Kirk-Othmer Encyclopedia of Chemical Technology.

COAL CONVERSION PROCESSES, CARBONIZATION

Coal carbonization is the process for producing metallurgical coke for use in iron-making blast furnaces and other metal smelting processes. Carbonization of coal (qv) entails heating coal to temperatures as high as 1100°C in the absence of oxygen in order to distill out tars and light oils (see Tar and pitch). A gaseous by-product referred to as coke oven gas (COG) along with ammonia, water, and sulfur compounds are also thermally removed from the coal. The coke that remains after this distillation largely consists of carbon (qv), in various crystallographic forms, but also contains the thermally modified remains of various minerals that were in the original coal. These mineral remains, commonly referred to as coke ash, do not combust and are left as a residue after the coke is burned. Coke also contains a portion of the sulfur from the coal. Coke is principally used as a fuel, reductant, and support for other raw materials in ironmaking blast furnaces (see Furnaces, fuel-fired; Iron). A much smaller tonnage of coke is similarly used in cupola furnaces in the foundry industry. The carbonization by-products are usually refined, within the coke plant, into commodity chemicals such as elemental sulfur (qv), ammonium sulfate, benzene, toluene, xylene, and naphthalene (qv) (see also Ammonium compounds; BTX processing). Subsequent processing of these chemicals produces a host of other chemicals and materials. The COG is a valuable heating fuel used mainly within steel (qv) plants for such purposes as firing blast furnace stoves, soaking furnaces for semifinished steel, annealing furnaces, and lime kilns as well as heating the coke ovens themselves.

Coke making dates to seventeenth century England where it was discovered that interrupting the burning of coal heaps produced solid blocks of carbon from the botton of the heap (1). This carbon quickly supplanted wood charcoal as the main blast furnace fuel. The first commercially successful coal carbonization plant was developed in 1709 (2). Subsequent generations of cokemaking facilities proceeded to ever more effectively exclude air (oxygen) from contact with the carbonizing coal. These facilities evolved from the initial coal heaps first to pits, then to masonry-walled nonroofed ovens. Dome-shaped mud-walled ovens, and then domed refractory brick ovens, commonly called beehive ovens, appeared by 1840 (1). At about this same time, rectangular-shaped ovens having arched roofs and removable doors on one or both ends of the oven appeared. This latter type allowed for pushing the coke out of the oven so that the coke could be quenched with water. Earlier ovens were designed for quenching the coke within the oven, necessitating subsequent reheating of the oven as well as repair of damage caused by thermal shock to the oven structure.

Within 15 years, the enclosing of the coal during carbonization allowed for the first attempts at profitably recovering the off-gases from the coking process. Commercial success in this endeavor is generally credited to Germany's by-product coke ovens of the early 1880s (1) which led to rapid growth in the steel industry as well as to development of chemical industry for use of the cokemaking by-products. Carbonization facilities at different locations in various countries aimed at different products depending on local needs. For some facilities, COG (also called coal gas) for street lights, etc was the prime product and the coke produced was a troublesome by-product. Production of COG or illuminating gas began about 1800 and was accomplished by heating coal in iron or steel retorts. Other facilities concentrated on producing tar and oil for use as rope preservatives. But a growing proportion of cokemaking facilities concentrated on quality coke for blast furnaces and used sale of the other carbonization products to offset the coke costs.

Developments in cokemaking technology in the United States closely followed those elsewhere. By the mid-1800s, coke had displaced charcoal as the principal smelting fuel (1) coinciding with application of hot blast principles to iron smelting. The first U.S. use of beehive ovens occurred in 1833 in Pennsylvania and in 1893 Semet-Solvay constructed the first narrow vertical slot by-product ovens in the United States (1). These coke ovens were built in Syracuse, New York and were designed for recovering ammonia for the Solvay soda-ash process. United States Steel Corp. shortly thereafter built the first vertical coke ovens for production of blast furnace coke near Joliet, Illinois. Annual construction of beehive coke ovens in the United States continued to grow through 1910, but most coke in the United States was produced via vertical by-product coke ovens by about 1920 (1).

Lack of availability of coal-derived chemicals from Germany during World War I led to rapid development of the by-product cokemaking industry in the United States during this period. This included production of blast furnace coke to support steelmaking, recovery of numerous organic liquids to support the chemical self-sufficiency effort, and recovery of by-product gas for industrial and home lighting. These products were in high demand until the availability of large quantities of low cost natural gas (see Gas, natural) and petroleum(qv) products from the southwestern United States became available in the mid-1940s.

As sof this writing, coke oven batteries are almost entirely of the vertical by-product oven type. Numerous alternative cokemaking processes, such as formcoke processes, have had some success, but widespread adoption has not occurred.

1. Supply and Demand

The vast majority of coke is produced from slot-type by-product coke ovens. Total coke production worldwide was about 378×10^6 t in 1990 (3). As shown in Table 1, this tonnage has remained relatively stable for the last two decades. In 1990, the former USSR (CIS) was the largest coke producer, producing 80×10^6 t, followed closely by the People's Republic of China, producing 73×10^6 t. Japan produced 53×10^6 t and the United States produced about 27×10^6. Since 1970, CIS production has remained in the 75–85 million metric ton range, but massive shifts in production have occurred in the United States, Japan, and the People's Republic of China. Since 1970, United States production has decreased by more than 50%; Japanese production has increased by 50%. During the same time period, the People's Republic of China increased coke production by over 300%. Thus the United States dropped from being the No. 2 producer in 1970 to being the No. 4 producer in 1990.

Worldwide demand for blast furnace coke has decreased over the past decade. Although, as shown in Figure 1, blast furnace hot metal production (pig iron) increased by about 4% from 1980 to 1990, coke production decreased by about 2% over the same time period (3). This discrepancy of increased hot metal and decreased coke production is accounted for by steady improvement in the amounts of coke required to produce pig iron. Increased technical capabilities, although not universally implemented, have allowed for about a 10% decrease in coke rate, ie, coke consumed per pig iron produced, because of better specification of coke quality and improvements in blast furnace instrumentation, understanding, and operation methods (4). As more blast furnaces implement injection of coal into blast furnaces, additional reduction in coke rate is expected. In some countries that have aggressively adopted coal injection techniques, coke rates have been lowered by 25% (4).

Production of coke is expected to continue to decrease unless new cokemaking facilities are constructed, because the effective production capacities of coke plants decrease as the coke plants age. This situation is particularly acute in North America where the majority of coke plants are over 25 years in age (5) and the economic life spans of conventional coke batteries average about 20 years.

Table 1. Production of Blast Furnace Coke, $t \times 10^6$[a]

Country	1970	1980	1985	1987	1988	1989	1990
North America	69.7	47.2	30.7	30.0	30.3	34.7	30.9
Western Europe	98.6	78.1	70.7	63.5	62.6	60.1	58.5
Japan	36.4	54.4	51.7	46.4	50.6	51.6	53.0
others[b]	10.1	9.6	5.9	7.5	8.4	8.5	8.5
Total industrial countries	*214.8*	*189.3*	*159.0*	*147.4*	*151.9*	*154.9*	*150.9*
Latin America	4.4	7.7	10.6	9.8	11.7	11.6	11.4
Asia	8.9	17.0	19.9	21.5	23.2	23.6	25.0
Africa and Middle East	0.6	2.2	2.2	2.1	2.1	2.2	2.2
Total developing countries	*13.9*	*26.9*	*32.7*	*33.4*	*37.0*	*37.4*	*38.6*
Total Western World	*228.7*	*216.2*	*191.7*	*180.8*	*188.9*	*192.3*	*189.5*
China, etc	25.5	46.4	51.4	61.4	64.6	69.7	76.7
Russia and Eastern Europe	102.8	122.5	119.5	120.9	120.8	115.2	111.7
Total Eastern countries	*128.3*	*168.9*	*170.9*	*182.3*	*185.4*	*184.9*	*188.4*
World Total	*357.0*	*385.1*	*362.6*	*363.3*	*374.3*	*377.2*	*377.9*

[a] Ref. 4.

