

3. THE BY-PRODUCT COKE INDUSTRY

3.1 GENERAL

Coke is one of the basic materials used in blast furnaces for the conversion of iron ore into iron. The major portion (93 percent in 1978) of the coke produced in the United States is used for this purpose. Most of the iron is subsequently processed into steel, and an adequate supply of coke is necessary to assure a continuing steel supply. Coke also is used by a number of other industries, principally iron foundries, nonferrous smelters, and chemical plants.

Coke is produced in the United States by two methods: the original beehive process and the contemporary by-product recovery or slot oven process. Approximately 99 percent of U.S. annual coke production is produced by the slot oven process. This conversion of coal to coke is performed in long, narrow slot ovens which are designed to permit separation and recovery of the volatile materials (by-products) evolved from coal during the coking process.

In 1975 it was estimated that in the United States there were 62 operating by-product coke plants which consisted of 231 batteries containing 13,324 ovens.¹ However, by 1978 only 60 by-product coke plants remained in operation.² The industry has two sectors, and plants are classified generally as "furnace" and "merchant." Furnace plants are owned by or affiliated with iron- and steel-producing companies which produce coke primarily for consumption in their own blast furnaces, although they also engage in some intercompany sales among steel firms with excesses or deficits in coke capacity. In 1978 there were 47 furnace plants which accounted for 93 percent of the total coke production.

Independent merchant plants which produce coke for sale on the open market are typically owned by chemical or coal firms. The 13 merchant

plants operating in 1978 accounted for 7 percent of the total coke produced. These firms sell most of their products to other firms engaged in blast furnace, foundry, and nonferrous smelting operations. Chemical companies have entered the coke industry to obtain the by-product hydrocarbon gases that are released when coal is converted into coke; coal firms have entered the coke industry as a form of downstream vertical integration.

In 1978, 43.8 million megagrams of coke were produced in slot ovens in the United States. This production was less than the 1977 production level of 48.1 million megagrams and was 16 percent less than the 1976 production level of 52.4 million megagrams.³ In 1978 furnace plants produced 40.7 million megagrams of coke and merchant plants produced 3.1 million megagrams of coke. Principal markets for merchant coke were blast furnaces not associated with integrated coke producing facilities, independent gray-iron foundries, nonferrous smelters, chemical plants, and affiliated foundries. The production of coke from the beehive process accounted for only 0.3 million megagrams, which was 0.7 percent of the total coke production during 1978.³ A production and consumption history of coke in the United States since 1970 is presented in Table 3-1.

Although coke was produced in 18 States in 1976, 57 percent of the production occurred in three eastern States: Pennsylvania, Ohio, and Indiana.² Pennsylvania, with 14.7 million megagrams of output, was the leading coke producing State and accounted for 28 percent of U.S. coke production. Ohio produced 7.6 million megagrams of coke while Indiana produced 7.5 million megagrams of coke. The relative amounts of coke produced in the various States have changed little in the past decade. The geographical distribution of coke oven facilities reflects the locations of coal deposits and steelmaking facilities. Table 3-2 shows the geographical distribution of coke production in the United States from 1971 through 1976.^{2 3 4}

The yield of coke from coal, approximately 69 percent, has remained nearly constant during the past decade.^{3 4} This production does not include breeze, the undersize coke which results from the crushing and screening of the coke after it is removed from the oven. Although not completely standardized, the term breeze is generally applied to coke that will pass

through a half-inch screen. In 1976, coke plants produced 3.9 million megagrams of breeze, which is equivalent to 51 kg/Mg of coal carbonized.³ Because of its small size, breeze is not suitable for use in ferrous blast furnaces. However, it is used for the sintering of iron bearing dust and fine ores, boiler fuel, and for other industrial purposes.

After separation and recovery, the by-products that evolved during the coking process are used within the facility or are marketed. Typical products and by-products from the production of coke during 1978 are presented in Table 3-3.³

Approximately 93 percent (47.3 million megagrams) of the coke distributed by U.S. producers in 1978 was shipped to blast furnace plants, 5 percent went to foundries, and the remainder went to other industrial plants.³ Apparent consumption (or total consumption) of coke in the United States equaled 51 million megagrams in 1978 and 48.2 million megagrams in 1977. The apparent consumption is a quantity which includes domestic production plus imports, minus exports, plus or minus any net change in stocks. Apparent consumption, linked closely with iron demand, increased from 1975 to 1976, corresponding to an 8.8 percent increase in blast furnace iron production. As iron production declined in 1977, apparent consumption decreased from the 1976 level. Both apparent consumption and blast furnace iron production increased in 1978.

