Coke Oven Emissions*

Known to be a human carcinogen
First Listed in the *Second Annual Report on Carcinogens* (1981)

Carcinogenicity

Coke oven emissions are *known to be human carcinogens* based on sufficient evidence of carcinogenicity in humans that indicates a causal relationship between exposure and cancer in humans. Prior to 1950, there were numerous case reports that linked employment in coke production with cancers of the skin, bladder, and respiratory tract. Since then, several cohort studies conducted in the United States, United Kingdom, Japan, and Sweden have reported an increased risk of lung cancer in humans exposed to coke oven emissions. Smoking was accounted for in some of these studies and was not found to be a significant confounding factor. A large cohort study of 59,000 steel workers reported that lung cancer risk increased with increasing duration of exposure to coke-oven fumes or intensity of exposure. Several studies of coke plant workers have reported an increased risk for kidney cancer. An excess of cancer at other sites (prostate, large intestine, and pancreas) was reported in single studies (IARC 1984, 1987).

There is sufficient evidence for the carcinogenicity of coke oven emissions in experimental animals. The carcinogenicity of coke oven emissions has been tested in mice (inhalation and skin application) and rats (inhalation) (IARC 1984, 1987). Coke oven emission samples applied weekly to the skin of mice for up to 52 weeks caused malignant skin tumors. These samples also showed tumor-initiating activity in mice. Several inhalation studies, using coal tar aerosols generated by samples collected from coke ovens, caused both benign and malignant lung tumors in rats and mice, and skin tumors in female mice. Chemical analyses of coke oven emissions revealed the presence of numerous known carcinogens and potentially carcinogenic chemicals, including several polycyclic aromatic hydrocarbons (PAHs), nitrosamines, coal tar, arsenic compounds, and benzene. In addition to these carcinogens, coke oven emissions contain several agents known to enhance the effect of chemical carcinogens, especially on the respiratory tract.

Properties

Coke is produced by blending and heating bituminous coals to 1,000 to 1,400°C in the absence of oxygen. Tars and light oils are distilled out of the coal, and gases are generated during this process. Coke oven emissions are defined as the benzene-soluble fraction of total particulate matter generated during coke production. These emissions are complex mixtures of dusts, vapors, and gases that typically include PAHs, formaldehyde, acrolein, aliphatic aldehydes, ammonia, carbon monoxide, nitrogen oxides, phenol, cadmium, arsenic, and mercury. More than 60 organic compounds, including more than 40 PAHs, have been identified in air samples collected at coke plants. One metric ton of coal yields approximately 545 to 635 kg of coke, 45 to 90 kg of coke breeze (large coke particulates), 7 to 9 kg of ammonium sulfate, 27.5 to 34 L of coke-oven gas tar, 55 to 135 L of ammonia liquor, and 8 to 12.5 L of light oil. Approximately 20% to 35% of the initial coal charge is emitted as gases and vapors. Most of these gases and vapors are collected in by-product coke production. Coke oven gas includes hydrogen, methane, ethane, carbon monoxide, carbon dioxide, ethylene, propylene, butylene, acetylene, hydrogen sulfide, ammonia, oxygen, and nitrogen. Coke-oven gas tar includes pyridine, tar acids, naphthalene, creosote oil, and coal-tar pitch. Benzene, xylene, toluene, and solvent naphthas may be extracted from the light oil fraction (IARC 1984).

Use

The primary use of coke is as a fuel reductant and support for other raw materials in iron-making blast furnaces (Kirk-Othmer 1999). Coke also is used to synthesize calcium carbide and to manufacture graphite and electrodes, and coke-oven gas is used as a fuel (IARC 1984). By-products of coke production may be refined into commodity chemicals (e.g., benzene, toluene, naphthalene, sulfur, ammonium sulfate, etc.) (Kirk-Othmer 1999).