[b] Mainly Australia and South Africa.

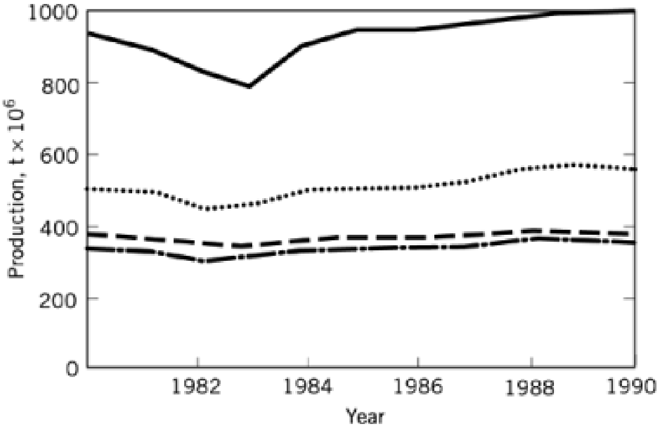

Fig. 1. World production trends in steelmaking raw materials where (—) represents iron ore production; (.....), pig iron (hot metal) production; (_ _ _), coke production; and (_._.), scrap consumption (3).

2. Coals for Cokemaking

Known world coal reserves in 1990 were estimated to be about 1000–1600 billion metric tons (4). The geographic distribution of these reserves is widespread, but about two-thirds of this coal resides in the United States, People's Republic of China, and the Commonwealth of Independent States. Some 637–1075 billion metric tons is classified as anthracite and bituminous coals of which 10% is estimated to be suitable for cokemaking. Thus this 60–108 billion metric tons of coking coal, if recovered in a fully useful form, represents enough coal to supply coke plants at 1990 consumption rates for about 100–200 years. North America is estimated to possess about 130 billion metric tons of bituminous coal of which, perhaps, one-tenth would be classified as coking coal, most of which resides in the United States (4).

For by-product coke ovens, it is general practice to blend two or more types of coals that have complimentary technical as well as economic characteristics. Because most by-product coke plants are located near the large industrial users of the coke and by-products, coals usually have to be transported from the coal mines

Table 2. Classification of Coals by Rank[a]

Class	Fixed carbon limits, %[b]	Volatile matter limits range, %[b]	Calorific value limits, J/kg[c,d]
Anthracitic coals[e]			
meta-anthracite	98[f]	2[g]	
anthracite	92–98	2–8	
semianthracite	86–92	8–14	
Bituminous coals[h]			
low volatile	78–86	14–22	
medium volatile	69–78	22–31	
high volatile A	69[g]	31[f]	14000[f]
high volatile B			13000–14000
high volatile C			11500–13000, 10500–11500
Subbituminous coals[e]			
subbituminous A			10500–11500
subbituminous B			9500–10500
subbituminous C			8300–9500
Lignitic coals[e]			
lignite A			6300–8300
lignite B			6300[g]

[a] Ref. 7.
[b] Dry, mineral-matter-free basis.
[c] Moist, mineral-matter-free basis.
[d] To convert J to cal, divide by 4.184.
[e] Nonagglomerating.
[f] Value is equal or greater than.
[g] Value is less than.
[h] Commonly agglomerating.

to the coke plants. Thus coal blends are designed on integration of coke quality needs, by-product quality needs, coal costs, transportation costs, impacts of productivity, and impacts on the coke ovens themselves. The physical behavior of coal blends during coking can damage coke ovens.

The United States possesses a wealth of good quality coking coals in the Appalachian states as well as in locations in some southern and western states (4) (see Coal). Coal blends normally consist of higher rank (more metamorphosed) coals in minor proportion relative to certain lower rank coals. The higher rank coals are referred to as medium volatile and low volatile according to the classification system shown in Table 2. Similarly, the lower rank coking coals are referred to as high volatile. The reference to volatility reflects the relative amounts of by-products derived from the coals. High volatile coals generate more gas and tar during coking than do the medium and low volatile coals. Coals having either very low or very high volatile contents are not extensively used in cokemaking for technical reasons.

Medium and low volatile coals contribute great strengthening components to the resultant coke. High volatile coals provide the background network of coke structure because of the high propensity to become fluid and to intermix with other coals during coking including the reactives–inerts theory in which coking coals are thought of as contributing aggregate and cementlike materials that, if properly balanced, produce a strong concretelike product. However, as other coke properties besides cold strength have gained importance, basic research on coal carbonization behavior has shown the carbonization mechanisms to be much more complex than is considered in the current views of coal blending technology (6).

From a bulk chemical standpoint, coking coals may be considered to consist of irregular macromolecules that are nearly two-dimensional and are held together by noncovalent bonds. Up to 80% of the carbon is hydroaromatic or aromatic. This percentage of aromatic molecules, versus aliphatic ones, increases with coal rank. The aromatics are of a condensed angular ring structure and are often connected together via aliphatic or ether bridges. These linked rings form chains of molecules along which exist short methyl, ethyl, or hydroxyl side chains. These chains may also contain other elements such as oxygen and sulfur. Coals having lower rank than about high volatile A are generally considered noncoking in that the individual coal particles only weakly, or not at all, fuse together under standard coking conditions. Lower rank coals have a lower aromaticity to the point that most of the carbonization decomposition products consist of low molecular-weight hydrocarbons that are gaseous, thus little or no plastic material is generated. Coals higher in rank than low volatile are similarly viewed because their highly aromatic molecules are strongly cross-linked, as a result of the coalification process, which prevents generation of much plastic behavior during coking.

The smallest semihomogeneous components of coal identified are a group of materials of microscopic size called macerals. Coal, formed from geological processes acting for hundreds of millions of years on remains of ancient plant life, is a complex, heterogeneous material. Indeed, microscopically, coal can be seen to be composed of different groups of materials that, within a group, have uniform and unique combinations of color, texture, and structure. These macerals, the organic analogues to the inorganic minerals, are routinely quantified when coals are characterized in support of determining coking abilities and suitability for blending with other coals. For simplicity, macerals are discussed in terms of the three main groups, although it is clear that different macerals within a group may actually possess quite distinct behaviors during carbonization (6). Petrographic characterization of coking coal is the main science used worldwide to design coal blends for metallurgical cokemaking.

In most coals, the predominant group maceral is vitrinite, largely derived from the woody parts of the plants from which coal originates. Under standard microscope techniques, vitrinite appears as an intermediate gray material of relatively uniform mixture. Owing to its molecular structure, vitrinite is semistable when subjected, in the absence of oxygen, to the conditions of cokemaking. As the less stable portions of the heated vitrinite decompose to form volatile compounds that are eventually recovered as part of the cokemaking by-products, the particles soften. Vitrinite particles can become fluid and act as a solvent relative to other coal components. This mobility and ability to interact with other coal constituents results in fusing of adjacent coal particles to form coherent large carbon-rich structures that account for most of the carbon in coke. In the process, small optically active liquid crystal spheres of aromatic molecules, called mesophase, promote crystallographic alignment of the carbon atoms into locally oriented regions known as mosaics. These mosaic structures have unique optical, chemical, and structural properties. Among these properties is anisotropy, the ability to reflect light to different degrees depending on orientation of the material. This crystallinity has a profound impact on the subsequent behavior of coke in the blast furnace.

Another group maceral is inertinite which results from coal-forming dehydrogenation processes, whether chemical or thermal, acting on virtually any type of plant material. As the name implies, inertinite generally is thermally stable at cokemaking temperature and does not become fluid or even appreciably soften. Inertinite macerals may originate from any part of the original plants, but these plant parts were chemically altered during the coalification process. Any structure, such as plant cell walls, present in the archetypical inertinite can still be present in the material after it has been coked. Inertinite macerals, however, do evolve gaseous hydrocarbon compounds during carbonization. The remaining molecules are not normally mobile in inertinite and the heterogeneous carbon arrangement results in an isotropic type of carbon that performs quite differently in the blast furnace than does anisotropic carbon from other macerals. Microstructural analysis of coke is widely used to characterize carbon forms and spacial distribution, in order to better understand the suitability of the coke for blast furnace use.