Consumption of coke in iron furnaces has decreased partly because of decreases in the coke rate for these furnaces. The coke rate is the ratio between the coke consumed in blast furnaces and blast furnace output. Although the output of pig iron and ferroalloys from blast furnaces has

TABLE 3-3. COKE AND COAL CHEMICALS PRODUCED BY U.S. COKE PLANTS IN 1978³

Product	Total production
Coke	43.8 million megagrams
Breeze	2.2 million megagrams
Crude tar	2,050 million liters
Crude light oil	623.6 million liters
Ammonia (sulfate equivalent)	0.4 million megagrams
Coke oven gas ^a	22 billion cubic meters

^aEstimated from the 1976 ratio of gas to coke.

increased significantly during the past 2 decades, the blast furnace coke rate has declined. In 1976, an average of only 593.5 kg of coke was required to produce 1 Mg of pig iron and ferroalloys, compared with 860.0 kg in 1956.⁵ Various factors have contributed to this reduction, but the primary causes are higher grade ore burdens and the use of increased quantities of supplemental fuels.

Supplemental fuels, which consist primarily of fuel oil, tar, and natural gas, can reduce the coke requirements for the ore reduction process. The use of supplemental fuels has increased significantly in the past 10 years, and in 1975 it resulted in a decreased need for blast furnace coke of approximately 3.6 million megagrams.⁵ The application of supplemental fuels to replace coke used in blast furnaces is inherently limited because coke is the principal agent in reducing iron ore. Therefore, even though the supplemental fuels are cheaper than coke on a heat-content basis, they will not be able to replace coke in this vital application. In the near future, however, these fuels may help to offset the deficit in projected coke production levels.

3.2 BY-PRODUCT COKING PROCESS

Figure 3-1 illustrates the major process equipment in a schematic diagram of a by-product coke battery. Note that the coke side is the side where the coke is quenched and dumped, and the pusher side is the side from which the pushing ram operates. A flow sheet is provided in Figure 3-2 to give an overview of the process from coal charging to by-product recovery. This operation will be discussed in greater detail in three major subprocesses: coal preparation and charging, thermal distillation and pushing, and by-product recovery.

3.2.1 Coal Preparation and Charging

The coal that is charged to the by-product coke ovens is usually a blend of two or more low, medium, or high volatile coals that are generally low in sulfur and ash. Blending is required to control the properties of the resulting coke, to optimize the quality and quantity of by-products, and to avoid the expansion exhibited by types of coal that may cause excessive pressure on the oven walls during the coking process.

Coal is usually received on railroad cars or barges. Conveyor belts transfer the coal as needed from the barges or from a coal storage pile to

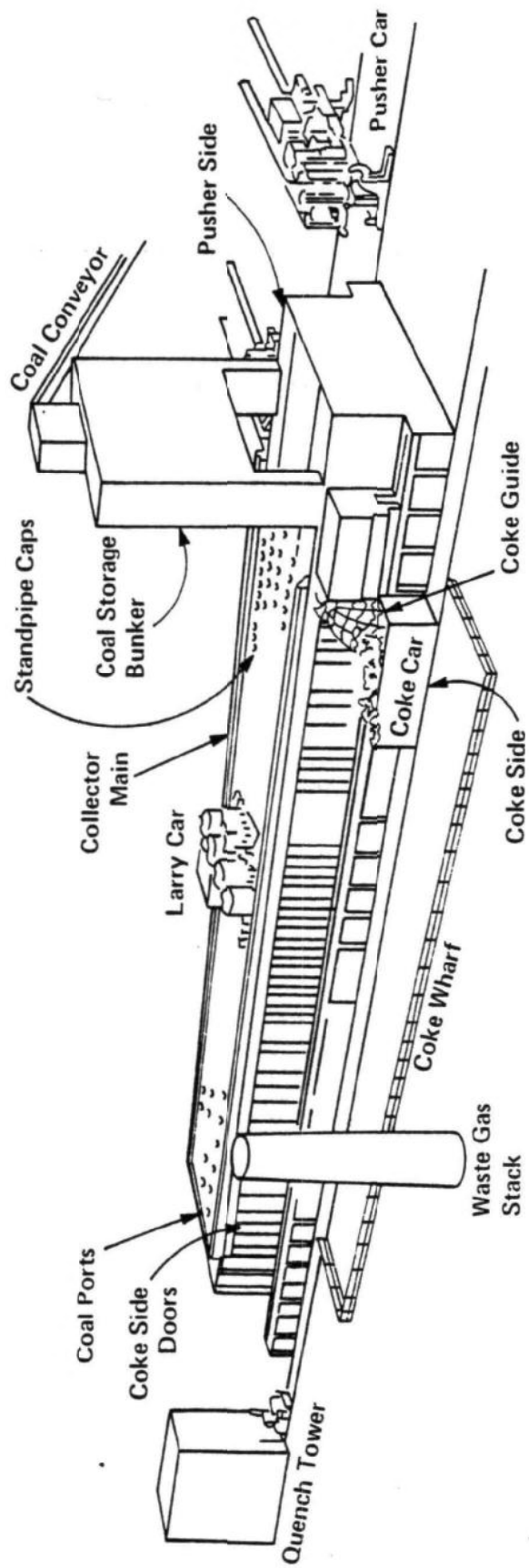


Figure 3-1. Schematic diagram of by-product coke battery.

