Nickel Compounds and Metallic Nickel

Introduction

Nickel compounds and metallic nickel have many industrial and commercial applications including use in stainless steels and other nickel alloys, catalysts, batteries, pigments, and ceramics. Nickel and "certain nickel compounds" were first listed in the *First Annual Report on Carcinogens* (1980) as *reasonably anticipated to be human carcinogens.* Nickel compounds as a class were first listed as *known to be human carcinogens* in the *Tenth Report on Carcinogens* (2002); this listing supersedes the listing of certain nickel compounds and applies to all members of the class. Metallic Nickel was reevaluated in 2000 and remains listed as *reasonably anticipated to be a human carcinogen.* Nickel alloys were reviewed in 2000 but were not recommended for listing in the Report on Carcinogens (see Appendix C).

The profile for nickel compounds and metallic nickel follow this introduction. The evidence for the carcinogenicity of nickel compounds and metallic nickel is discussed separately. However, most of the information on additional information relevant to carcinogenicity, properties, use, production, exposure and regulations is common to both nickel compounds and metallic nickel and therefore has been combined into one section following the carcinogenicity discussions.

Nickel Compounds*

Known to be human carcinogens
First listed in the *Tenth Report on Carcinogens* (2002)

Carcinogenicity

Nickel compounds are *known to be human carcinogens* based on sufficient evidence of carcinogenicity from studies in humans, including epidemiological and mechanistic information, which indicates a causal relationship between exposure to nickel compounds and human cancer. The findings of increased risk of cancer in exposed workers are supported by evidence from experimental animals that shows that exposure to an assortment of nickel compounds by multiple routes causes malignant tumors to form at various sites in multiple species of experimental animals. The combined results of epidemiological studies, mechanistic studies, and carcinogenesis studies in rodents support the concept that nickel compounds generate nickel ions in target cells at sites critical for carcinogenesis, thus allowing consideration and evaluation of these compounds as a single group. The IARC (1990) evaluation of nickel and nickel compounds concluded that nickel compounds are carcinogenic to humans based on sufficient evidence for the carcinogenicity of nickel compounds in the nickel refining industry and very strong evidence of carcinogenicity of a variety of nickel compounds in experimental studies in rodents.

Several cohort studies of workers exposed to various nickel compounds showed an elevated risk of death from lung cancer and nasal cancer (IARC 1990). Although the precise nickel compound responsible for the carcinogenic effects in humans is not always clear, studies indicate that nickel sulfate and the combinations of nickel sulfides and oxides encountered in the nickel refining industries cause cancer in humans. IARC (1990) made the overall evaluation of nickel compounds as a group based on indications from mechanistic and animal studies that the event responsible for inducing cancer is generation of ionic nickel at the target site. Anderson *et al.* (1996) reported that nickel refinery workers exposed primarily to soluble nickel compounds had a significant excess risk for lung cancer and that smoking and nickel exposure have a multiplicative effect. An excess risk of nasal cancer was also observed in workers exposed to nickel compounds.

In rats and in some studies with mice, inhalation or intratracheal instillation of nickel subsulfide or nickel oxide led to dose-related induction of benign and malignant lung tumors, including carcinoma (IARC 1990, NTP 1996a,b). Inhalation of nickel compounds also causes tumors to form in organs other than the lung, in particular, malignant and benign pheochromocytoma in rats (NTP 1996a, 1996b). Injection of various nickel compounds has repeatedly been shown to produce dose-dependent increases in tumors at a variety of sites in several species of experimental animals. Subcutaneous, intramuscular, intraperitoneal, subperiosteal, intrafemoral, intrapleural, intracerebral, intrarenal, intratesticular, and intraocular injections of nickel compounds all have caused malignant tumors to form at the site of injection. These tumors are usually sarcomas, but other types also develop. Injection of nickel produces distant tumors of the liver in some strains of mice (IARC 1990). Soluble nickel acetate is an effective, complete transplacental carcinogen in rats, and brief intraperitoneal exposure during pregnancy to this soluble nickel salt induces malignant pituitary tumors in the offspring. Additionally, exposure to nickel acetate through the placenta followed by exposure of the offspring to barbital (a known tumor promoter) produces tumors of the kidney (renal cortical and pelvic tumors) (Diwan *et al.* 1992). In adult rats, injection of soluble nickel salts followed by barbital exposure caused kidney cancer (renal cortical adenocarcinomas) that frequently metastasized to the lung, liver, and spleen (Kasprzak *et al.* 1990). No adequate data were available to evaluate the carcinogenicity of nickel compounds in animals by the oral or dermal routes of exposure.