Yet another group maceral, exinite (also called liptinite), represents the waxy and resinous plant components and is largely aliphatic and very unstable at coking temperatures. These macerals, in general, almost totally decompose into gases during carbonization and very little, if any, of a given exinite maceral remains in the product coke. Other types of maceral behaviors, which are not easily classified, have also been found. All ranges of behavior intermediate to those of the vitrinites, inertinites, and exinites exist and some macerals can influence the carbonization behavior of others. For example, some inertinite particles have been found to soften and fuse if located adjacent to some exinite particles. The resulting carbon from these inertinites can become aligned in the process and be optically anisotropic, similar to the carbon derived from some vitrinites. A host of other material interactions, including those that inhibit coalescence of adjacent softened particles, are also known (6).

Coal arrives at the coke plant by ship, rail, conveyor, or truck. Each type of coal is unloaded into a separate stockpile in the coal field. Reclaiming of coal from the stockpile can be accomplished using mobile equipment or bridge-mounted hoists. Coal of each type is moved to its coal bunker. In some plants, it is possible to crush each coal independently prior to it reaching the coal bunker. This crushing is often done in two stages. The first stage may be to simply ensure that no large, ie, usually no larger than about 25 mm, coal lumps remain and to ensure that large pieces of rock or foreign material are removed. The second stage of crushing takes place in a hammermill or similar facility that is equipped to pulverize the coal. It is common practice to pulverize coal for cokemaking to more than 80%, being less than 3 mm in size. In other plants, crushing of the coal takes place after the various coals have been blended. This blending is accomplished by discharging measured, either mass or volumetric, amounts of each coal into mixing bins. This may be accomplished through use of intermediate conveyor belt systems as well. The coal blend is then withdrawn from the mix bins and is transported to the coal blend silo at the coke battery. This material flow is depicted in Figure 2.

Coals are not usually stored at coke plants for lengthy time periods. Besides the costs to maintain such inventories, coal undergoes low temperature oxidation that can adversely impact its coking behavior (8). Oxygen can form cross-links in the coal molecules and inhibit the softening character needed for coke formation. Also, coke shrinkage can be significantly destroyed, leading to coke oven damage as the coke is pushed after the end of the carbonization cycle.

3. Coking Mechanism

There are several necessary conditions for coal to be transformed into coke. These include a heat supply, enclosure, or blanketing to prevent oxygen contact with the coal, and close contact between the coal particles during the carbonization process. In conventional vertical coke ovens these conditions are readily met. The heat is supplied from gas-burning flues located within the walls of each oven. Loading, called charging, of the coal into the oven, and retrieving, called pushing, of the product coke from the oven are accomplished via openings in the oven that can be sealed to prevent incursion of air. Finally, the coal particles are charged into the oven by being dropped from a height so that the particles are packed together between the opposite walls of the oven, causing contact between particles. In this configuration, even for cubic particles and excluding contact with gas pockets, each particle, on average, comes into contact with six other particles.

Upon heating, coal molecules undergo many reactions. The primary reactions involve pyrolysis and formation of radicals having lower molecular weight than in the original coal. Some of the radicals, enriched with hydrogen, form liquid and gaseous products. In other reactions some radicals form more stable substances of higher molecular weight and less hydrogen content. Surface tension on the liquid components promotes additional contact between these components to further facilitate fusing the coal particles as they are heated.

When coal is charged into the hot coke oven, the coal particles adjacent to the coke oven walls and doors begin to devolatilize and soften immediately. The softened, or fluidized, particles sinter into each other and are further devolatilized to form a layer of fully sintered coal particles, ie, coke against the oven walls and doors. Away from these hot surfaces are successive layers of coal in various stages of softening, melting, fusing, and resolidifying. This arrangement results in the existence of an envelope of “plastic” coal that continues to move inward, away from the heated surfaces, until the plastic envelope converges at the center of the coal charge. What results are three separate regimes of coal/coke transformation that occur simultaneously in a given coke oven until the plastic envelope is consumed. Formation and movement of the plastic envelope is shown in Figure 3.

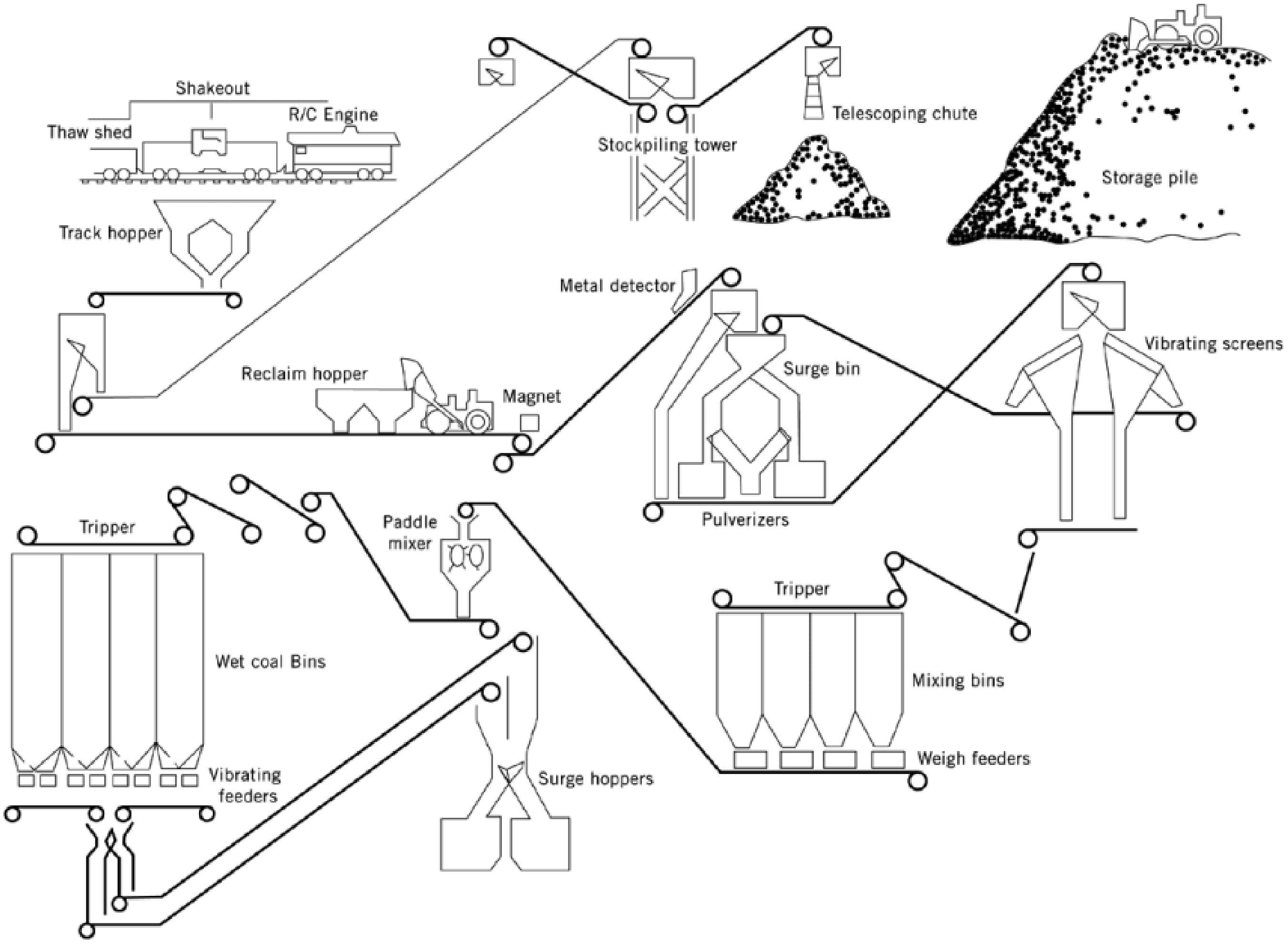

Fig. 2. Coal handling system for cokemaking.