mixing bins where the various types of coal are stored. The coal is transferred from the mixing bins to the crusher where it is pulverized to a preselected size between 0.15 and 3.2 mm. The desired size depends on the response of the coal to coking reactions and the ultimate coke strength that is required. For example, low volatile coals coke more readily if the particle size is small, and smaller particles are reported to give greater strength to the coke.

The pulverized coal is then mixed and blended, and sometimes water and oil are added to control the bulk density of the mixture. The prepared coal mixture is transported to the coal storage bunkers on the coke oven batteries as shown in Figure 3-1.⁶ A weighed amount or volume of prepared coal is discharged from the bunker into a larry car, a vehicle which is driven by electric motors and travels the length of the battery top on a wide gauge railroad track. The larry car is positioned over the empty, hot oven, the lids on the charging ports are removed, and the coal is discharged from the hoppers of the larry car through discharge chutes. The flow rate from the hoppers to the oven may be controlled by gravity, a rotary table, or screw feeders. To prevent gases from escaping during charging, a steam-jet aspirator is used in most plants to draw gases from the space above the charged coal into the collecting main.⁷

Peaks of coal will form directly under the charging ports as the oven is filled. As shown in Figure 3-3, these peaks are leveled by a steel bar that is cantilevered from the pusher machine through an opening called the chuck door on the pusher side of the battery. This leveling process provides a clear vapor space and exit tunnel for the gases that evolve during coking to flow to the standpipes and aids in the uniform coking of the coal.⁷ After filling, the chuck door and the topside charging ports are closed; the latter may be sealed with a wet clay mixture called luting.

3.2.2 Thermal Distillation

The thermal distillation of coal to separate volatile and nonvolatile components takes place in coke ovens that are grouped in batteries. A battery consists of 20 to 100 adjacent ovens with common side walls which are made of high quality silica and other types of refractory brick and contain integral flues. Typically, the individual slot ovens are 11 to 16.8 m long, 0.35 to 0.5 m wide, and 3.0 to 6.7 m high. The heating systems fall into two general classes: underjet and gun-flue. In the underjet

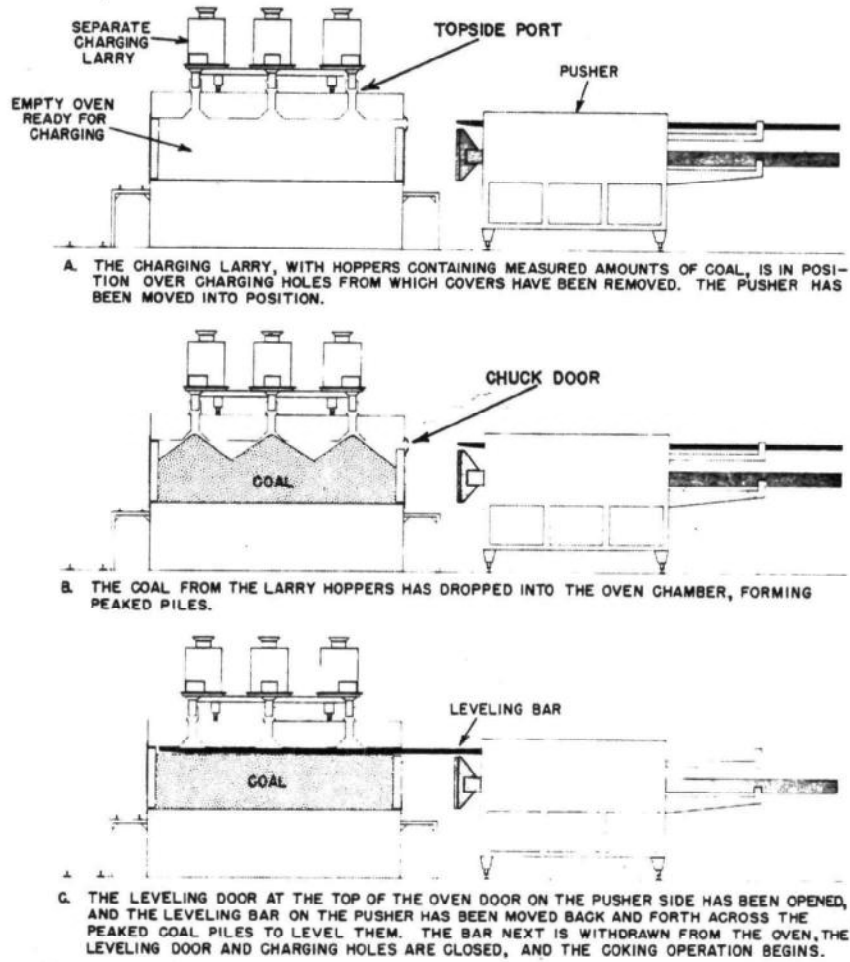


Figure 3-3. Charging and leveling operations. (copyright 1971 by United States Steel Corporation)