Metallic Nickel
CAS No. 7440-02-0

Reasonably anticipated to be a human carcinogen
First Listed in the *First Annual Report on Carcinogens* (1980)

Carcinogenicity

Metallic nickel is *reasonably anticipated to be a human carcinogen* based on sufficient evidence of carcinogenicity from studies in experimental animals, which indicates there is an increased incidence of malignant and/or a combination of malignant and benign tumors at multiple tissue sites in multiple species of experimental animals. A variety of carcinogenicity studies in rodents indicate that metallic nickel powder can produce tumors when given by intratracheal instillation or subcutaneous, intramuscular, or intraperitoneal injection. Intratracheal instillation of metallic nickel powder induces primarily adenocarcinoma, whereas injection most frequently induces sarcoma, demonstrating that metallic nickel can induce both epithelial and connective-tissue tumors. Tumors have been produced by metallic nickel exposure in both rats and hamsters (IARC 1990).

The available data from human studies of metallic nickel exposures are less informative. The available epidemiological studies of workers are limited by inadequate exposure information, low exposures, short follow-up periods, and small numbers of cases.

Nickel Compounds and Metallic Nickel

Additional Information Relevant to Carcinogenicity

Many studies in cultured rodent and human cells have shown that a variety of nickel compounds, including both soluble and insoluble forms of nickel, damage genetic material. DNA strand breaks, mutations, chromosomal damage, cell transformation, and disrupted DNA repair have been observed in cell-culture studies. Nickel can bind ionically to cellular components, including DNA. The reduction–oxidation activity of the nickel ion may produce reactive oxygen species that attack DNA, and 8-hydroxy-2′-deoxyguanosine can be produced *in vitro* and *in vivo* in target tissues for cancers caused by nickel (IARC 1990, Kasprzak *et al.* 1990). Nickel can induce chromosomal aberrations in exposed humans.

The carcinogenic potency of various nickel compounds varies widely, based on solubility properties and speciation. Studies indicate that soluble nickel salts can be complete carcinogens (Diwan *et al.* 1992) and/or initiators of carcinogenesis (Kasprzak *et al.* 1990) at sites distant from the application site, which confirms that ionic nickel is the carcinogenic species. Differences in potency of nickel compounds may relate to the specific properties of the compounds that affect the availability of ionic nickel at target sites. The listing is based on a large body of scientific evidence supporting the concept that the nickel ion is carcinogenic. The hazard associated with a particular nickel compound largely relates to the propensity for the compound to release ionic nickel in the body. The evidence suggests that the relatively insoluble metallic nickel is less likely to present a carcinogenic hazard than are the nickel compounds that tend to release proportionately more nickel ion. This view agrees with that expressed by the International Agency for Research on Cancer (IARC) (IARC 1990), which based its overall evaluation of the carcinogenicity of nickel compounds as a group on the combined results of human epidemiological studies, carcinogenicity studies in experimental animals, and other data supporting the "underlying concept that nickel compounds can generate nickel ions at critical sites in their target cells." The IARC review group correctly pointed out that the carcinogenicity of nickel compounds depends not solely on their capacity to release ionic nickel, but also on factors that promote localization of high concentrations of nickel ions at critical tissue sites. This conclusion is consistent with evidence from experimental animals indicating that nickel compounds of moderate solubility can, under certain exposure conditions, be more carcinogenic than compounds that are more soluble. Thus, it is difficult to predict with any certainty the relative carcinogenic hazard posed by a particular nickel compound without a full understanding of its ability to release ionic nickel under specific exposure conditions.

The available evidence suggests that metallic nickel has carcinogenic properties because it can slowly dissolve in the body and release ionic nickel, an active genotoxic and carcinogenic form of nickel. No available data suggest that mechanisms by which nickel induces cancer in experimental animals would not also operate in humans.

Properties

Metallic nickel is a group 10 metallic element. It is a lustrous silvery hard ferromagnetic metal or a gray powder with an atomic weight of 58.7 a melting point of 1,455°C, and a boiling point of 2,730°C. It has a vapor pressure of 1 mm Hg at 1,810°C and a specific gravity of 8.91. Metallic nickel is soluble in dilute nitric acid, slightly soluble in hydrochloric acid and sulfuric acid, and insoluble in water and ammonia. It is resistant to attack by air and water at standard temperatures. However, powdered nickel is reactive in air and may ignite spontaneously (IARC 1990, ATSDR 1997, HSDB 2003).