The plastic envelope represents a barrier to gas movement. Although gases generated in the envelope move out in both directions, gases generated on either side of the envelope do not generally cross this barrier. On the hotter side of the envelope, toward the heating surfaces, decomposition of the envelope leaves a porous solid carbon often referred to as semicoke. The semicoke adjacent to the envelope still contains much volatile gas which continues to be driven off as it reaches higher temperatures from heat transfer from the oven walls and doors. The remaining volatiles in this semicoke decrease to nearly zero as proximity to the hot surfaces increases. During this heating, the carbon crystal structure grows and becomes increasingly oriented, and the porosity of the carbon decreases as the pore walls thicken and densify. This process continues even to very high temperatures, but conventional cooking is normally considered to have concluded by the time the carbon reaches about 1000°C.

On the cooler side of the plastic envelope, toward the center of the coal charge, the coal remains at least as cool as about 100°C until all of the water in the coal, both chemically bound and on the surface of the coal particles, is converted to steam and flows out of the coal mass. This process also occurs progressively in layers

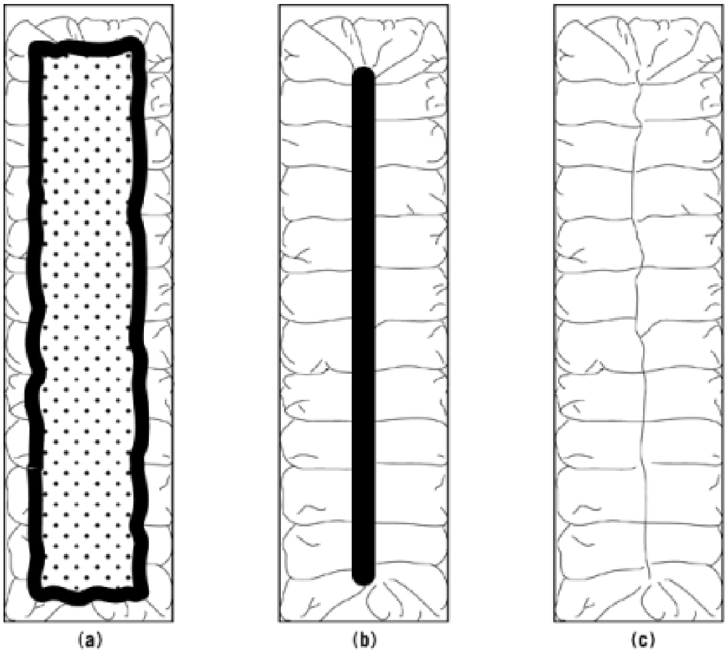

Fig. 3. Development of plastic layer movement during coking: (**a**), about midway in coking cycle; (**b**), convergence of plastic envelope; and (**c**), end of coking cycle. The thick, dark, solid line represents the plastic envelope, defining the boundary between coal and semicoke; and ⊡ represents the plasticized coal.

away from the plastic layer. Immediately adjacent to the colder side of the plastic layer, the coal particles are completely dry and elevated to a temperature just below that needed to cause the particles to soften. At the center of the coal charge, temperatures may not rise above that of the boiling point of water for several hours after the coal is charged into the oven. For coke oven wall temperatures of about 1200°C, the complete coking cycle requires 18 hours or more. This cycle starts when coal is charged into the hot oven and ends when the last of the volatiles are degassed from the coke at the center of the charge, which is the coolest part of the charge.

After semicoke has been formed and continues to degas, it tends to physically shrink. The volume of this material is lowered as the carbon atoms align into more compact forms. This effect of itself would tend to cause the coke mass to contract away from the oven walls and doors. However, buildup of gas pressure within the plastic layer and thermal expansion of the coal particles produce forces that tend to continue pressing the coke in contact with the oven walls and doors, as shown in Figure 4. The force keeping the coke in contact with the walls and doors acts to maintain good heat transfer from the oven surfaces into the coke mass. However, if this pressure is high, the oven surfaces, in particular the walls, can themselves be deflected. The walls are constructed of brittle refractory materials (see Refractories) and such deflection leads to a gradual deterioration of the strength of the oven structure. Moreover, high instantaneous wall pressures can cause catastrophic failure of the oven walls in a matter of hours. Thus coal blends and coking conditions must be carefully matched to ensure that the pressures attained are not excessive. Additionally, if the coke mass remains in intimate contact with the coke oven walls through the coking cycle, friction between the coke and walls as the coke is pushed from the oven can also damage the walls. Thus the final balance of pressure and contraction should favor contraction so that the coke surfaces have moved away from the oven surfaces prior to pushing of the coke from the oven. In actual practice, wall pressure and coke shrinkage requirements place a significant restriction on usable coal blends for vertical oven cokemaking.

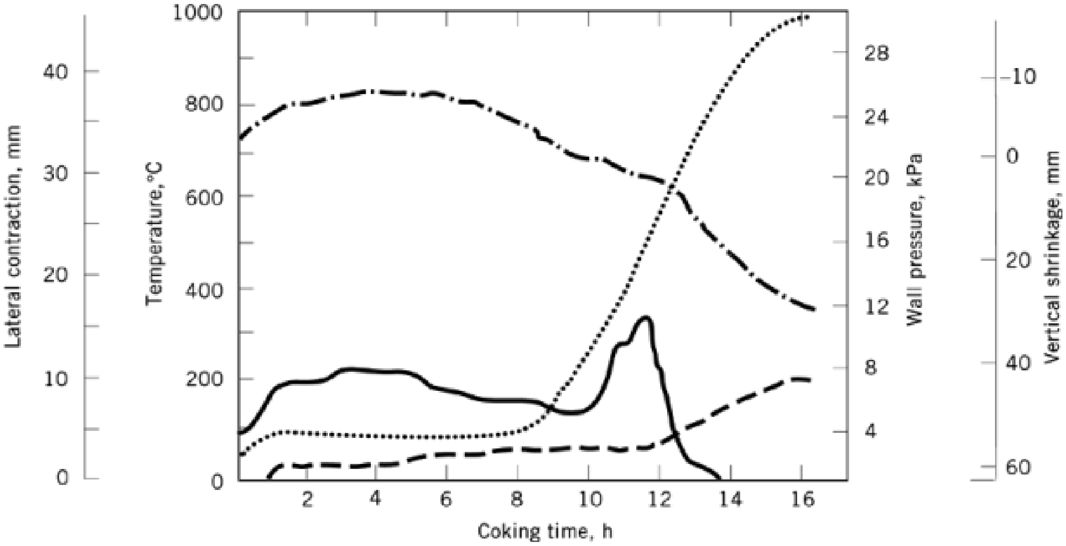

Fig. 4. Parameters in a coking cycle where (—) represents coke oven wall pressure; (....) coal charge center temperature; (_ _ _) coke mass lateral contraction; and (_._.), coke mass vertical shrinkage. To convert kPa to psi, multiply by 0.145.

4. Coke Ovens and Battery Operation

Figure 5 shows a schematic of a modern coke oven. Individual coke ovens are constructed of interlocking silica bricks that are produced in numerous shapes for special purposes. It is not uncommon for modern coke oven batteries to contain 2000 different shapes and sizes of brick. Typical coke ovens are 12–14 m in length, 4–6 m in internal height, and have less than 0.5 m internal width. On each side of the oven are heating flues also constructed of silica brick. Batteries of adjacent ovens, where ovens share heating flues, contain as many as about 85 ovens. At each end of each oven, refractory-lined steel doors are removed and reseated for each oven charge and push. Beneath each oven is a refractory substructure of the heating system regenerator checkers and sole flues for heating the oven floors. Combustion air, and sometimes combustion gases, are preheated in the regenerator. Reversing equipment periodically, perhaps twice per hour, reverses gas and air flow to the oven flues in order to maintain uniform temperature distributions in all of the flues. A concrete basement in which various battery equipment and portions of the heating system are contained is also standard. Coke batteries are generally heated with part of the coke oven gas generated in the cokemaking process, however, they can be heated using blast furnace gas and natural gas also. Once heated, the battery generally remains hot for its entire life because cooling of the silica brick causes a mineralogical change in the silica that lowers the strength of the brick. This effect is not reversed upon reheating, thus unexpected, sustained loss of heat can be catastrophic to the ovens.

