,00                                    |  |  |
| Exploration for new deposits                                  |   |  |  |
| Mining  |   |  |  |
| Milling of the ore  |   |  |  |
| Copper smelting   |   |  |  |
| Iron sinter   |   |  |  |
| Ferric sulfate (Ferri-Floc)                                   |   |  |  |
| Sulfuric acid   |   |  |  |
| The contact acid process                                      |   |  |  |
| The contact acid process                                      |   |  |  |
| Copper sulfate  |   |  |  |
| Fungicides  |   |  |  |
| Organic chemicals   |   |  |  |
| Sodium hydrosulfite   |   |  |  |
| Marketing   |   |  |  |
| Marketing   | .19                                     |  |  |
| Copper in general19   |   |  |  |
| Price   | 110000000000000000000000000000000000000 |  |  |
| Tariffs   |   |  |  |
| Products other than copper23                                  |   |  |  |
| Sulfuric acid   |   |  |  |
| Iron sinter24   |   |  |  |
| Zinc24  |   |  |  |
| Economic significance   |   |  |  |
| Uses of copper24  |   |  |  |
| Uses of sulfuric acid   |   |  |  |
| Uses of liquid sulfur dioxide25                               |   |  |  |
| Potential and outlook   |   |  |  |
| Economic contribution by the industry27                       |   |  |  |
| Selected references   | .27                                     |  |  |
|   |   |  |  |
| ILLUSTRATIONS   |   |  |  |
|   |   |  |  |
| Figure 1. Topographic map of the Copper Basin area            |   |  |  |
| 2. Generalized flow sheet of milling and processing           | .15                                     |  |  |
| 3. Yearly average price of copper, f. o. b.                   |   |  |  |
| refineries, in cents per pound                                | .22                                     |  |  |
| MADYE   |   |  |  |
| TABLE   |   |  |  |
|   | 4.0                                     |  |  |
| 1. Copper (recoverable content of ores) produced in Tennessee | .10                                     |  |  |

# THE COPPER-SULFURIC ACID INDUSTRY IN TENNESSEE

By

# STUART W. MAHER<sup>1</sup>

# HISTORY AND PRODUCTION

# Early Industry

The area of Tennessee that was destined to become known as the Copper Basin lies in Polk County. In the early 19th century this mountainous section was heavily forested and inhabited chiefly by the Cherokee Indians. In 1838 these Indians were moved by the United States Army to territory west of the Mississippi River, and the land was made available to white settlers. To some extent removal of the Indians was effected at this time because of the discovery in 1827 of gold-bearing gravels on Coker Creek and the ensuing rush of prospectors into the area organized into Polk and Monroe Counties (Polk County was organized in 1839 and Monroe County in 1819).

Safford (1869, p. 471) attributes the discovery of copper to a gold prospector named either Semmons or Lemmons who in 1843 recovered native copper from a stream near the future site of the Hiwassee mine. Later others discovered "black copper" (chalcocite) ore, but the significance of these discoveries was not recognized. The earliest recorded shipment of copper ore was made in 1847 by a German, variously identified as "Mr. Weber," "Webber," and "A. J. Weaver," who leased the site of the "black ore" from the owners and shipped 90 casks of ore weighing some 31,000 pounds to a smelter near Boston. The casks were divided into two lots. One lot of 18,750 pounds averaged 32.5 percent copper, and the other lot of 12,460 pounds averaged 14.5 percent copper

<sup>&</sup>lt;sup>1</sup> Principal Geologist, Tennessee Division of Geology, Knoxville.

(Safford, 1869, p. 471-472). This shipment is said to have been hauled by mules from the mine to the railroad at Dalton, Georgia.

In the same year (1847) B. C. Duggar built an iron furnace near the mouth of Potato Creek to smelt ore from the gossan later developed into the Cherokee mine. Unfortunately for Duggar, his iron ore was taken from the lower part of the gossan and was relatively rich in copper. This rendered the iron brittle or "redshort" and consequently unusable. Had Duggar's ore come from higher in the gossan zone, his enterprise probably would have succeeded.

By 1850 the significance of the Ducktown deposits was becoming appreciated, and in that year the Hiwassee mine was opened by T. H. Calloway and the Cocheco mine by J. V. Symons (Emmons and Laney, 1926, p. 30).

Another pioneer miner was John Caldwell, who began mining the old Tennessee lode about 1850 and also opened the Polk County mine in 1852. Caldwell has left an interesting record of his entry into the mining business in the form of a letter reproduced by Safford (1869, p. 472-473):

Gentlemen:—I came to Ducktown in 1849, scouting for copper, and found some five or six tons in a cabin, ten feet square, on the property now known as the Hiwassee. I found the country unexplored—the school section, a property now worth a million of dollars, attracting little or no attention. Sat down in the woods for three hours, to mature a plan to control and open the section. I owned, at the time, one twenty dollar bill. After three hours' reflection, resolved to call a meeting of the citizens of the township, and make a speech explanatory of the value of the school section, and of the importance of leasing it for mining purposes. Told the people that as soon as the mines could be opened, their condition would be improved, and that civilization, intelligence, comfort and wealth, would be the inevitable results. At the conclusion of this remark, a speaker arose in the crowd, and informed me that a large portion of the inhabitants had come here to get away from civilization, and if it followed them, they would run again.

After the speech was made, drew up a memorial to the Legislature, praying the passage of a law authorizing the commissioners to give a mining lease on the school section. The memorial was signed by a majority of the citizens, and, on personal application, the law was passed, and under it the lease was taken.

In May, 1850, commenced mining in the woods. In the same year sunk two shafts, and obtained copper from both of them. The excavations made did not exceed twelve feet—at that depth the copper being found. Commenced mining at the Hiwassee Mine in 1851, in connection with S. Congdon, the

agent of the Tennessee Mining Company. Built a double cabin, and taught Sabbath-school in the kitchen end of the establishment, aided by young Mr. Walter Congdon.

Perhaps the most difficult problem that faced these early copper miners was the lack of roads and railroads into the Copper Basin. Caldwell began construction of a wagon road in 1851 from the Basin along the Ocoee River gorge to Cleveland, a railroad station 30 miles closer to the mines than Dalton, Georgia. Caldwell was assisted in the later stages by the Tennessee Company and the Hiwassee Company; the road was completed in 1853 at a cost of \$22,000 (Safford, p. 473). This road, in conjunction with the extension of the railroad to Cleveland, led to a boom in the development of the Copper Basin. By 1855 all the major lodes in Tennessee were known, and Safford (p. 475) lists 14 mines which had been opened by that year and reports they had shipped 14,291 tons of ore.