heating system, illustrated in Figure 3-4, the flue gas is introduced into each flue from piping in the basement of the battery. The gas flow to each flue can be metered and controlled. The gun-flue heating system, shown in Figure 3-5, introduces the gas through a horizontal gas duct extending the length of each wall slightly below the oven floorline. Short ducts lead upward to a nozzle brick at the bottom of each of the vertical flues.⁷

Heat for the coking operation is provided by a regenerative combustion system located below the ovens. Because the combustion flue gas contains a significant amount of process heat, two heat regenerators are used for recovery. These regenerators are located below each oven, one for combustion air and one for the combustion waste gas, and the flow is alternated between the two at about 30 min intervals. The slot ovens operate like chemical retorts in that they are both batch operated, fitted with exhaust flues (standpipes), and function without the addition of any reagent.

The operation of each oven in the battery is cyclic, but the batteries usually contain a sufficiently large number of ovens (an average of 57) so that the yield of by-products is essentially continuous. The individual ovens are charged and discharged at approximately equal time intervals during the coking cycle. The resultant constant flow of evolved gases from all the ovens in a battery helps to maintain a balance of pressure in the flues, collecting main, and stack. All of the ovens are fired continuously at a constant rate, irrespective of a particular oven's stage in the coking cycle. If damage to the refractory occurs in inaccessible locations, through overheating or expansion of coal, repairs may be extremely difficult. A cooldown takes from 5 to 7 weeks, so a battery shutdown is undertaken only as a last alternative.

After the ovens are filled, coking proceeds for 15 to 18 hr to produce blast furnace coke and 25 to 30 hr to produce foundry coke. The coking time is determined by the coal mixture, moisture content of the coal, rate of underfiring, and the desired properties of the coke. The coking temperatures generally range from 900° to 1,100° C and are kept on the high side of the range to produce blast furnace coke. Air is prevented from leaking into the ovens by maintaining a positive back pressure of about 10 mm water. The gases and hydrocarbons that are evolved during the thermal distillation are removed through the offtake main and sent to the by-product plant for recovery.

At the end of the coking cycle, doors at both ends of the oven are removed and the incandescent coke is pushed out the coke side of the oven by a ram which is extended from the pusher machine. This operation is illustrated in Figure 3-6. The coke is pushed through a coke guide into a special railroad car, called a quench car, which traverses the coke side of the battery. The quench car carries the coke to the end of the battery to a quench tower where it is deluged with water so that it will not continue to burn after being exposed to air. The quenched coke is discharged onto an inclined "coke wharf" to allow excess water to drain and to cool the coke to a reasonable handling temperature.

Gates along the lower edge of the wharf control the rate of coke falling on a conveyor belt which carries it to the crushing and screening system. The coke is then crushed and screened to obtain the optimum size for the particular blast furnace operation in which it is to be used.⁷ The undersize coke generated by the crushing and screening operations is used in other steel plant processes, stockpiled, or sold.

3.2.3 By-Product Collection

Gases evolved during coking leave the coke oven through the stand-pipes, pass into goosenecks, and travel through a damper valve to the gas collection main which directs them to the by-product plant. These gases account for 20 to 35 percent by weight of the initial coal charge and are composed of water vapor, tar, light oils, heavy hydrocarbons, and other chemical compounds.

The raw coke oven gas exits at temperatures estimated at 760° to 870° C and is shock cooled by spraying recycled "flushing liquor" in the gooseneck. This spray cools the gas to 80° to 100° C, precipitates tar, condenses various vapors, and serves as the carrying medium for the condensed compounds. These products are separated from the liquor in a decanter (Figure 3-2) and are subsequently processed to yield tar and tar derivatives.⁷

The gas is then passed either to a final tar extractor or an electrostatic precipitator for additional tar removal. When the gas leaves the tar extractor, it carries three-fourths of the ammonia and 95 percent of the light oil originally present when leaving the oven.