Above the ovens is a roof system capable of supporting the moving Larry car from which coal is discharged into each oven through 3–5 charging holes in the roof of each oven. The Larry car itself is filled, for each oven charge, from a large blended coal silo that is constructed above the travel of the Larry car, usually at one end of the coke battery. Modern Larry car technology includes telescopic charging chutes for minimizing dust emissions during charging. Many facilities also include automatic charging hole lid removal and reseating. Considerable attention is given to the order in which coal is charged through each charging hole, overlapping of charging through the different holes, etc in order to produce as uniform a charge as possible and minimal emissions. After completion of charging and reseating of the charging hole lids, a small subdoor at the top of

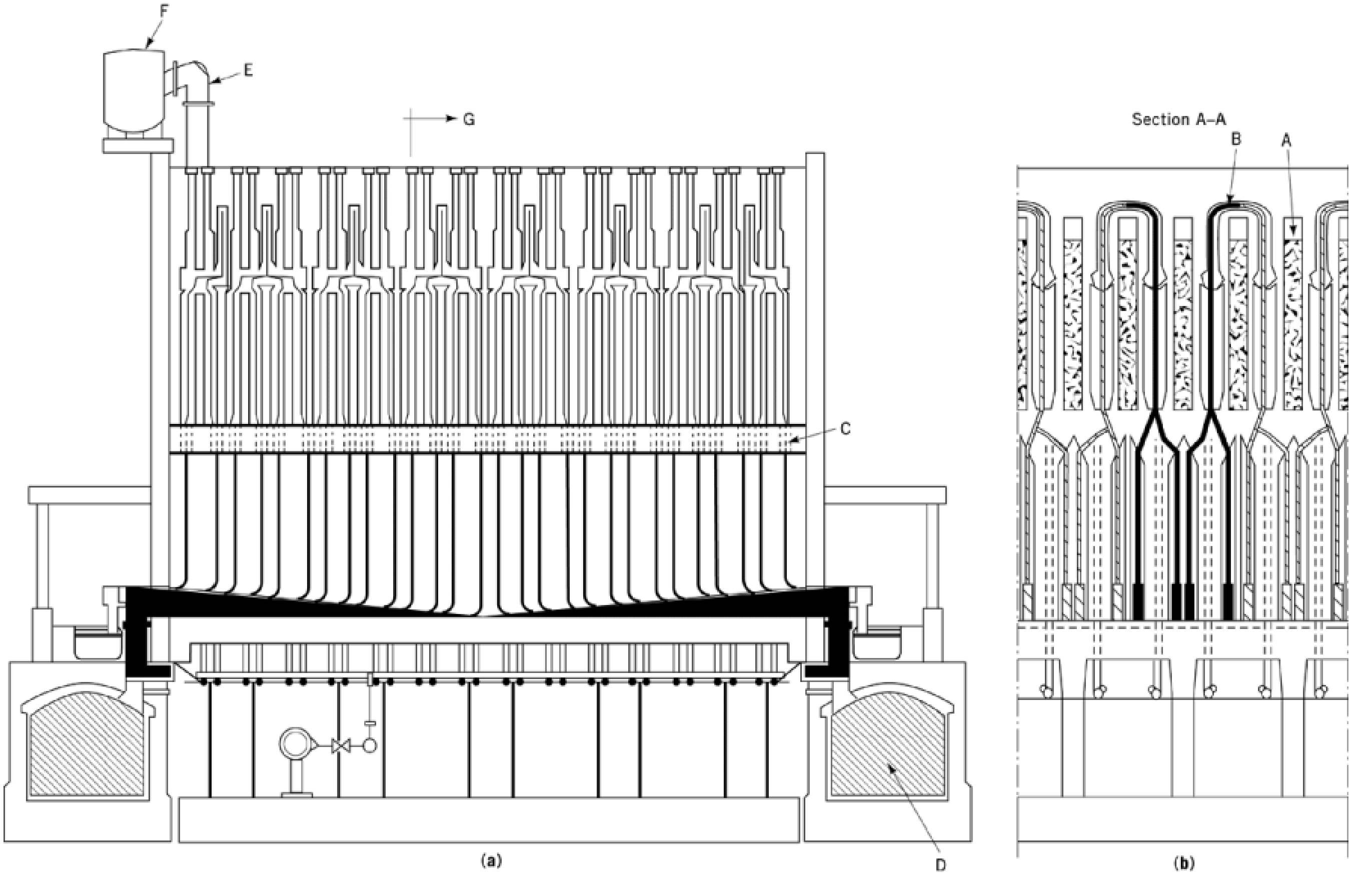

Fig. 5. (**a**) By-product coke oven of the Koppers-Becker type and (**b**) a section therein, where A represents the coke oven chamber containing coal; B, oven wall heating flue; C, sole heating flue; D, air preheating; E, standpipe; F, collecting main; and G, relationship between the two sections.

one of the oven doors is opened and a steel leveling bar is inserted along the length of the oven at the top of the coal charge. The leveling bar is moved back and forth over the coal charge to produce a level coal charge having sufficient free space above the charge. This free space is important in ensuring balanced heating of the coal and is needed for conveying the carbonization volatiles out of the oven. Most coke batteries charge wet coal into the ovens, however, a few facilities are equipped with coal preheaters that not only remove all moisture from the coal, but preheat it to 150–200°C in order to quicken the carbonization process. The preheat charge facilities function very similarly to wet charge facilities with the exception of more attention being paid to potentially higher charging emissions because of the dryness of the coal.

On the battery top, at either one or both ends of each oven, are refractory-lined standpipes mounted on additional roof openings into each oven. The volatile gases generated from the coal during carbonization flow to the top of the oven, into the free space, and out the standpipes. The standpipes are all connected to huge collecting mains that run the length of the battery. These mains transport the gases to the by-product plant in which the gases are processed into various materials. Cooling water is sprayed into the mains in order to cool the gases and to condense some of the tar out of the gas. A typical flow diagram for a modern by-product coke plant is shown in Figure 6.