The first smelter was built on Potato Creek in 1854 near the Old Tennessee mine, but it was not operated successfully until 1856. In 1855 other smelters were erected and operated at the Eureka, Hiwassee, and Polk County mines and another was built on Potato Creek.

A consolidation of the Old Tennessee, Mary, Calloway, Isabella, Cherokee, and other properties was effected in 1858 to form the Union Consolidated Company. This company began recovering copper from mine water so successfully that Safford reports 40,000 pounds a month was thus produced at three mines in 1859. In the same year two of their smelters produced the first ingot copper (Safford, p. 475).

The Union Consolidated Company and others joined to build a refinery at Cleveland, which led another company to establish a wire and rolling mill there.

The outbreak of hostilities in 1861 initially stimulated the young industry and about 1,000 people were employed, but by 1862 its operations were being slowed through losses of skilled labor. In 1863 the Federals occupied Cleveland and destroyed the refinery and rolling mill. This ended mining in the Basin.

By this time the inroads on the forest made by the cutting of trees for fuel and by the destruction of trees resulting from poisonous fumes driven off in smelting the ores began to be apparent.

The Union Consolidated Company resumed its activities in 1866 under the management of Julius E. Raht, a young German engineer who had been active in the Basin since 1854. Under his vigorous leadership the years from 1866 to 1877 were marked by great progress. In this period the principal smelters were located at Isabella and near the Old Tennessee mine on Potato Creek. Increase of production led to exhaustion of the high-grade "black ores" (chalcocite), and mining of primary yellow sulfides (chalcopyrite) began at the Mary and East Tennessee mines. Three stamp mills and jigs were installed. These mills worked successfully on ore from the East Tennessee mine, but the ores from the Mary and Isabella mines contained too much brittle pyrite and pyrrhotite to be amenable to stamping. Furthermore, the Basin's timber supply had been so reduced by cutting for fuel that by 1876 cordwood was being cut in Fannin County, Georgia, and floated down the Toccoa River to the Basin.

The depletion of the high-grade ore and lower prices for copper metal led to litigation and receivership for the Union Consolidated Company in 1877; similarly, the Polk County Mining Company failed in 1878 or 1879. From the War Between the States to this closing of the mines 24 million pounds of copper was produced, and about 50 square miles of the Basin was stripped of trees for fuel. No mining or development took place from 1879 to 1890.

The Marietta & North Georgia Railroad (subsequently the L. & N.), connecting Knoxville with Marietta and Atlanta, was completed in 1890. This made it possible to ship coke and other supplies to the Basin at low cost; and taken in conjunction with improved smelting technology, caused renewed interest in the ores of the district.

The Union Consolidated Company's holdings were acquired by the Ducktown Sulphur, Copper and Iron Company of London, England. In 1890 this company reopened the Mary mine and soon thereafter built a Herreshoff copper furnace of 100 tons daily capacity at Isabella. This furnace was designed for the successfull smelting of the primary sulfide ores of the district. In 1893 the Ducktown Sulphur, Copper and Iron Company shipped 632,000 pounds of copper. A second furnace was built, and by 1901 production was 3 million pounds of copper annually. Later this company erected a 200-ton sulfuric acid plant to utilize the sulfur in the ores.

A second company, the Pittsburgh and Tennessee Copper Company, leased the Old Tennessee mine in 1891 and subsequently the Polk County mine. A mill was installed in 1894.

As related above, an effort to mine and smelt the gossan iron was made in 1847 but failed because the ore mined was taken from too near the copper zone. Some iron ore was mined successfully from the gossans during the War Between the States, but as in the instance of copper, the main iron mining period began with railroad access to the basin. In the early 1890's the London Iron & Coal Company mined the Isabella gossan under terms of a lease and shipped iron ore to furnaces in Tennessee and Virginia.

Virginia Iron, Coal and Coke Company began mining gossan iron in 1894 and ended their operations in 1907. These gossan ores are said to have been higher in iron than most southeastern limonite and red hematite ores, and also notably low in phosphorus. Emmons and Laney (1926, p. 33) estimate that 1.5 million tons of iron ore averaging 43 percent iron was mined from the gossans.

Gossan ore was exhausted in 1907; but, as previously indicated, a high-grade iron sinter has been prepared by Tennessee Copper Company since 1925.

### Modern Industry

Extensive drilling of the Burra Burra and London lodes beginning in 1897 led to the formation in 1899 of the Tennessee Copper Company. This company purchased the Burra Burra, London, Eureka, Boyd, and Culchote mines and leased the Old Tennessee and Polk County mines. A new smelter was installed at Copperhill, and a railroad was built from Ducktown to Copperhill. Mining began in 1901 at Burra Burra, and by 1903 annual production reached 10 million pounds of copper.

The "open roasting" of ores ended in 1904, when the pyritic process of smelting was begun successfully at Isabella. Thus, in 1906 Tennessee Copper Company began construction at Copperhill of a chamber process acid plant which began production in late 1907. This ended the discharge of sulfurous gases to the air. A second unit was installed in 1910. This plant contained nearly 8 million pounds of lead and cost \$1,689,925. Its annual capacity was 168,000 tons of 60° acid.

Similarly, the Ducktown Sulphur, Copper and Iron Company began construction of an acid plant in July 1908 and began production of acid in June 1909.

The combined output of these plants in 1911 was estimated at 205,000 tons of acid (Nelson, 1912, p. 30-34). This made Tennessee

the site of one of the largest acid plants in the world, a situation still maintained.

A major improvement in ore processing came with the construction of the London Flotation plant in 1922. This made possible the recovery of an iron concentrate suitable for making iron sinter, a high-grade iron oxide first produced in 1925. Flotation also led to recovery of zinc concentrates beginning in 1927. Previously zinc had been lost in milling the ore, which contains about 1 percent zinc.

In 1922 Tennessee Copper Company began production of copper sulfate, by using copper and sulfuric acid produced locally.

The final consolidation of property in the Copper Basin took place in 1936, when Tennessee Copper Company purchased the Ducktown Chemical & Iron Company's holdings.

Modernization of mining and milling procedures, and the manufacture of new products, continued in the 1940's. In 1940 Tennessee Copper Company began operating a reverberatory furnace for the production of matte, the first stage in making blister copper. The Basin's acid-making capacity was supplemented in 1942 by construction of a large contact sulfuric acid plant at Copperhill. In 1949 liquid sulfur dioxide production was started from a new plant.