Nickel oxides and hydroxides are practically insoluble in water and soluble in acids and ammonium hydroxide. Nickel monoxide is a green to black powder that becomes yellow when heated. It has a molecular weight of 74.7 and a specific gravity of 6.72. The temperature at which the crystal is formed determines the color of the crystal. It is soluble in acids and ammonium hydroxide. The melting point is 1,955°C. Nickel monoxide reacts with acids to form nickel salts and soaps, and mixtures of nickel monoxide and barium oxide react violently with iodine and hydrogen sulfide in air. Nickel hydroxide occurs either as green crystals or as a black powder. It has a molecular weight of 92.7 and a specific gravity of 4.1. Nickel hydroxide does not burn, but it may produce toxic gases when heated to decomposition (> 230°C). It is available at 97% purity (IARC 1990, HSDB 2003).

Nickel sulfides are insoluble in water, and some occur in different forms. Nickel subsulfide (α-form) occurs as lustrous pale yellowish or bronze crystals that are soluble in nitric acid. Nickel sulfide occurs in three forms (α, β, and amorphous) as dark green to black crystals or powder. Nickel disulfide occurs as black crystals or powder and decomposes at temperatures above 400°C (IARC 1990).

Nickel salts are green to yellow crystals that generally are soluble in water and decompose when heated. Nickel acetate has a molecular weight of 176.8, a boiling point of 16.6°C, and a specific gravity of 1.79. It occurs as a dull-green powder that effloresces somewhat in air. It is available as the tetrahydrate in a grade at greater than 97.0% purity. Nickel chloride occurs as yellow (anhydrous) or green (hexahydrate) deliquescent crystals. It has a molecular weight of 129.6, a specific gravity of 3.51, and a melting point of 1,001°C. Nickel chloride is soluble in ethanol and ammonium hydroxide and insoluble in ammonia. The hexahydrate form is available as a laboratory reagent at greater than 99% purity or as industrial products containing approximately 24.7% nickel. Nickel sulfate occurs as yellow, green, or blue crystals and is available in anhydrous, hexahydrate, or heptahydrate forms. The anhydrous form has a molecular weight of 154.8, a specific gravity of 4.01, and decomposes at 848°C. The hexahydrate form melts at 53.3°C and the heptahydrate form at 99°C; both forms are available at greater than 99% purity. Nickel carbonate occurs as light green rhombic crystals. It has a molecular weight of 118.7 and a specific gravity of 4.39. It is practically insoluble in water but soluble in dilute acids and ammonia. Laboratory reagent grades contain 45% or 47.5% nickel, and industrial grades contain approximately 45% nickel. Nickel carbonate decomposes before reaching a melting point (IARC 1990, HSDB 2003).

Nickel carbonyl occurs as a colorless volatile, highly flammable liquid with a musty odor. It has a molecular weight of 170.7, a specific gravity of 1.32 at 17°C, a melting point of -19°C, and a boiling point of 43°C. It is practically insoluble in water but soluble in alcohol, benzene, chloroform, acetone, and carbon tetrachloride, and insoluble in dilute acids and dilute alkalies. It is available in a technical grade at greater than 99% purity. Nickel carbonyl may decompose violently when exposed to heat or flame in the presence of air or oxygen. When heated or on contact with acid or acid fumes, nickel carbonyl emits toxic carbon monoxide fumes. It decays spontaneously in air (HSDB 2003).

Nickelocene occurs as dark green crystals. It is insoluble in water but soluble in common organic solvents. It is a highly reactive compound that decomposes in air, acetone, alcohol, and ether. It is available in solid form at greater than 90% purity or as an 8% to 10% solution in toluene (IARC 1990).

Use

Nickel has many uses in industry because of its unique properties. The majority (about 80%) of all nickel is used in alloys, because it imparts such properties as corrosion resistance, heat resistance, hardness, and strength (ATSDR 1997). The main uses of nickel are in the production of stainless steel, copper–nickel alloys, and other corrosion-resistant alloys. Pure nickel metal is used in electroplating, as a chemical catalyst, and in the manufacture of alkaline batteries, coins, welding products, magnets, electrical contacts and electrodes, spark plugs, machinery parts, and surgical and dental prostheses (IARC 1990, HSDB 2003).

Data on the uses of nickel from 2002 indicate that 42% is used in stainless and alloy steel production, 38% in nonferrous alloys and superalloys, 14% in electroplating, and 6% in other uses. The ultimate end uses in 2003 were transportation, 32%; chemical industry, 13%; electrical equipment, 10%; construction, 9%;

fabricated metal products, 8%; petroleum, 6%; household appliances, 7%; machinery, 6%; and other uses, 9% (USGS 2003a).