Production

Coke production in the United States increased steadily between 1880 and the early 1950s, peaking at 72 million tons (65 million metric tons) in 1951. In 1976, the United States ranked number two in the world with 52.9 million tons (48 million metric tons) of coke, or about 14.4% of the world production (Kirk-Othmer 1979). By 1990, the United States produced 27 million tons (24 million metric tons) and was ranked fourth in the world. A continuing gradual decline in production has occurred as production has decreased from 22 million tons (20 million metric tons) in 1997 to 16.8 million tons (15.2 million metric tons) in 2002 (EIA 2003). Demand for blast furnace coke also has declined in recent years because technological improvements have reduced the coke rates (i.e., the amount of coke consumed per amount of iron produced) by 10% to 25% (Kirk-Othmer 1999). Consumption for 1997 to 2002, however, exceeded production by approximately 1 to 3 million tons (0.9 to 2.7 million metric tons) per year. As a result, imports, which ranged from 2.5 to 3.8 million tons per year (2.3 to 3.4 million metric tons per year) for 1997 to 2002, consistently exceeded exports, which were in the range of 0.8 to 1.3 million tons per year (0.7 to 1.2 million metric tons per year) for the same time period.

An estimated 330,000 to 3.5 million pounds (150 to 1,600 metric tons) of coke oven emissions were produced annually in the United States in 1984 (CEN 1984). Although the by-product process is designed to collect the volatile materials given off during the coking process, emissions escape because of structural defects around the doors or charging lids, improper use of engineering controls, improper work practices, and insufficient engineering controls (IARC 1984).

Exposure

The primary routes of potential human exposure to coke oven emissions are inhalation and dermal contact. Occupational exposure may occur during the production of coke from coal or while using coke to extract metals from their ores, to synthesize calcium carbide, or to manufacture graphite and electrodes. Workers at coking plants and coal tar production plants, as well as the residents surrounding these plants, have a high risk of possible exposure to coke oven emissions. In 1970, there were more than 13,000 coke ovens at 64 plants with an estimated 10,000 coke oven workers that were potentially exposed to coke oven emissions (NIOSH 1973). This number was essentially unchanged by 1975 but had declined to 23 coke plants operating about 3,800 ovens in 1998 (EPA 2001).

A study presenting the 1979 to 1983 measurements of exposure of employees to coke oven emissions at a steel plant found the levels among selected job classifications to be as expected given the job descriptions and the coking process (Keimig *et al.* 1986). Approximately 60% of the total emissions occur during charging, 30% during pushing, and 10% during quenching the coke (Kirk-Othmer 1979). Larry car operators, lidmen, and door machine operators stationed very close to the oven are exposed to volatiles released from the topside and side during charging and/or coke pushing and, therefore, have the highest mean breathing zone concentrations. Intermediate in the exposure rankings are the benchman-coke side and benchman-pusher side, who are exposed to volatiles through door leakage but are able to move away during the pushing operation. The group exposed to the lowest concentrations consists of the pusher operator, quencher car operator, heater, and heater helper; the operators do not work close to the coke ovens, while the heater and heater helper, who regulate gas reversals and check the oven temperatures, are found mainly in the control room. Data compiled by the International Agency for Research on Cancer (IARC, 1984) indicated that average concentrations of coke oven emissions in the breathing zones of workers were the lowest for the pusher-machine operator (0.39 mg/m^3) and highest for lidman (3.22 mg/m^3), tar chaser (3.14 mg/m^3), and larry car operator (3.05 mg/m^3). During the past several decades, pollution control efforts have reduced coke oven emissions (Kirk-Othmer 1979, Costantino *et al.* 1995).

Regulations

EPA

Clean Air Act

NESHAP: Listed as a Hazardous Air Pollutant (HAP)

Urban Air Toxics Strategy: Identified as one of 33 HAPs that present the greatest threat to public health in urban areas

Comprehensive Environmental Response, Compensation, and Liability Act

Reportable Quantity (RQ) = 1 lb

OSHA

Permissible Exposure Limit (PEL) = 0.150 mg/m^3 (benzene-soluble fraction)

"Comprehensive Standards" for occupational exposure to this substance have been developed

Guidelines

NIOSH

Recommended Exposure Limit (time-weighted-average workday) = 0.2 mg/m^3 (benzene-soluble fraction)

Listed as a potential occupational carcinogen

*No separate CAS registry number is assigned to coke oven emissions.

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