Improved mining and milling techniques, which provide for better separation of ore minerals from waste rock, have led to the mining of large bodies which 30 years ago were without value. Mining these large low-grade ore bodies (which average 26 percent sulfur, 36 percent iron, and less than 1 percent copper and zinc) permits increased mechanization in mining and consolidation of underground operations.

Recently new plants have been built to produce organic sulfonates (1952) and flotation reagents (1959); and a new shaft was sunk (the Cherokee) to reach ore on the "School" property. Also a plant to utilize iron oxide and acid to make "Ferri-Floc," a water purifier, was constructed in 1959. In 1958 all flotation was consolidated in the London mill.

The Tennessee Copper Company is a subsidiary of Tennessee Corporation (formerly Tennessee Copper and Chemical Corporation). In 1962 discussions began between Tennessee Corporation and Cities Service Company concerning a merger. Tennessee Corporation stockholders approved the merger March 19, 1963. The combination was effected June 14, 1963, by acquiring the Tennessee

see Corporation as a wholly-owned subsidiary of Cities Service, and exchanging shares of Tennessee Corporation stock for a new issue of callable, cumulative, preference Cities Service stock. At the date of the Cities Service merger, Tennessee Corporation consisted of three operating divisions: Tennessee Copper; U. S. Phosphoric Products, Tampa; and Miami Copper, Miami, Arizona (T. C. Topics).

#### Present Mines and Mills

All mines and mills currently operating in Polk County are owned by Tennessee Copper Company. During the 1950-1960 decade this company recovered ore from the Boyd, Burra Burra, Calloway, Eureka, and Mary-Polk County mines (fig. 1). The Burra Burra was closed in July 1958, after being operated from 1850 (as an open-cut 1859 to 1899) and having the longest record of continuous production and the largest production of any mine in the district.

Development of the Cherokee-School property, as related previously, began with shaft sinking in 1959.

Tennessee Copper Company operates a flotation mill at London to classify the raw ore into copper, iron, and zinc concentrates and waste; a copper smelter and converter at Copperhill; and five contact acid plants at Copperhill and Isabella. The liquid sulfur dioxide, copper sulfate, detergents, and organic chemicals plants are located at Copperhill. Iron sintering is done at Copperhill and Isabella. Most recently a plant to manufacture flotation chemicals has begun production at London, and a plant to make "Ferri-Floc" was constructed at Copperhill in January 1959.

The flotation plant has a rated daily capacity of 4,800 tons; the copper smelter is rated at 11,000 tons annually. The capacity of the acid plants was reported to be 765,500 tons annually, 100 percent acid basis (Jermain, 1953). However, another contact plant was placed in operation in 1954.

A major change in sulfuric acid manufacture in the Copper Basin was effected in July 1964. The chamber process plant rated at 850 tons daily capacity was replaced by an equivalent sized contact plant. This development means that all acid manufacture is by the contact process, which results in a more concentrated (98 percent), pure acid. The Tennessee Copper Company says it this way: "From beginning to the final products (usually 98 percent acid), the process is a highly automatic one, of push-button efficiency typical of sulfuric acid production today. Acid now being

made at No. 4 plant is crystal clear, as compared to weak, 77.7 percent, and dingy product of the chamber process." (T. C. Topics, vol. 13, No. 5, August 1964).

Sulfuric acid plants also are located in Nashville and Memphis as well as in the Copper Basin. However, these plants use elemental sulfur from the Gulf Coast as raw material, rather than sulfide ore minerals. Capacity of these plants in 1953 was 46,267 tons (Nashville) and 12,500 tons (Memphis), annually (Jermain, 1953).

#### **GEOLOGY**

#### General

A group of copper-bearing ore deposits lie along the Appalachian Mountain chain from central Virginia to eastern Alabama (Ross, 1935, p. 17). These deposits have many similar geologic features; and because of size and large-scale development, the deposit at Ducktown has commonly come to be chosen to typify these related ore deposits. Thus, the geologic literature uses the expression "Ducktown-type deposits" for them.

Ducktown-type deposits are found in strongly faulted and folded rocks that are also pervasively metamorphosed. The enclosing rocks are chiefly ancient sediments, originally conglomerates, sandstones, and shales, subsequently altered to slates, gneisses, and reconstituted conglomerates. The metamorphic processes also produced minerals not in the original sediments, notably micas, garnets, and staurolite. Two episodes of metamorphism are evident.

The host rocks of the ores not only were altered metamorphically, but also were dislocated, moved, folded and faulted by the processes that formed the Appalachian Mountains. As a consequence of this history the geology of the Ducktown-type deposits is complex; and the history and origin of the ore minerals themselves is not completely known and agreed upon by various workers.

The ores occur in the metamorphosed host rocks as veins and massive lodes of sulfide minerals below the zone of weathering. The principal sulfides are those of iron, pyrite and pyrrhotite; but the copper sulfide, chalcopyrite, the zinc sulfide, sphalerite, and locally lead sulfide, galena, also are found. Smaller amounts of the iron oxide, magnetite, and of gold and silver also are found in many of the deposits.

This complex ore assemblage originally was introduced into the rocks well below the depth of weathering by ore-bearing solutions of unknown origin. Subsequent uplift of the entire mineralized rock mass and erosion brought the deposits under the influence of atmospheric oxygen and downward percolating water of surface origin. In such an environment sulfides are unstable and alter to secondary iron and copper minerals, such as limonite (iron hydroxide), chalcocite (Cu<sub>2</sub>S), covellite (CuS), and cuprite (Cu2O). Through this process a zone enriched in iron ores is formed at or near the surface, with an underlying zone of copper enrichment beneath the iron ores and extending beneath the water table. Below the zone of water saturation the primary leaner sulfide ores occur. The weathered, oxidized, and enriched zone is termed a "gossan" from the Spanish word for iron hat. It was these gossan ores that were initially mined in Tennessee. They have long been exhausted, so that mining since the turn of the century has consisted essentially of recovery of the primary sulfide ores.

#### Tennessee

The Copper Basin of Polk County is the only known location in Tennessee where copper-bearing ores occur in commercial amount and grade. These deposits are similar to other Appalachian deposits discussed previously but are larger. Some other deposits were higher in the percentage of contained copper, but such grade of ore was rather quickly exhausted. Furthermore, Tennessee's production has been developed in such a way that all the values in the ore (sulfur, zinc, iron, and precious metals, as well as copper) are recovered (see Mining and Milling). To develop such an integrated recovery scheme successfully presupposes large reserves.