Nickel oxide sinters (a coarse form of nickel monoxide) are used in steel and alloy manufacturing. Green nickel monoxide is used in electronics, in fuel cell electrodes, as a colorant in ceramics and glass, and to make nickel catalysts. Black nickel monoxide is used in the ceramics industry, to manufacture nickel catalysts, and to manufacture nickel salts. Nickel hydroxide is used in nickel-cadmium batteries and as a catalyst intermediate (IARC 1990).

Nickel sulfides are used as catalysts in the petrochemical industry when high concentrations of sulfur are present in the distillates and as intermediates in hydrometallurgical processing of silicate-oxide nickel ores (IARC 1990). Nickel subsulfide is used in lithium batteries (HSDB 2003).

Nickel salts are widely used in industry. Nickel acetate is used as a catalyst intermediate, as a dye fixative in the textile industry, in electroplating, and as a sealer for anodized aluminum. Nickel chloride is used in nickel catalysts, to absorb ammonia in industrial gas masks, and in electroplating. Nickel sulfates are used in electroplating and electrodeless nickel plating, as chemical intermediates to produce other nickel compounds, and in nickel flashings on steel to prepare it to be porcelain-enameled. Nickel carbonate is used to prepare nickel monoxide, nickel powder, nickel catalysts, colored glass, and certain nickel pigments. It also is used in electroplating and as a catalyst to remove organic contaminants from water (IARC 1990, HSDB 2003).

Nickel carbonyl is used in the production of high-purity nickel powder by the Mond process and for continuous nickel coatings on steel and other metals. It also has many small-scale applications, such as vapor plating of nickel and depositing of nickel in semiconductor manufacturing. Nickelocene is used as a catalyst and complexing agent (IARC 1990).

Production

Nickel is refined from either sulfide or silicate-oxide ore. These ores generally contain no more than 3% nickel. Magmatic sulfide ores are mined underground or by open-pit methods. Pentlandite ($[NiFe]_9S_8$) is the principal sulfide ore; the largest known deposit is in Ontario, Canada, and substantial deposits are found in Minnesota, South Africa, Russia, Finland, and western Australia. Silicate oxide ores, or garnierites, originate in (current or former) humid tropical regions and are surface mined by open-pit methods (IARC 1990, ATSDR 1997).

Primary nickel production from mines in the United States was steady between the mid 1950s and 1980, ranging from approximately 10,000 to 14,000 metric tons (22 million to 31 million lb) per year. After 1980, primary production of nickel in the United States declined rapidly. Production from secondary ferrous sources (scrap metal recycling) ranged from approximately 25,000 to 37,600 metric tons (55 to 83 million lb) per year from 1980 to 1990, whereas secondary production from nonferrous sources declined from approximately 16,700 metric tons (37 million lb) in 1980 to 6,300 metric tons (14 million lb) in 1990. In addition, relatively small quantities of nickel are recovered as a by-product at copper and precious metals refineries or from reclamation of spent catalysts. Between 1970 and 1990, the United States imported approximately 100,000 to 170,000 metric tons (220 to 375 million lb) of nickel per year and exported between 8,000 and 40,000 metric tons (18 to 88 million lb) per year (USGS 2003a, 2003b).

Primary production of nickel in the United States ceased in 1986; one mine restarted mining and smelting operations in 1989, but this mine closed in 1998 (ATSDR 1997, USGS 2003b). From 1998 to 2002, secondary nickel production in the United States ranged from approximately 90,000 to 145,000 metric tons (198 to 320 million lb) per year. Annual U.S. imports (primary and secondary sources combined) totaled approximately 131,000 to 167,000 metric tons (289 to 368 million lb) between 1998 and 2002, and annual U.S. exports were approximately 39,000 to 58,000 metric tons (86 to 128 million lb) (USGS 2003b). Nickel demand in the United States is expected to grow because of increased demand for stainless steel, nickel-bearing superalloys used in aircraft engines, and nickel-based batteries (Kuck 2001).

Exposure

Environmental exposure to nickel occurs through inhalation, ingestion, and dermal contact. The general population is exposed to low levels of nickel because it is widely present in air, water, food, and consumer products. The general population takes in most nickel through food, with the average daily intake from food in the United States estimated to be 150-168 μg. Typical intakes from drinking water and air are 2 μg and 0.1-1 μg, respectively The general population also is exposed to nickel in nickel alloys and nickel-plated materials such as coins, steel, and jewelry, and residual nickel may be found in soaps, fats, and oils (ATSDR 1997).

EPA's Toxic Chemical Release Inventory (TRI) estimated that in the United States in 2001, 2,258 facilities released 4,481,059 lb (2,033 metric tons) of nickel, while 1,324 facilities released 9,799,196 lb (4,445 metric tons) of nickel compounds to the environment. From 1988 to 2001, the amount of nickel reported released by facilities was reduced by approximately half, while the release of nickel compounds did not change significantly (TRI01 2003).