The ammonia is recovered either as an aqueous solution by water absorption or as ammonium sulfate salt. Ammonium sulfate is crystallized in a

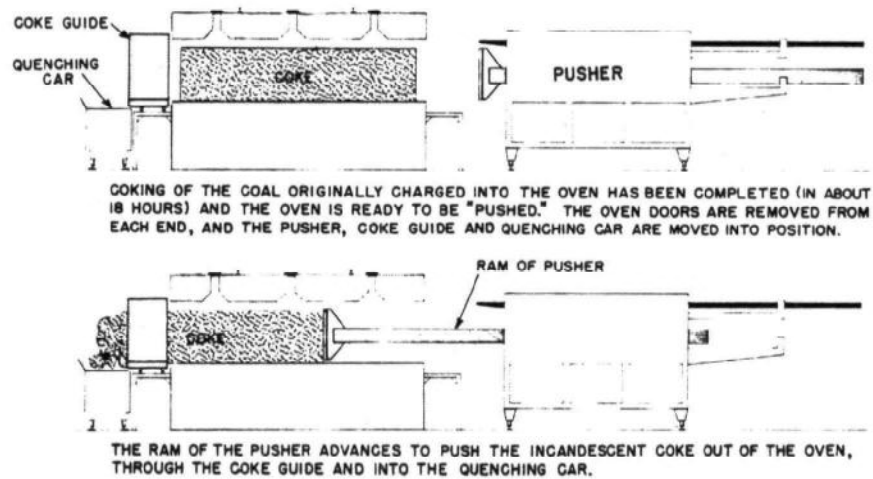


Figure 3-6. Schematic representation of the pushing operation. (copyright 1971 by United States Steel Corporation)

saturator which contains a solution of 5 to 10 percent sulfuric acid and is removed by an air injector or centrifugal pump. The salt is dried in a centrifuge and packaged.

The gas leaving the saturator at about 60° C is taken to final coolers or condensers, where it is typically cooled with water to approximately 24° C. During this cooling, some naphthalene separates and is carried along with the wastewater and recovered. The remaining gas is passed into a light oil or benzol scrubber, over which is circulated a heavy petroleum fraction called wash oil or a coal-tar oil which serves as the absorbent medium. The oil is sprayed in the top of the packed absorption tower while the gas flows up through the tower. The wash oil absorbs about 2 to 3 percent of its weight of light oil, with a removal efficiency of about 95 percent of the light oil vapor in the gas. The rich wash oil is passed to a countercurrent steam stripping column. The steam and light oil vapors pass upward from the still through a heat exchanger to a condenser and water separator. The light oil may be sold as crude or processed to recover benzene, toluene, xylene, and solvent naphtha.⁷

After tar, ammonia, and light oil removal, the gas undergoes a final desulfurization process at some coke plants before being used as fuel. The coke oven gas has a rather high heating value, on the order of 20 MJ/Nm³ (550 Btu/stdft³). Typically, 35 to 40 percent of the gas is returned to fuel the coke oven combustion system, and the remainder is used for other heating needs.

3.3 COKE OVEN CHARGING, TOPSIDE, AND DOOR EMISSIONS

Coke oven emissions consist of a yellow-brown gas which contains over 10,000 compounds as gases, condensable vapors, and particulates. The components that primarily concern public health include benzene and the other known or suspected carcinogens belonging to a class of compounds termed polycyclic organic matter (POM). POM, which condenses on fine particulates at ambient temperatures, consists of compounds with two or more fused rings. There are thousands of POM compounds which vary widely in physical and chemical characteristics. These potential pollutants are sometimes reported as benzene soluble organics (BSO) or by the quantity of a specific surrogate compound, such as benzo(a)pyrene (BaP). BSO is composed

12.2 Coke Production

12.2.1 General

Metallurgical coke is produced by destructive distillation of coal in coke ovens. Prepared coal is "coked", or heated in an oxygen-free atmosphere until all volatile components in the coal evaporate. The material remaining is called coke.

Most metallurgical coke is used in iron and steel industry processes such as blast furnaces, sinter plants, and foundries to reduce iron ore to iron. Over 90 percent of the total metallurgical coke production is dedicated to blast furnace operations.

Most coke plants are co-located with iron and steel production facilities. Coke demand is dependent on the iron and steel industry. This represents a continuing decline from the about 40 plants that were operating in 1987.

12.2.2 Process Description^{1,2}

All metallurgical coke is produced using the "byproduct" method. Destructive distillation ("coking") of coal occurs in coke ovens without contact with air. Most U. S. coke plants use the Kopper-Becker byproduct oven. These ovens must remain airtight under the cyclic stress of expansion and contraction. Each oven has 3 main parts: coking chambers, heating chambers, and regenerative chambers. All of the chambers are lined with refractory (silica) brick. The coking chamber has ports in the top for charging of the coal.