The Copper Basin deposits originally produced from the enriched gossan ores (see History) but the mines now, and for many years past, produce primary sulfide ores entirely. These ores are found in a sequence of shales, sandstones, and conglomerates metamorphosed to metagraywackes and intruded locally by gabbro dikes. The rocks also have been deformed intensely. Simmons (1950) has discussed the relations of rock structure and alteration to ore localization and recovery; and Hernon (open-file maps) has mapped the geology in the vicinity of the mines. Earlier reports by Emmons and Laney (1926) and Ross (1935) present studies of the geology, paragenesis, and origin of the deposits. Furthermore, the mines are under continuous study by geologists of the operating

company. Even so, no generally accepted theory of the origin and localization of the ores has resulted.

The Copper Basin deposits lie in a series of northeastward trending belts. A given belt or lode may be a few thousand feet long and as wide as 300 feet. Mining extends to 2,400 feet below sea level. The lodes are therefore great lenses of heavy sulfide ore.

The amount of ore in a particular lode or portion thereof can be enormous. Total production from Burra was 15,636,000 tons of ore from total ore reserve of 19,090,000 tons, a recovery of 82 percent (most of the unrecovered ore was in the form of support pillars). The average grade of the ore, estimated from available data, was 1.61 percent copper, 23.5 percent sulfur, 31.3 percent iron.

Copper in ore mined from Burra was 511,122,200 pounds, and sulfur in ore produced since sulfur recovery started in 1907 was 3,485,350 tons. Iron in ore since recovery of iron was started in 1925 was 2,008,060 tons, and zinc in ore since recovery started in 1927 was 196,825,000 pounds. (Data from Tennessee Copper Company, 1958)

The U. S. Bureau of Mines reports that in 1963 the various mines in the Basin produced 1,431,271 tons of ore that contained 13,717 short tons of recoverable copper metal (table 1), an average grade of 0.96 percent.

TABLE 1. COPPER (RECOVERABLE CONTENT OF ORES)
PRODUCED IN TENNESSEE.

| Year      | Short Tons | Value         |
|-----------|------------|---------------|
| 1948      | 6,693      | \$2,904,762   |
| 1949      | 6,489      | 2,556,666     |
| 1950      | 6,851      | 2,850,016     |
| 1951      | 7,069      | 3,421,396     |
| 1952      | 7,620      | 3,688,080     |
| 1953      | 7,829      | 4,493,846     |
| 1954      | 9,087      | 5,361,861     |
| 1955      | 9,911      | 7,393,569     |
| 1956      | 10,449     | 8,881,650     |
| 1957      | 9,790      | 5,893,580     |
| 1958      | 9,109      | 4,791,334     |
| 1959      | 11,490     | 7,054,860     |
| 1960      | 12,723     | 8,168,000     |
| 1961      | 12,272     | 7,363,000     |
| 1962      | 14,298     | 8,808,000     |
| 1963      | 13,717     | 8,450,000     |
| 1831-1963 | 547,095    | \$202,924,000 |

Copper minerals are known to occur in a few places outside the Copper Basin, but none of these prospects has indicated sufficient tonnage of ore grade to encourage development.

Pyrite was mined in Carter County in Strong Creek valley about 1900. This activity produced about 1,000 tons of iron sulfide but no copper (King and others, 1944, p. 188-189; anonymous, 1912, p. 71). Similarly, some pyrite was recovered in coal washing in the World War I period (Holbrook and Nelson, 1919). In both instances, the pyrite was sold to sulfuric acid plants and yielded no copper.

### Exploration for New Deposits

The Ducktown deposits are the largest known orebodies in a group of similar deposits that extend along the Appalachians from Alabama to Virginia. Similar deposits also are known in Vermont and Quebec (Ross, 1935, p. 17). Hence, a large area is regarded as favorable for prospecting. Obviously, smaller areas with known exposures of ore minerals in this belt are even more favorable. Deep soil cover, dense vegetation, and poor access make much of the region comparatively little known and difficult to explore. Furthermore, successful exploration not only involves arduous labor under difficult living conditions but requires considerable capital for geophysical surveying equipment and core drilling. If a potentially valuable deposit is located, high development costs are necessary to bring it into production.

# MINING 1

The ore from which our products are made begins its journey in one of our five mines. From this ore we produce copper, copper sulfate, iron sinter, sulfuric acids, fungicides, zinc concentrate, ferric sulfate, slag, liquid sulfur dioxide, sodium hydrosulfite, and organic chemicals. Except for some ingredients in the organic chemicals, sodium hydrosulfite, and fungicides, all the raw materials come from sulfide ore mined in the Copper Basin at the rate of about 1,300,000 tons a year.

Up to about 35 years ago copper and sulfur were the only

<sup>&</sup>lt;sup>1</sup> This section is quoted verbatim from *The Tennessee Copper Company Story*, A Handbook for Employees of the Tennessee Copper Company.

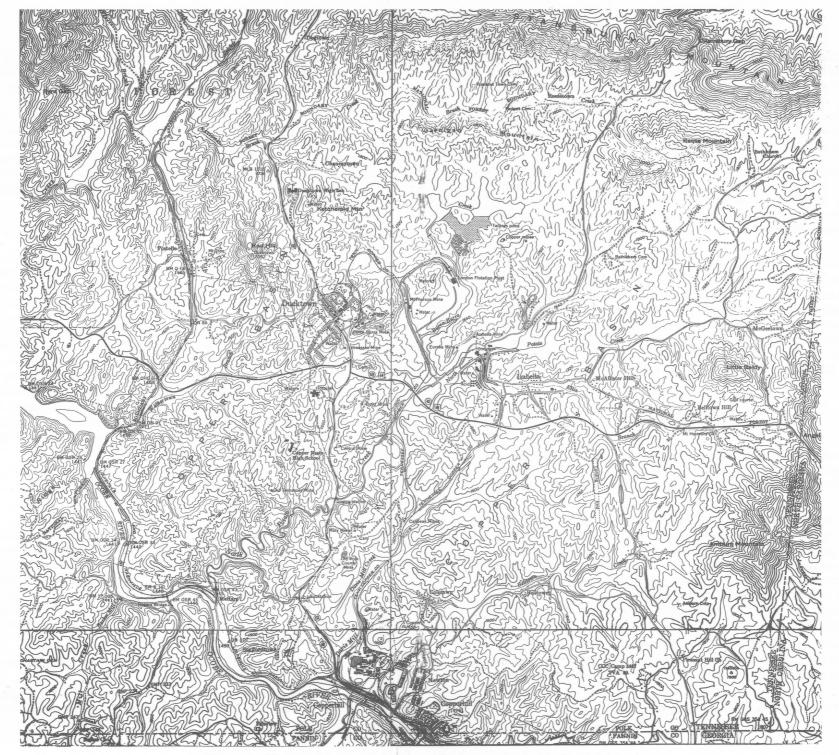


Figure 1. Topographic map of the Copper Basin area (scale 1 inch = 4,000 feet).

