

Coke-Oven Emissions

CAS No.: none assigned

Known to be human carcinogens

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 from studies in humans.

Cancer Studies in Humans

Before 1950, numerous case reports linked employment in coke production with cancer of the skin, urinary bladder, and respiratory tract. Since then, several cohort studies conducted in the United States, the 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 published in 1969 reported that lung-cancer risk increased with increasing duration or intensity of exposure to coke oven fumes. Several studies of coking-plant workers reported an increased risk of kidney cancer. An excess of cancer at other tissue sites (prostate, large intestine, and pancreas) was reported in no more than one study for each site (IARC 1984, 1987).

Cancer Studies in Experimental Animals

There is sufficient evidence for the carcinogenicity of coke-oven emissions from studies in experimental animals. Exposure to coke-oven emissions caused tumors in two rodent species, at two different tissue sites, and by two different routes of exposure. Coke-oven emission samples applied weekly to the skin of mice for up to 52 weeks caused skin cancer, and these samples also showed tumor-initiating activity in initiation-promotion studies in mice. In several studies, inhalation exposure to coal-tar aerosols generated from samples collected from coke ovens caused benign and malignant lung tumors in rats and mice and skin tumors in female mice (IARC 1984).

Studies on Mechanisms of Carcinogenesis

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, coke-oven emissions contain several agents known to enhance the effect of chemical carcinogens, especially on the respiratory tract (IARC 1984).

Properties

Coke is produced by blending and heating bituminous coals to 1,000°C 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 (1,200 to 1,400 lb) of coke, 45 to 90 kg (100 to 200 lb) of coke breeze (large coke particulates), 7 to 9 kg (15 to 20 lb) of ammonium sulfate, 27.5 to 34 L (7.3 to 9.8 gal) of coke oven gas tar, 55 to 135 L (14.5 to 35.7 gal) of am-

monia liquor, and 8 to 12.5 L (2.1 to 3.3 gal) of light oil. About 20% to 35% of the initial coal charge is emitted as gases and vapors, most of which 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. Coke is also used to synthesize calcium carbide and to manufacture graphite and electrodes, and coke-oven gas is used as a fuel. By-products of coke production may be refined into commodity chemicals (such as benzene, toluene, naphthalene, sulfur, and ammonium sulfate) (IARC 1984, Kaegi *et al.* 2000).

Production

Coke production in the United States increased steadily between 1880 and the early 1950s, peaking at 72 million tons in 1951. In 1976, the United States ranked second in the world in coke production, producing 52.9 million tons, or about 14.4% of world production (Kaegi *et al.* 2000). In 1990, U.S. production was 27 million tons, fourth highest worldwide. Production gradually declined from 22 million tons in 1997 to 16.8 million tons in 2002 (EIA 2003). Demand for blast-furnace coke declined because technological improvements reduced the amount of coke consumed per amount of iron produced by 10% to 25% (Kaegi *et al.* 2000). However, annual consumption from 1997 to 2002 exceeded production by 1 million to 3 million tons. Thus, for this period, U.S. imports (2.5 million to 3.8 million tons) consistently exceeded exports (0.8 to 1.3 million tons).

In 1984, it was estimated 330,000 lb to 3.5 million pounds of coke-oven emissions was produced annually in the United States (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 the use of coke to extract metals from ores, to synthesize calcium carbide, or to manufacture graphite and electrodes. Workers at coking plants and coal tar production plants, as well as people who live near these plants, have a high risk of possible exposure to coke-oven emissions. In 1970, the United States had 64 coking plants operating more than 13,000 coke ovens, with an estimated 10,000 coke-oven workers potentially exposed to coke-oven emissions (NIOSH 1973). The numbers of plants and ovens remained essentially the same through 1975 but by 1998 had declined to 23 coking plants operating about 3,800 ovens (EPA 2001). During the past several decades, pollution-control efforts have reduced coke-oven emissions (Costantino *et al.* 1995, Kaegi *et al.* 2000).

About 60% of total coke-oven emissions occur during charging, 30% during pushing, and 10% during quenching of the coke (Kaegi *et al.* 2000). A study reported measurements of exposure of employees to coke-oven emissions (average breathing-zone concentration) at a steel plant from 1979 to 1983, by job classification. The exposure

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levels depended on proximity to the oven during the coking process (Keimig *et al.* 1986). Exposure levels were highest for larry-car operator, lidman, and door-machine operator; intermediate for benchman-coke side and benchman-pusher side; and lowest for pusher operator, quencher-car operator, heater, and heater helper. 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 lowest for pusher-machine operator (0.39 mg/m³) and highest for lidman (3.22 mg/m³), tar chaser (3.14 mg/m³), and larry-car operator (3.05 mg/m³).

Regulations

Environmental Protection Agency (EPA)

Clean Air Act

National Emissions Standards for Hazardous Air Pollutants: Listed as a hazardous air pollutant.

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

Comprehensive Environmental Response, Compensation, and Liability Act

Reportable quantity (RQ) = 1 lb.

Occupational Safety and Health Administration (OSHA)

While this section accurately identifies OSHA's legally enforceable PELs for this substance in 2010, specific PELs may not reflect the more current studies and may not adequately protect workers.

Permissible exposure limit (PEL) = 0.15 mg/m³ for the benzene-soluble fraction.

Comprehensive standards for occupational exposure to coke-oven emissions have been developed.

Guidelines

National Institute for Occupational Safety and Health (NIOSH)

Recommended exposure limit (time-weighted-average workday) = 0.2 mg/m³ for the benzene-soluble fraction.

Listed as a potential occupational carcinogen.

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