Occupational exposure to nickel occurs mainly by inhalation of dust particles and fumes or by dermal contact. Nickel workers also can ingest nickel-containing dusts. Occupational exposure is common for workers involved in mining, smelting, welding, casting, spray painting and grinding, electroplating, production and use of nickel catalysts, polishing of nickel-containing alloys, and other jobs where nickel and nickel compounds are produced or used (HSDB 2003). The National Institute for Occupational Safety and Health (NIOSH) conducted the National Occupational Exposure Survey (NOES) from 1981 to 1983, and estimated that 507,681 workers, including 19,673 women, potentially were exposed to nickel and nickel compounds. NIOSH's National Occupational Hazard Survey (NOHS), conducted from 1972-1974, estimated that 23,272 workers were potentially exposed to nickel and nickel compounds.

Regulations

DOT

Nickel carbonyl, nickel cyanide, nickel nitrate, nickel nitrite, and nickel picrate are considered hazardous materials and requirements have been prescribed for shipping papers, package marking, labeling, and transport vehicle placarding for the shipment and transportation of these hazardous materials

Nickel carbonyl, nickel cyanide, and nickel tetracarbonyl are considered marine pollutants and requirements have been prescribed for marking the packaging and transport vehicles containing these materials

EPA

Clean Air Act

Mobile Source Air Toxics: Nickel Compounds listed as Mobile Source Air Toxics for which regulations are to be developed

NESHAP: Nickel Compounds listed as Hazardous Air Pollutants (HAPs)

Prevention of Accidental Release: Threshold Quantity (TQ) = 1,000 lb (nickel carbonyl)

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

Clean Water Act

Biosolids Rule: Ceiling concentration of nickel (type not specified) for land application = 420 mg/kg

Effluent Guidelines: Nickel and nickel compounds listed as Toxic Pollutants

Water Quality Criteria: Based on fish/shellfish and water consumption = 610 μg/L (nickel, type not specified); based on fish/shellfish consumption only = 4,600 μg/L (nickel, type not specified)

Comprehensive Environmental Response, Compensation, and Liability Act

Reportable Quantity (RQ) = 100 lb (nickel, nickel ammonium sulfate, nickel chloride, nickel nitrate, nickel sulfate); 10 lb (nickel carbonyl, nickel cyanide, nickel hydroxide)

Emergency Planning and Community Right-To-Know Act

Toxics Release Inventory: Listed substances subject to reporting requirements (nickel, nickel compounds, nickel ammonium sulfate, nickel carbonyl, nickel chloride, nickel cyanide, nickel hydroxide, nickel nitrate, nickel sulfate)

Threshold Planning Quantity (TPQ) = 1 lb (nickel carbonyl)

Reportable Quantity (RQ) = 10 lb (nickel carbonyl)

Resource Conservation and Recovery Act

Listed Hazardous Waste: Waste codes in which listing is based wholly or partly on substance - P073, P074, F006

Listed as a Hazardous Constituent of Waste (nickel, nickel compounds, nickel carbonyl, nickel cyanide)

FDA

Maximum permissible level of nickel in bottled water = 0.1 mg/L

The color additives ferric ammonium ferrocyanide and ferric ferrocyanide may contain nickel at levels no greater than 200 ppm

Menhaden oil may contain nickel at concentrations not to exceed 0.5 ppm

OSHA

Permissible Exposure Limit (PEL) = 1 mg/m^3 (metallic nickel and compounds other than nickel carbonyl); 0.001 ppm (0.007 mg/m^3) (nickel carbonyl)

Guidelines

ACGIH

Threshold Limit Value - Time-Weighted Average Limit (TLV-TWA) = 1.5 mg/m^3 (elemental nickel); 0.1 mg/m^3 (soluble inorganic compounds & nickel subsulfide); 0.2 mg/m^3 (insoluble inorganic compounds); 0.05 ppm (nickel carbonyl)

NIOSH

Recommended Exposure Limit (REL) = 0.015 mg/m^3 (elemental nickel, nickel compounds other than nickel carbonyl); 0.001 ppm (0.007 mg/m^3) (nickel carbonyl)

Immediately Dangerous to Life and Health (IDLH) = 10 mg/m^3 (elemental nickel, nickel compounds other than nickel carbonyl); 2 ppm (nickel carbonyl)

Listed as a potential occupational carcinogen (elemental nickel, nickel compounds other than nickel carbonyl)

*No separate CAS registry number is assigned to nickel compounds

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