A coke oven battery is a series of 10 to 100 coke ovens operated together. Figure 12.2-1 illustrates a byproduct coke oven battery. Each oven holds between 9 to 32 megagrams (Mg) (10 to 35 tons) of coal. Offtake flues on either end remove gases produced. Process heat comes from the combustion of gases between the coke chambers. Individual coke ovens operate intermittently, with run times of each oven coordinated to ensure a consistent flow of collectible gas. Approximately 40 percent of cleaned oven gas (after the removal of its byproducts) is used to heat the coke ovens. The rest is either used in other production processes related to steel production or sold. Coke oven gas is the most common fuel for underfiring coke ovens.

A typical coke manufacturing process is shown schematically in Figure 12.2-2. Coke manufacturing includes preparing, charging, and heating the coal; removing and cooling the coke product; and cooling, cleaning, and recycling the oven gas.

Coal is prepared for coking by pulverizing so that 80 to 90 percent passes through a 3.2 millimeter (1/8 inch) screen. Several types of coal may be blended to produce the desired properties, or to control the expansion of the coal mixture in the oven. Water or oil may be added to adjust the density of the coal to control expansion and prevent damage to the oven.

Coal may be added to the ovens in either a dry or wet state. Prepared wet coal is finely crushed before charging to the oven. Flash-dried coal may be transported directly to the ovens by the hot gases used for moisture removal. Wall temperatures should stay above 1100°C (2000°F) during loading operations and actual coking. The ports are closed after charging and sealed with luting ("mud") material.

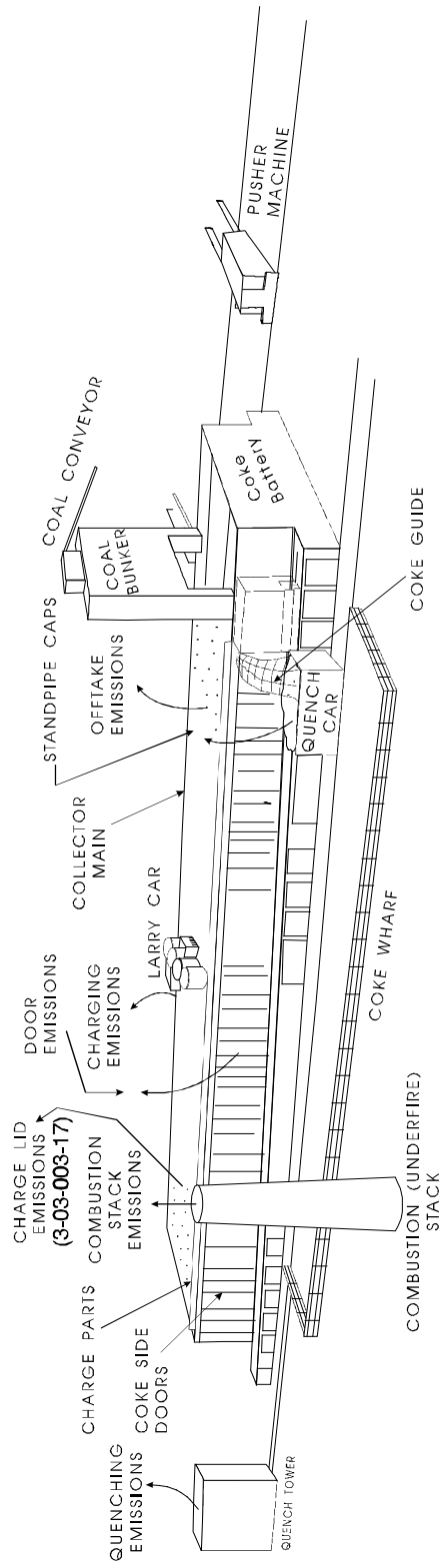


Figure 12.2-1. Byproduct coke oven battery showing major emission points. (Source Classification Codes in parentheses.)