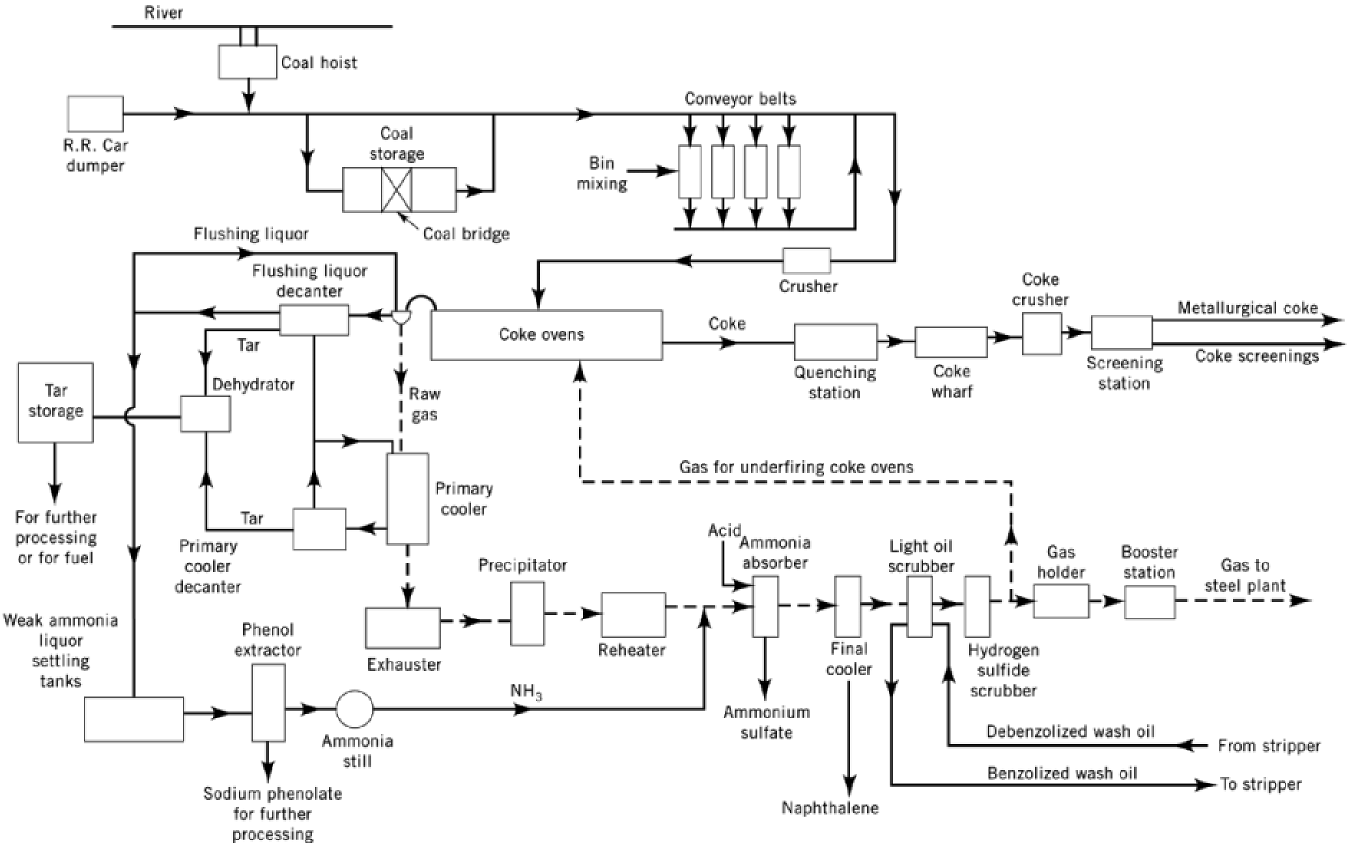

Fig. 6. Schematic for a by-product coke plant (9).

During charging, standpipe valves are positioned so that all gases pass directly into the collecting main. This includes the volume of air displaced from the oven by the coal, coal dust generated during charging, and steam and other gases generated during initial contact of the coal with the oven surfaces. To prevent gas pressure in the oven from building up during charging to the point that gas is forced past the doors, aspiration nozzles in the standpipes use steam to maintain a slight suction on the oven during charging. After pushing, standpipe valves are generally positioned to allow escape to the atmosphere of carbon dioxide gas produced from combustion of wall carbon while the oven is empty.

At the end of each oven's coking cycle, which ranges from about 16 to 24 hours depending on production needs and battery condition, the doors are removed from the oven. A pusher machine equipped with a large water-cooled ram then pushes the coke from the oven into a hot or quench car. After the coke is pushed from the oven, the doors are replaced to maintain oven heat and for maintenance of oven carbon. Oven carbon refers to carbon from the coal that coats the internal surfaces of the oven. Because the refractory bricks are essentially mortarless, the carbon acts to seal the oven wall and prevent cross leakage of gases between the ovens and the flues. Too much carbon buildup, however, can interfere with heat transfer, particularly at the oven top, and reduces the oven volume. Adjustments of the time during which each oven is empty, and the internal conditions of the oven, are made to maintain a balance between carbon burnoff in the empty oven and carbon buildup in the charged oven. The hot car may or may not be constructed with a moveable roof or partial roof to minimize gaseous and particulate emissions. The car moves on rails and positions the hot coke beneath a large water tank equipped with nozzles on its underside. Water flow is timed to quench the coke with a minimal amount of excess water remaining on the cooled coke. After quenching, the hot car again moves to dump the coke onto a refractory covered coke wharf sloped away from the hot car. The coke flows to the bottom of the wharf at which point it drops onto a conveyor system for transportation to blast furnace, storage pile, or for further transportation out of the plant.

Coke ovens in a battery are charged with coal and pushed according to planned schedules. These schedules attempt to ensure that wall pressures generated in adjacent ovens are balanced to prevent wall movement, and that heat utilization and movement of charging and pushing equipment are optimized. To balance heat utilization from the flues, it is undesirable to charge ovens sequentially because each flue would be trying to heat ambient, wet coal in both of its ovens. Therefore, ovens are pushed in any one of a number of pushing series which may consist of pushing every tenth oven, every seventh oven, odd ovens, etc depending on productivity, battery life, and heating impacts on the facility. In modern coke plants, computerized control systems manage oven scheduling and heating.

5. Coke Properties and Use

Coke, used in ironmaking blast furnaces, provides three primary functions. First, coke is the fuel that is burned in the blast furnace. The heat generated by combustion of coke provides the energy needed for the various reactions in the process including the melting of iron raw materials and the elevation of liquid iron to the temperatures required for downstream processing into steel. Second, the gases produced from combustion and gasification of coke are the reducing agents to remove oxygen from the iron raw materials in the blast furnace. Third, coke is the only blast furnace material that remains solid at the high temperatures that exist in the lower portions of the furnaces. This means that the coke can support the rest of the materials and provide passageways for the ascending gases and descending iron droplets to meet and interact. The ability to maintain permeability in the blast furnace is perhaps the most important function of coke. These functions and interactions are shown in Figure 7.

The combustion and reduction functions of coke are enhanced by maximization of the carbon in the coke. This means that the other chemical constituents of coke derived from the coal sulfur and coal minerals should be as low as possible as the presence of these impurities dilutes the amount of carbon in coke. Additionally, these impurities must be melted, prevented from entering the molten product iron, and must then be removed from the blast furnace. This is accomplished by maintaining a molten slag layer that floats on the molten iron and periodically “tapping” this slag from the furnace. The slag chemistry and properties are continually adjusted to drive the coke impurities, as well as impurities from other raw materials, into the slag rather than into the pig iron. The materials added to the blast furnace in order to effect this slag volume, chemistry, and properties must also be melted. Slag components arising from coke impurities create a thermal drain on the blast furnace and occupy furnace volume that could have otherwise contributed to productivity. Thus coke impurities have a twofold negative effect on the blast furnace: dilution of the useful coke, and increased consumption of the useful coke in order to melt the impurities and associated slag materials. Of special concern are phosphorus and alkalies. The boiling points of most alkali compounds result in recirculation of some alkali in the blast furnace. The refractory lining materials used in blast furnaces can be attacked, consumed, and weakened by these alkalies. Phosphorus, which does not readily combine with blast furnace slag, largely exits the blast furnace in the hot metal. The phosphorus content of steel has a significant impact on the properties of the steel, so hot metal phosphorus must be controlled through blast furnace input levels or through expensive hot metal or liquid steel dephosphorization processes.