elements of value recovered from the ore. Consequently the orebodies with higher copper content were mined. As processes were perfected for successfully separating and processing iron and zinc minerals, other Basin orebodies of lower copper content became of commercial importance. These orebodies were larger and required improvements in mining methods and the installation of heavier equipment for profitable operation.

Whereas originally each mine was operated as a separate unit, improvements in development of the orebodies for mining and installation of larger hoisting equipment has made it practical to connect the various mines underground, and thereby increase efficiency through the use of common ore crushing and hoisting equipment.

Mining operations at TCC involve five stages for production of ore: development (getting to the orebodies); stoping (drilling and blasting); loading; hauling; crushing and hoisting. When ore is blasted it tumbles down to "draw points" where it is loaded by power shovels and drags into tram cars and then hauled by battery-powered motors to storage pockets near a hoisting shaft. Here it is fed through crushers, then hoisted to the surface, and hauled from mine to flotation plant by the TCC railroad.

# MILLING OF THE ORE 1

In the London Flotation Plant, the ore is processed to separate the mineral values from gangue (worthless rock), and then from each other, thereby obtaining copper, iron and zinc sulfide concentrates.

First, the ore is crushed and then ground finely in revolving rod and ball mills. In these mills, water is added to produce a pulp which is ground to the fineness necessary to free the minerals. Chemicals are added and the mixture moves into flotation machines which, by a combination of chemicals, mechanical agitation, and the release of compressed air, cause a heavy froth to rise to the surface, carrying with it the particular mineral or minerals to be concentrated.

The first step, "bulk flotation," removes all minerals from the worthless gangue (fig. 2). Subsequent steps separate and concentrate the sulfide minerals of copper, iron and zinc, which are then

<sup>&</sup>lt;sup>1</sup> This section was written by The Tennessee Copper Company.

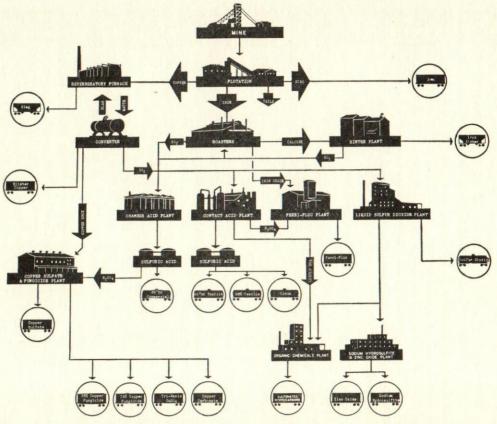


Figure 2. Generalized flow sheet of milling and processing (from The TCC Story).

dewatered, filtered and stored temporarily in bins. Copper and iron concentrates are hauled in Tennessee Copper Company railroad cars to the Smelting Department for further processing. Zinc concentrate is sold without further treatment to various zinc smelters. In the "flotation" process waste matter does not float, but in pulverized form is drawn off at the bottom of the float machines and pumped to a waste disposal lake, the "tailings pond." Flotation was introduced at Tennessee Copper Company in 1922 and constituted one of the most important technical changes ever made by the Company. Until that time, neither the iron nor the zinc in Basin ores could be recovered in the form of salable products, so that only copper, and beginning in 1907, sulfuric acid, were produced.

# Copper Smelting

From the mill the copper concentrate goes by rail to the Copperhill smelter, where it is first melted in a reverberatory furnace. The furnace is so named because its heat is reflected from roof and walls. Fuel used is pulverized coal. For transfer to the next process, the molten concentrate, "matte," is tapped or drawn out of the furnace into lined steel pots of 10 tons capacity.

The matte is treated in the Pierce-Smith converter, a barrel-shaped, bricklined vessel, in which compressed air is blown through the matte to burn out sulfur and produce sulfur dioxide gas, which then goes by flue to the Acid Plant for use in producing sulfuric acid. As a result of the heat generated in this process, other impurities are combined with silica flux, forming slag. Considerably lighter than the copper, the slag is readily skimmed off into pots and transferred back to the furnace where some residual copper is settled out of it. The slag is finally granulated by being poured into a stream of water, after which it is sold as an ingredient for cement.

The material remaining is molten copper sulfide. Blowing the material with air continues until all sulfur has been removed and the final product, "blister copper," is left. Blister copper, more than 99 percent pure, is solidified in either of two ways: into 2,500-pound rectangular slabs or "pigs" shaped in molds and shipped in the same form; or into pellets called "shot copper," used as a raw material in the Copper Sulfate Plant at Copperhill.

#### Iron Sinter

The iron sulfide concentrate from the flotation process goes to the Copperhill or Isabella plant for final treatment by roasting furnaces. This concentrate is burned much like coal in a blast of air. Large quantities of sulfur dioxide gas are thereby generated and drawn off through dust-cleaning apparatus before being conveyed through flues to the Acid Plants. The roasted concentrate (calcine) is flumed with water to large concrete tanks, then removed from these settling tanks by overhead crane. After dewatering, the calcine is transferred to the Sintering Plants.

Residual sulfur is burned and the fine particles are fused into lumps by the sintering process through application of intense heat to prepared calcines which move along a traveling grate. The resulting product is a spongelike mass called iron sinter, which falls from the traveling grate into railroad cars and is ready for shipment. TCC iron sinter is a high-grade iron-oxide product, assaying 68-70 percent iron, and is used by TCC customers in producing iron and steel.

### Ferric Sulfate (Ferri-Floc)

The sulfur dioxide gases that are liberated in the roasting and sintering of the iron sulfides contain high concentrations of iron oxide dust which are removed before the gases are suitable for conversion into sulfuric acid. These minute particles are called "flue dust," and are mixed with sulfuric acid and water to manufacture a partially hydrated ferric sulfate. This product is marketed under the trade name "Ferri-Floc" and is used principally as a coagulating agent in water and sewage treatment.