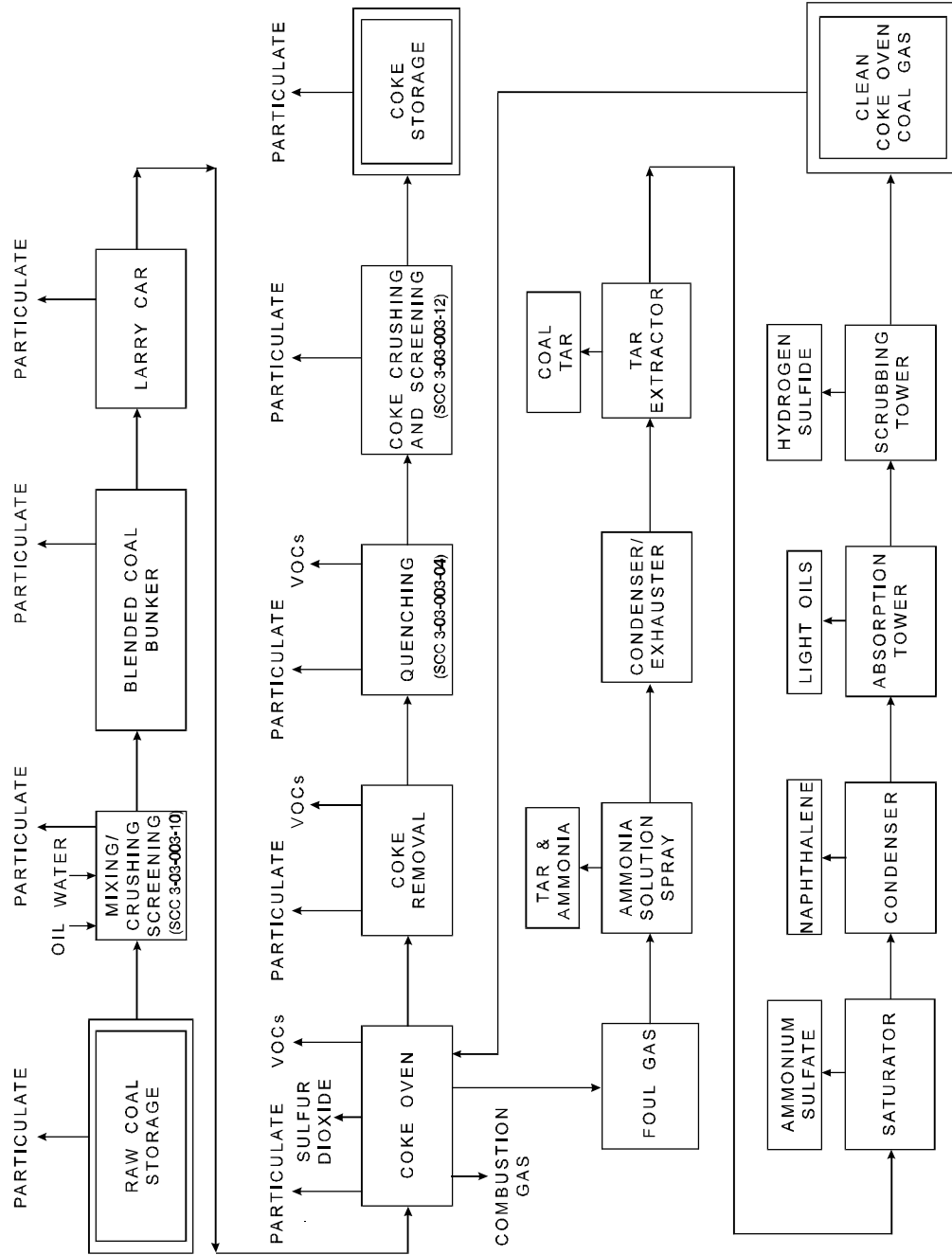


Figure 12.2-2. Flow diagram of coke manufacturing. VOC = volatile organic compound. (Source Classification Codes in parentheses.)

The blended coal mass is heated for 12 to 20 hours for metallurgical coke. Thermal energy from the walls of the coke chamber heats the coal mass by conduction from the sides to the middle of the coke chamber. During the coking process, the charge is in direct contact with the heated wall surfaces and develops into an aggregate "plastic zone". As additional thermal energy is absorbed, the plastic zone thickens and merges toward the middle of the charge. Volatile gases escape in front of the developing zone due to heat progression from the side walls. The maximum temperature attained at the center of the coke mass is usually 1100 to 1150°C (2000 to 2100°F). This distills all volatile matter from the coal mass and forms a high-quality metallurgical coke.

After coking is completed (no volatiles remain), the coke in the chamber is ready to be removed. Doors on both sides of the chamber are opened and a ram is inserted into the chamber. The coke is pushed out of the oven in less than 1 minute, through the coke guide and into a quench car. After the coke is pushed from the oven, the doors are cleaned and repositioned. The oven is then ready to receive another charge of coal.

The quench car carrying the hot coke moves along the battery tracks to a quench tower where approximately 1130 liters (L) of water per Mg of coke (270 gallons of water per ton) are sprayed onto the coke mass to cool it from about 1100 to 80°C (2000 to 180°F) and to prevent it from igniting. The quench car may rely on a movable hood to collect particulate emissions, or it may have a scrubber car attached. The car then discharges the coke onto a wharf to drain and continue cooling. Gates on the wharf are opened to allow the coke to fall onto a conveyor that carries it to the crushing and screening station. After sizing, coke is sent to the blast furnace or to storage.

The primary purpose of modern coke ovens is the production of quality coke for the iron and steel industry. The recovery of coal chemicals is an economical necessity, as they equal approximately 35 percent of the value of the coal.