The burden support and permeability function of coke is enhanced by the coke degrading in size as little as possible as it progresses downward through the blast furnace. This means that, in addition to minimum

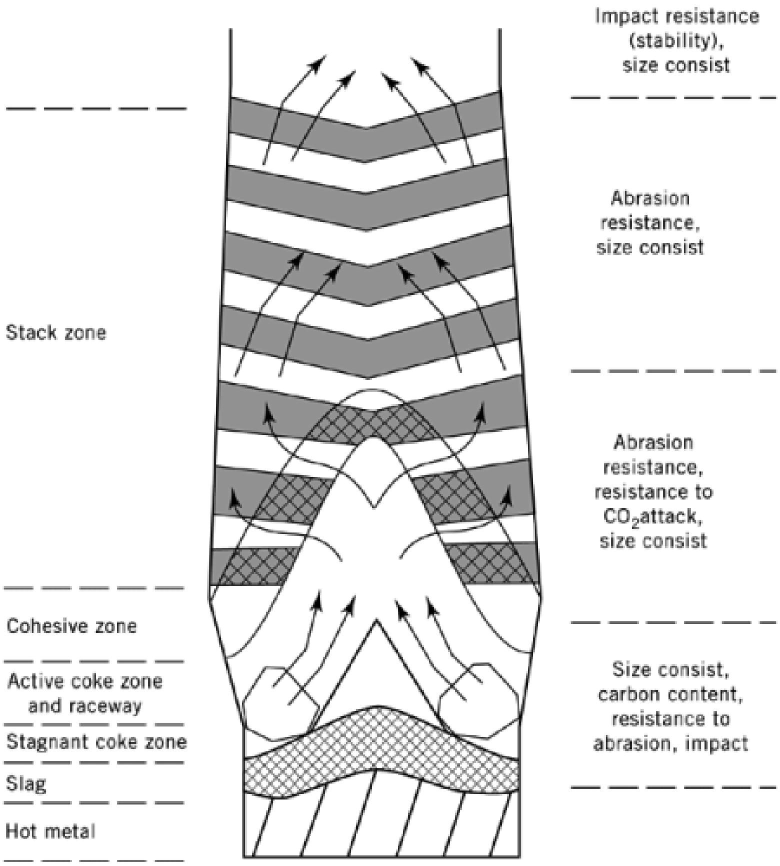

Fig. 7. Primary functions of coke in a blast furnace showing the various furnace zones where arrows indicate direction of gas flow. The term size consist indicates the presence of a distribution of sizes.

breakage as the coke is transported from coke plant to blast furnace, the coke should be as resistant as possible to all of the blast furnace conditions that act to degrade the coke.

When coke is first charged into the blast furnace, it falls through some distance before coming to rest on top of other burden materials in the blast furnace. This acts to break the coke at the relatively cool temperatures that exist at the furnace top. Various laboratory tests exist that attempt to gauge the ability of coke to resist this breakage. In North America the most widely used of these tests is the Tumbler Test, which measures coke stability, standardized by ASTM (7). Elsewhere in the world, similar tests such as the Micum, JIS, and Irsid tests gauge coke resistance to breakage in tumbler-type machines (8). The results of these tests have been statistically correlated to blast furnace performance, ie, to coke consumption per unit of pig iron and blast furnace productivity, even though the breakage phenomena are known to only partially reflect the actual performance. Most cokes presently measure between 55 and 65 stability. Values of over 60 are usually desired for use in large modern blast furnaces.

Coke degradation upon charging into the blast furnace is known to be only a minor effect compared to other degradation (10). These other mechanisms include thermal shock of the coke, gasification of the coke, attack by molten iron and slag, intercalation of alkalies into the coke crystal structure, carbon attack via oxygen liberated from coke impurities, and abrasion at various temperatures and atmospheres in the blast furnace

(11). Only the effect of gasification on coke degradation has been studied to the point that a widely accepted laboratory test of this coke characteristic has been developed. The coke strength after reaction (CSR) test, developed by Japanese steel companies and building on earlier reactivity tests, subjects coke to a prescribed gasification and subsequent measurement of abrasion resistance (12). The higher the CSR, the better resistance to degradation stemming from gasification. Typical CSR values range from about 50 to 65. In large, modern blast furnaces, CSR values in excess of 60 are generally desired. All of the coke degradation mechanisms and ways to meaningfully characterize coke are under continued investigation. These studies are expected to generate additional coke quality measurement techniques (of an empirical nature), but are ultimately aimed at fundamental understanding.

6. Other Cokemaking Technology

Owing to the importance of coke to the steel industry, means for improving the quality of coke, lowering its cost of production, and developing cleaner cokemaking processes are always under investigation. Alternative technologies include modifications to by-product vertical coke oven processes, completely new process designs, and modifications to cokemaking processes used in the past.

One modification to the vertical coke oven process, coal preheating, gained attention and acceptance in the late 1960s and early 1970s. Several coke plants were built around the world in which the coal blend was thoroughly dried and preheated before it was charged into the oven via special Larry cars, enclosed conveyors, or pneumatic transport. The stated benefits of this technology were to shorten coking times to increase productivity, and to allow for use of marginal quality coals. By preheating the coal outside of the coke oven, coking cycles could be shortened by six hours (35%) or more and substantial reductions in coke battery operating costs could be realized. This preheating also changed carbonization conditions in the coke ovens such that use of lower rank and lower cost coals was possible while maintaining coke quality. Over the years, however, most of these facilities shut down as it was realized that costs of operating and maintaining the preheaters and additional battery maintenance negated the benefits of shortened coking cycles.

Another modification to the vertical coke oven process, dry quenching of the coke as first developed in the CIS (13), started becoming of interest in the 1960s and has continued to grow steadily. Using dry quenching, the coke is discharged into a hot car and is quickly transported and dumped into a sealed vessel. Contact with cooling gases, of various sorts, accomplishes slow cooling of the coke rather than the more conventional rapid quenching with water. In this way, the coke is dry when used at the blast furnace. Also, there are some claims of coke strength improvements resulting from dry quenching. Some facilities recover the heat from the cooling gases and make use of this heat for steam raising or electricity generation. Besides plants in the CIS, Japanese coke plants have extensively adopted this technology as have some European ones.

Extensions to the size of vertical coke ovens have been developed and this idea continues to be evaluated. The largest ovens actually implemented are in Germany. Rather than the conventional limit of 6-m oven heights, the Huckingen Plant contains a battery of ovens that are nearly 8 m in height (14). Also, beyond the conventional 460-mm mean oven width, the Prosper plant contains batteries of ovens tht are 590-mm in width (14). Such large ovens can hold more than twice the coal of conventional coke ovens and offer an advantage of fewer openings that can leak emissions per ton of production. These facilities were quite expensive to build, however, and wear and tear of operation over the years remains to be evaluated. Further extension of oven dimensions is planned for a jumbo reactor in Germany (15).

6.1. Formcoke Processes

A completely different approach to making coke is embodied in the various types of formcoke processes which produce coke briquettes in a series of reactors and vessels. The formcoke process, such as that shown in