Ferri-Floc also is used in the manufacture of pigments, inks, the pickling of stainless steel and copper, weed control, and fertilizers.

Production of Ferri-Floc at the Tennessee Copper Company was started in 1959. Prior to that time flue dust from the Copper-hill plant was shipped to the Corporation's East Point, Georgia, and Lockland, Ohio, plants for conversion to this product.

#### Sulfuric Acid

Tennessee Copper Company's most widely known product, sulfuric acid, is made at the Copperhill and Isabella Acid Plants from gases captured during the smelting, roasting, and sintering processes. It is industry's most important chemical, being necessary to the manufacture of fertilizers, iron and steel, petroleum products, textiles, automobile batteries, and hundreds of other

articles for everyday living. One of the largest consumers is Tennessee Corporation, which uses it principally in the acidulation of phosphate rock to produce fertilizers.

#### The Contact Acid Process

Contact plants at Copperhill and Isabella produce acid of strengths ranging from 78 percent to the oleums, or fuming acids, which are 100 percent acid with additional amounts of sulfur trioxide gas dissolved in the acid.

In the two contact plants at Isabella and the three much larger ones at Copperhill, gases are cooled and cleaned of dust by scrubbing with water and then dried by scrubbing with sulfuric acid. This dried gas is noncorrosive and can be handled through ordinary steel apparatus. The sulfur dioxide gas (SO<sub>2</sub>) is converted to the trioxide (SO<sub>3</sub>) by passage through converters packed with a vanadium oxide catalyst. The trioxide is absorbed in towers through which a large volume of strong acid is circulated. Although the acid's strength tends to increase as the gas is absorbed, constant strength of about 99 percent is maintained by the addition of water. Volume increase is bled off as marketable acid and stored in large tanks, awaiting shipment in railroad tank cars and trucks.

# Liquid Sulfur Dioxide

Production of liquid sulfur dioxide, one of the newer Tennessee Copper Company products, was begun in Copperhill in the year 1949. This product is made by extracting pure sulfur dioxide gas from roaster gas. It is shipped by tank truck, railroad tank cars, drums, and cylinders of various sizes. Liquid sulfur dioxide has many industrial uses: as a bleaching agent in textile mills and sugar refineries; as an aid in extracting vegetable oil from cotton-seed and other agricultural products, and one of the latest uses—as a preservative for silage.

# Copper Sulfate

The copper sulfate plant uses two TCC products, shot copper and sulfuric acid, as basic materials. At the copper sulfate plant, shot copper is dissolved in hot sulfuric acid agitated with compressed air, copper sulfate crystals forming when the solution is cooled. Copper sulfate is used in fertilizer mixtures, chemical processing, plating, flotation metallurgy, inks, animal feeds, and for algae control in water purification. These crystals are produced in several sizes to meet customer requirements.

#### **Fungicides**

Some of the copper sulfate solution is used in the Tennessee Copper Company Fungicide Plant where several copper products are created by various chemical additions. One of the best known Tennessee Copper Company fungicides, Tri-Basic Copper Sulfate, is of special value to farmers and gardeners in controlling tomato blight.

### Organic Chemicals

An organic chemicals plant was built in 1952 at Copperhill to utilize established Tennessee Copper Company products in combination with purchased raw materials to form new products. The first of these were Sul-Fon-Ate AA-9 (a detergent) and Sulfonic Acids.

#### Sodium Hydrosulfite

Production of sodium hydrosulfite began at TCC in 1956. In this plant liquid sulfur dioxide is combined with purchased raw materials to produce sodium hydrosulfite. This product is a powerful reducing agent and is used extensively by the textile industry in vat color reduction. A by-product of this operation is zinc oxide, which is used in the manufacturing of rayon and other products.<sup>1</sup>

# MARKETING

# Copper in General

Copper ores are concentrated and smelted, as described in the section on milling, and generally are shipped to refineries for electrolytic processing. In 1958 nearly 90 percent of new domestic copper metal was produced by 10 electrolytic refineries or combined furnace-electrolytic refineries. These domestic refineries are located on the Atlantic Coast (5) and in Arizona, Montana, Texas,

<sup>&</sup>lt;sup>1</sup> End of section written by the Tennessee Copper Company.

and Utah (5). In addition 3 refineries treat Great Lakes ores by furnace methods only.

Electrolytic refining is employed because impurities in blister copper adversely affect the metal in many of its uses. Furthermore, the electrolytic process separates valuable by-products such as gold, silver, nickel, cobalt, and tellurium (if present) from the copper. Commonly, electrolytic copper is furnace-treated to remove any remaining sulfur and to regulate the oxygen content in preparation for casting.

Copper marketing differs greatly from that of most other commodities, because a few large, vertically integrated companies dominate the U. S. copper industry. These companies—Anaconda Copper Mining Company, Kennecott Copper Corporation, Phelps Dodge Corporation, and American Smelting and Refining Company—own nearly 95 percent of U. S. smelting capacity and 85 percent of U. S. refining capacity, and they also own or control more than 50 percent of the fabricating business. Consequently, these large concerns consume virtually all of their ore production and market their copper as finished products rather than as a raw material.

Many ore producers do not own smelting and refining plants. These mining companies, which account for about 25 percent of U. S. production, sell their concentrated ores to large companies or to companies that engage essentially in smelting and refining only. Alternatively, the producer may pay a smelting charge or toll and retain title to the copper. Such procedures are referred to as "custom smelting" and are governed by contractual agreements between the miner and the smelter. Such contracts cover prices paid, smelting charges, and penalties assessed or bonuses paid for various types and grades of ore.

A typical schedule in 1949 was as follows:

#### Charges:

Base treatment charge per ton \$4.00, up to gross value of \$25.00. Over \$25, add 10 percent of excess, up to maximum of \$6.00.

#### Payments:

Gold—Pay for 94 percent @ \$34.9125 for first ounces per ton, 95.5 percent for second ounces per ton, 97 percent for all over 10 per ton.

Silver—Pay for 95 percent @ \$0.77 per ounce. Minimum deduction 1 ounce per ton.

Copper—Pay for 100 percent, less pounds copper per ton @ market price, less 2.5 cents a pound.

Penalties per ton of ore:

Zinc-30 cents a unit (20 pounds) in excess of 6.