To produce quality metallurgical coke, a high-temperature carbonization process is used. High-temperature carbonization, which takes place above 900°C (1650°F), involves chemical conversion of coal into a mostly gaseous product. Gaseous products from high-temperature carbonization consist of hydrogen, methane, ethylene, carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia, and nitrogen. Liquid products include water, tar, and crude light oil. The coking process produces approximately 338,000 L of coke oven gas (COG) per megagram of coal charged (10,800 standard cubic feet of COG per ton).

During the coking cycle, volatile matter driven from the coal mass passes upward through cast iron "goosenecks" into a common horizontal steel pipe (called the collecting main), which connects all the ovens in series. This unpurified "foul" gas contains water vapor, tar, light oils, solid particulate of coal dust, heavy hydrocarbons, and complex carbon compounds. The condensable materials are removed from the exhaust gas to obtain purified coke oven gas.

As it leaves the coke chamber, coke oven coal gas is initially cleaned with a weak ammonia spray, which condenses some tar and ammonia from the gas. This liquid condensate flows down the collecting main until it reaches a settling tank. Collected ammonia is used in the weak ammonia spray, while the rest is pumped to an ammonia still. Collected coal tar is pumped to a storage tank and sold to tar distillers, or used as fuel.

The remaining gas is cooled as it passes through a condenser and then compressed by an exhaustor. Any remaining coal tar is removed by a tar extractor, either by impingement against a metal surface or collection by an electrostatic precipitator (ESP). The gas still contains 75 percent of original ammonia and 95 percent of the original light oils. Ammonia is removed by passing the gas

through a saturator containing a 5 to 10 percent solution of sulfuric acid. In the saturator, ammonia reacts with sulfuric acid to form ammonium sulfate. Ammonium sulfate is then crystallized and removed. The gas is further cooled, resulting in the condensation of naphthalene. The light oils are removed in an absorption tower containing water mixed with "straw oil" (a heavy fraction of petroleum). Straw oil acts as an absorbent for the light oils, and is later heated to release the light oils for recovery and refinement. The last cleaning step is the removal of hydrogen sulfide from the gas. This is normally done in a scrubbing tower containing a solution of ethanolamine (Girbotol), although several other methods have been used in the past. The clean coke oven coal gas is used as fuel for the coke ovens, other plant combustion processes, or sold.

12.2.3 Emissions And Controls

Particulate, VOCs, carbon monoxide and other emissions originate from several byproduct coking operations: (1) coal preparation, (2) coal preheating (if used), (3) coal charging, (4) oven leakage during the coking period, (5) coke removal, (6) hot coke quenching and (7) underfire combustion stacks. Gaseous emissions collected from the ovens during the coking process are subjected to various operations for separating ammonia, coke oven gas, tar, phenol, light oils (benzene, toluene, xylene), and pyridine. These unit operations are potential sources of VOC emissions. Small emissions may occur when transferring coal between conveyors or from conveyors to bunkers. Figure 12.2-2 portrays major emission points from a typical coke oven battery.

The emission factors available for coking operations for total particulate, sulfur dioxide, carbon monoxide, VOCs, nitrogen oxides, and ammonia are given in Tables 12.2-1 and 12.2-2. Tables 12.2-3 and 12.2-4 give size-specific emission factors for coking operations.

A few domestic plants preheat the coal to about 260°C (500°F) before charging, using a flash drying column heated by the combustion of coke oven gas or by natural gas. The air stream that conveys coal through the drying column usually passes through conventional wet scrubbers for particulate removal before discharging to the atmosphere. Leaks occasionally occur from charge lids and oven doors during pipeline charging due to the positive pressure. Emissions from the other methods are similar to conventional wet charging.

Oven charging can produce significant emissions of particulate matter and VOCs from coal decomposition if not properly controlled. Charging techniques can draw most charging emissions into the battery collecting main. Effective control requires that goosenecks and the collecting main passages be cleaned frequently to prevent obstructions.

During the coking cycle, VOC emissions from the thermal distillation process can occur through poorly sealed doors, charge lids, offtake caps, collecting main, and cracks that may develop in oven brickwork. Door leaks may be controlled by diligent door cleaning and maintenance, rebuilding doors, and, in some plants, by manual application of lute (seal) material. Charge lid and offtake leaks may be controlled by an effective patching and luting program. Pushing coke into the quench car is another major source of particulate emissions. If the coke mass is not fully coked, VOCs and combustion products will be emitted. Most facilities control pushing emissions by using mobile scrubber cars with hoods, shed enclosures evacuated to a gas cleaning device, or traveling hoods with a fixed duct leading to a stationary gas cleaner.

Coke quenching entrains particulate from the coke mass. In addition, dissolved solids from the quench water may become entrained in the steam plume rising from the tower. Trace organic compounds may also be present.