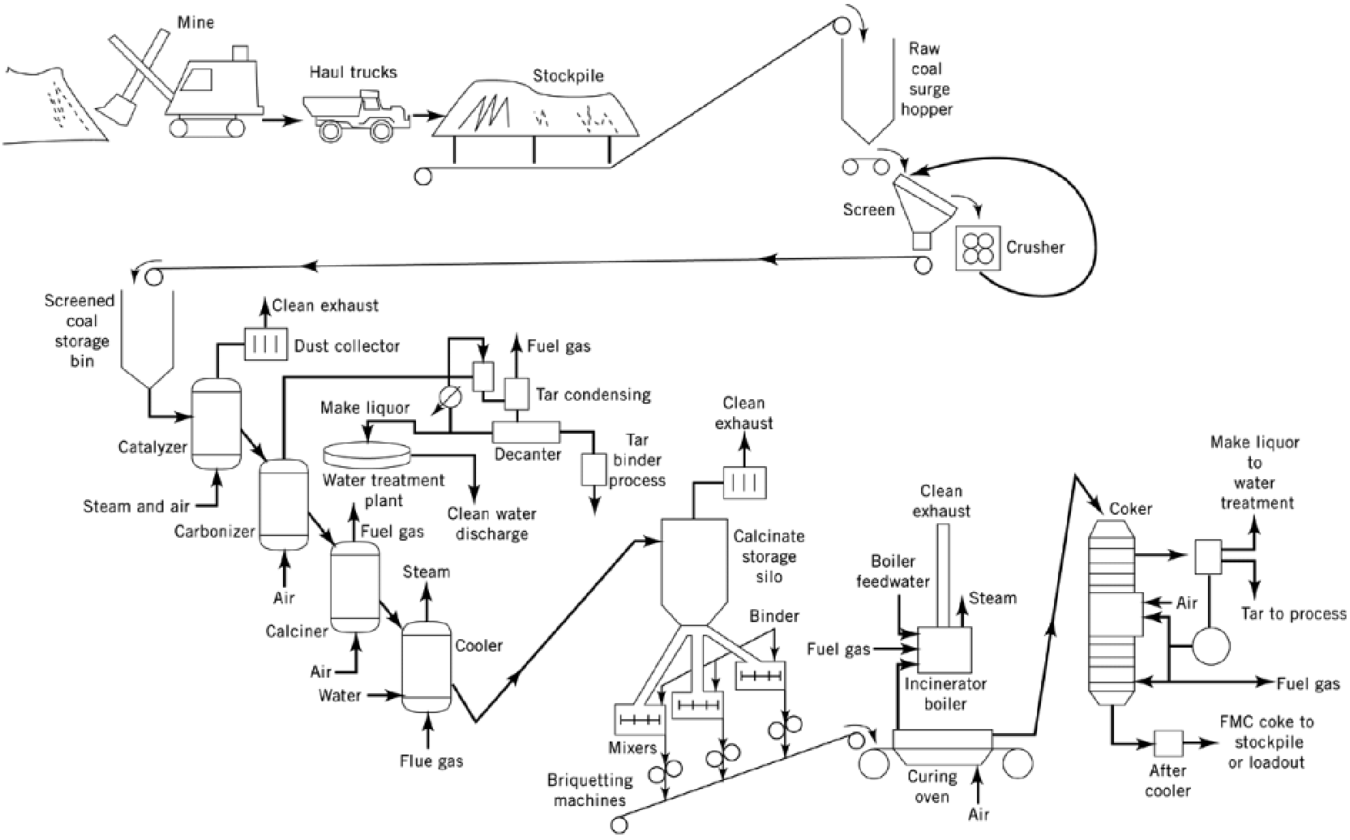

Fig. 8. Schematic of a formcoke process (16).

Figure 8, entails heating the coal, in a fluidized bed for example, to drive off some of the volatile matter. This volatile matter is collected and modified for future use. The remaining coal, referred to as char, can be prepared by crushing and screening and then mixed with an organic binder such as a petroleum product, a product of the volatile matter removed earlier in the formcoke process, or even a special type of highly fluid coal. The char/binder mixture is briquetted and the briquettes are further heated in a moving bed furnace to finish the carbonization cycle. The briquettes can be either dry or wet quenched. Alternatively, coals with or without additives may be briquetted in a hot briquetting press without need for the separate devolatilizing step. Formcoke offers the advantages of using a wide range of coals, minimizing emissions because of the closed vessels, and producing a uniform size coke product. In practice, the formcoke has not been considered suitable for general blast furnace use, however, because of its high degradation at higher temperatures. A few operating plants exist, but these mainly produce formcoke for nonblast furnace uses. Additional study may produce commercial formcoke plants for support of ironmaking blast furnaces (16).

6.2. Nonrecovery Cokemaking

Another cokemaking technology that is being practiced in various forms in several countries is nonrecovery cokemaking (17). This technology evolves around horizontal ovens somewhat similar to those that were used historically along with beehive ovens. In the People's Republic of China and other developing countries,

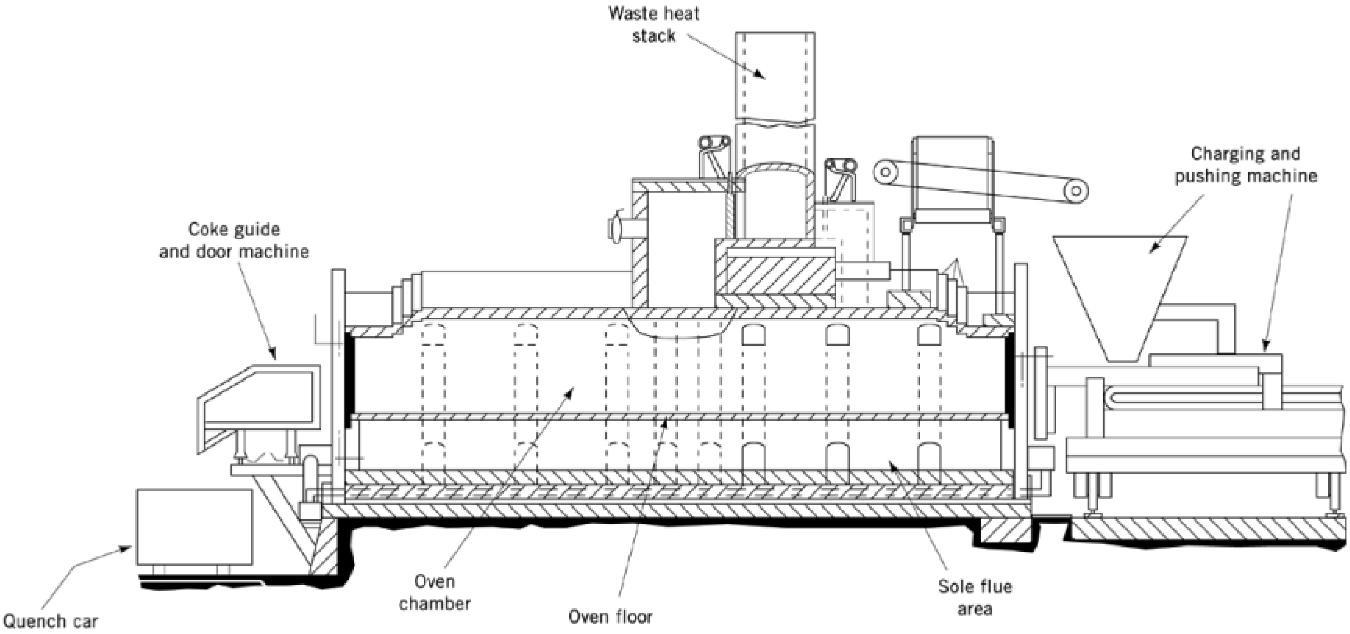

Fig. 9. Modern nonrecovery coke oven (19).

numerous coke plants exist based on oven designs that have changed little since the early 1800s. These consist of rectangular ovens constructed of simple clay bricks. The ovens can be on the order of 1–1.5 m high, 1.5–2.5 m in width, and 5–10 m in length. Coal is loaded into cold ovens and is covered with movable roofing material and/or mud and straw mixtures. The coal is then ignited through openings in the walls or roof. The coal in the vicinity of the openings burns and generates heat that is conducted into the rest of the oven to carbonize that coal. At an appropriate time, usually after several days, the roof materials are removed and the coke is water quenched while still in the horizontal ovens. After a few days of drying, the coke is then removed from the oven and the cycle is restarted. In these simple coke plants, most movement of coal and coke is done using manual labor, beasts of burden, and simple mechanized equipment.

Updated versions of horizontal coke ovens exist in developed countries including Australia and the United States (18). These nonrecovery ovens are constructed of silica brick and have permanent roofs. Doors at each end of each oven are removed for pushing, and, for some facilities, charging of coal into the ovens. The ovens remain hot at all times and are heated by a combination of heat from combustion of coal volatiles and coal in the oven itself and coal volatiles that are drafted through flue systems in the oven walls and floors. The existence of flues in the oven floors, also called soles, gives rise to another name for these ovens, sole flue ovens. These types of nonrecovery ovens have about the same dimensions as those of past generations, but the coke is pushed and water quenched outside of the oven as in modern vertical coke ovens. Though this cokemaking technology produces coke suitable for use in blast furnaces, it is not very prominent as of this writing. However, low costs and relative low emission of pollutants may stimulate future growth in use of the most technologically advanced versions of nonrecovery cokemaking. Figure 9 shows one of these nonrecovery coke ovens.

Other types of cokemaking technology include both batch and continuous processes, and processes that use electrical induction as the heat-transfer mechanism. Processes under development are further described in Reference 16.

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