Arsenic and antimony—50 cents a unit (20 pounds) in excess of 2. Penalties and payments for iron, zinc, lime, sulfur, and bismuth to be negotiated.

The raw copper market in the U. S. is composed of about 60 buyers including fabricators, both affiliated with primary producers and independents, and large electrical manufacturers. Approximately half the copper marketed is in the form of wire bars. Cakes, cathodes, and billets comprise about 10 percent each of other forms, and the remaining 20 percent is sold as ingots, ingot bars, and other shapes.

Copper metal is usually sold on a 90-day delivery basis, in carload lots f.o.b. cars at U. S. destinations for electrolytic copper in standard shapes. The price is determined by the price bid in cents per pound on the New York exchange. Prices for odd shapes, other forms of copper, and fire-refined copper are based on the price of electrolytic copper in ordinary forms.

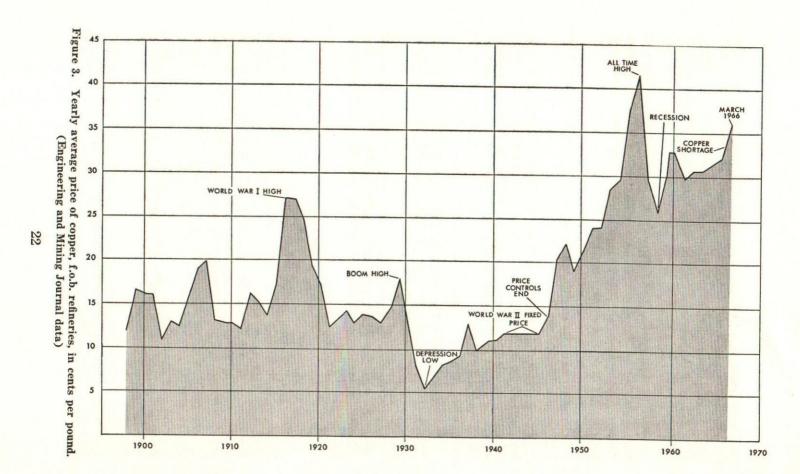
Production from Tennessee is shipped, as blister copper, to Phelps Dodge Corporation for refining, and sold by Adolph Lewisohn Selling Corporation.

Other Tennessee Copper Company metal products are sold directly from the plant as concentrates in the instance of zinc sulfides, or as beneficiated products in the case of iron sinter and slag.

#### Price

The price of copper flucuates daily and over longer periods in response to supply and demand and the general economic situation. The New York price is affected to a degree by the price on the London Metal Exchange, and by tariffs. The price of copper is a sensitive barometer of business conditions and outlook. It also is affected by lower cost substitutes, especially in recent years by competition from aluminum and plastics. The price of new copper also is affected by the supply and price of scrap copper. In 1958, for example, 797,000 tons of copper was recovered from scrap copper and copper alloys compared with 1,352,520 tons of new refined copper produced in the U. S. (U.S.B.M., 1959, p. 373 and 384).

At the beginning of the 20th century copper was priced at 16.5 cents per pound, and prior to World War I it was priced as



low as 13 cents. The highest price in World War I was 37 cents per pound in 1917, and this high was not exceeded until 1956. Just prior to the 1929 depression, copper was quoted at 23.9 cents, and it fell to a low of 4.9 cents in 1933. During World War II the price was fixed at 11.87 cents per pound, but production bonuses resulted in an average of 14.3 cents for the period 1941-1946. By 1950 the price advanced to 21.6 cents, and in March 1956 it reached an all-time high of 47.6 cents. In December 1965 copper was quoted at 36 cents per pound, f.o.b. New York. The price history is summarized in figure 3.

#### Tariffs

In July 1958, after a 7-year suspension, an excise tax was imposed on copper imports. The rate is 1.7 cents a pound when copper is selling at 24 cents a pound or higher and 2 cents a pound if copper falls below 24 cents.

# PRODUCTS OTHER THAN COPPER

Copper is obviously not the only material recovered in the Copper Basin. As has been shown iron, zinc, gold and silver are recovered, along with sulfur in various forms. The most important of these commercially is sulfur, recovered chiefly as sulfuric acid.

#### Sulfuric Acid

The smelting of metallic sulfides produces sulfurous gases that can be used to form sulfuric acid. This recovery has been practiced with increasing efficiency in the Copper Basin since 1907. Today sulfuric acid contributes so notably to the economics of the mining that it must be regarded as a co-product with the metals recovered.

Much of the sulfur in the ores occurs as pyrite ( $FeS_2$ ), which theoretically contains 53.7 percent sulfur. The pyrrhotite (FeS), and chalcopyrite ( $CuFe_2$ ), contain less sulfur but supply copper. Owing to the importance of a uniform sulfur content to plant operations, mining in the Basin is adjusted to supply a 35 percent sulfur assay ore to the mills. The copper and sulfur in the mill feed produce enough collective values to make the operation profitable, but both are necessary.

Sulfuric acid is produced in the smelting of sulfide ores, by burning native sulfur, and in refining "sour" natural gas. In the Southeast native sulfur offers the chief competitive acid raw material to sulfide ore producers. Sulfur-derived acid has made the manufacture of acid from copper-free pyrite unprofitable in recent years. Because of their copper and zinc content the Copper Basin ores compete successfully for acid-making, and Tennessee produces more pyrites (pyrite-pyrrhotite) than any other state.

#### Iron Sinter

Iron sinter from the smelters is shipped as a high-grade iron oxide that assays 68 to 70 percent iron. It finds a ready market in iron smelters in the Southeast, where it is blended with much lower grade natural ores to make suitable quality charges for the steel furnaces.

#### Zinc

Zinc recovered in the flotation plant is shipped as zinc sulfide concentrate to zinc smelters in other states. For a detailed discussion of zinc the reader is referred to Tennessee Division of Geology Information Circular 6, *The Zinc Industry of Tennessee*.

# ECONOMIC SIGNIFICANCE

# Uses of Copper

Copper generally is considered second only to iron as the most important metal. The U. S. Bureau of Mines (1964) reported that the United States produced 98.3 million tons of steel, 2.1 million tons of aluminum, 1.9 million tons of copper (including secondary recovery), 1.4 million tons of zinc, and 1.06 million tons of lead in 1962.

The properties of copper make it highly valuable in both peace and war. Its widespread usage arises from its electrical conductivity, corrosion resistance, ductility, and heat conductivity. It also is essential as an alloy: brass (copper and zinc), bronze (copper and tin); and in combination with beryllium, aluminum, nickel and lead.

Copper is surpassed only by silver as a conductor of electricity, and hence its principal use is in the electrical equipment and wiring industry. Most of the copper is refined electrolytically to produce the purest metal, which is required for these uses. The automobile and building-construction industries are the second and third largest consumers of copper in peacetime. In war, much copper is used to make brass for cartridge and shell cases; and in construction of ships, tanks, and aircraft.

Copper compounds also find wide applications, and the most common of these is copper sulfate. It is used as a fungicide, a plant food, in flotation ore dressing, in photography, and other chemical processes. Still other copper compounds are used in rayon manufacture, dyes, ceramics, electroplating, and as catalysts in organic chemistry.

#### Uses of Sulfuric Acid

Probably no compound is more basic to the chemical industry than sulfuric acid. Virtually no chemical processing plant fails to use large amounts of acid, and it is also used by other basic industries as well. It has been asserted that a nation's degree of civilization is directly measured by its sulfuric acid consumption.

Major uses, in order, are: fertilizers, chemicals, petroleum refining, paints and pigments, iron and steel treatment, rayon and film, explosives, metal finishes, and textiles. Sulfur compounds also are used in paper manufacture, insecticides, and metallurgical processes.

Much of the South's recent industrial growth has been in the chemical and paper fields. The availability of water, cotton, wood pulp and labor have been important in this development, but large acid production in the area also has been a factor. The availability of large quantities of sulfuric acid, together with the fact that Tennessee is the second state in phosphate rock production, has led to the development of a large fertilizer manufacturing industry in this State.

# Uses of Liquid Sulfur Dioxide

Liquid sulfur dioxide is made from gases driven off in smelting copper ores. The compressed gas is used by textile and sugar companies as a bleaching agent, in the extraction of cottonseed oil, and as a preservative.

# POTENTIAL AND OUTLOOK

The copper and sulfuric acid industry in Tennessee is in a strong position with respect to ore reserves. Although detailed reserve estimates are not available, enough is known to state that present production can be maintained for a prolonged period. Insofar as income from sulfuric acid is now more than the income from copper, demand and price are major considerations in the outlook for the industry; and to a degree, mining of ore to produce acid will affect the amount of copper produced. Or, stated in another way, the demand for and the price of acid will be a greater factor in the industry's future than the demand and price of copper.

Favorable factors are increases in chemical manufacturing requiring acid, especially growth of such industry near the Copper Basin; increasing markets for acidulated phosphate fertilizers; and the growth of the paper industry in the Southeast. Adverse factors for producers of acid from pyrite and other sulfide minerals are increases in mining costs and the ability of native sulfur to hold the cost down. This low-cost sulfur, especially where it is near water transportation routes, has led to new acid plants which compete effectively with Tennessee producers.

It seems probable at this time that in general demand for copper will continue at about the present level, but new mines in other countries are entering production. Some of these mines are located in areas of lower labor costs and are therefore highly competitive with domestic producers. Substitutes, such as aluminum, also have displaced copper in certain uses.

The industry in Tennessee is meeting these problems in two ways, in the first instance by improved mining and milling methods, e.g. the consolidation of ore hoisting in the Central Shaft, and flotation of all ore at the London mill; and by creating new products from raw materials available, e.g. liquid sulfur dioxide, sodium hydrosulfite, and Ferri-Floc (ferric sulfate).

It is noteworthy that the industry's geologic staff is actively engaged in the search for new deposits and in assisting the Mining Department in mining a chemically uniform grade of ore. Unless the composition of the ore is uniform, numerous and costly adjustments must be made in the mills.

# ECONOMIC CONTRIBUTION BY THE INDUSTRY

The copper and sulfuric acid industry makes a very significant contribution to the State. Capital investment in Tennessee is large; exact figures are not available, but the amount is measured in tens of millions of dollars.

Payrolls are also large. The Tennessee Copper Company employs 1900 people who earn approximately \$10 million annually. In addition the company spends about \$6 million for goods and services annually. These expenditures, taxes, insurance, and expansion costs represent a major contribution to the economy of the region.

The value of the commodities produces new wealth created by mining. These operations rank Polk County third in Tennessee in value of mineral production.

#### SELECTED REFERENCES

- Anonymous (1912) "Fools Gold": Tenn. Geol. Survey, Resources of Tenn. v. 2, p. 69-71.
- BATEMAN, A. M. (1942) Economic mineral deposits: New York, 898 p.
- EMMONS, W. H., AND LANEY, F. B. (1926) Geology and ore deposits of the Ducktown mining district, Tennessee: U.S. Geol. Survey Prof. Paper 139, 114 p.
- HOLBROOK, E. A., AND NELSON, W. A. (1919) The coal pyrite resources of Tennessee and tests on their availability: Tenn. Geol. Survey, Resources of Tenn. v. 9, p. 60-70.
- JERMAIN, G. D. (1953) Raw materials for the sulfuric acid industry, Region VII: U. S. Bureau of Mines, unpub. ms.
- KING, P. B., FERGUSON, H. W., CRAIG, L. C., AND RODGERS, JOHN (1944)

  Geology and manganese deposits of northeastern Tennessee: Tenn. Div.

  Geology Bull. 52, 283 p.
- NATIONAL SECURITY RESOURCES BOARD (1952) Copper materials survey: 553 p.
- Nelson, W. A. (1912) Manufacture of sulphuric acid in Tennessee for 1911: Tenn. Geol. Survey, Resources of Tenn., v. 2, p. 30-34.
- Ross, C. S. (1935) Origin of copper deposits of the Ducktown type in the southern Appalachian region: U. S. Geol. Survey Prof. Paper 179, 165 p.
- SAFFORD, J. M. (1869) Geology of Tennessee: Nashville, 550 p.

- SIMMONS, W. W. (1950) Recent geological investigations in the Ducktown mining district, Tennessee, in Snyder, F. G., ed., Symposium on mineral resources of the southeastern United States: Univ. of Tenn. Press., p. 67-71.
- TENNESSEE COPPER COMPANY (1960) The TCC story—a handbook for employees: 28 p.
- TOPICS: Company newsletter, published monthly.
- U. S. Bureau of Mines (1927-1934) Mineral resources of the United States for 1924-1931.
- ———— (1933-1959) Minerals yearbooks for 1932-1958.
- U. S. GEOLOGICAL SURVEY (1883-1927) Mineral resources of the United States for 1882-1923.