

III. EXTENT AND MEASUREMENT OF EXPOSURE

Uses of Cobalt

Cobalt (atomic number 27, atomic weight 58.93) is a transition element located between iron and nickel in group VIII of the periodic table. The metallic form is silver gray to bluish white and is magnetic. There are three oxides of cobalt: cobaltous oxide, CoO ; cobaltic oxide, Co_2O_3 ; and cobaltous cobaltic oxide, Co_3O_4 . Ionic cobalt can exist in either a divalent or a trivalent form. The cobaltous ion can form numerous inorganic and organic salts [247], and cobalt can form complexes with amines, nitrites, and cyanides [248]. Divalent cobalt can have a coordination number of either 4 or 6, whereas trivalent cobalt has a coordination number of 6 [2]. The physical and chemical properties of some cobalt compounds are given in Table IX-3, and substances containing cobalt that are listed in the Toxic Substances Control Act Chemical Substance Inventory [249] are listed in Tables IX-4 to IX-6.

Cobalt is a byproduct or coproduct of the refining of other mined metals such as copper and nickel. Some of the commercially mined ores are carrollite, CuCo_2S_4 ; smaltite, CoAs_2 ; cobaltite, CoAsS ; siegenite, $(\text{Co}, \text{Ni})_3\text{S}_4$; and sphaerocobaltite, CoCO_3 [1,5]. The amount of cobalt mined is relatively small in comparison with copper or nickel, and the cobalt supply depends to a large extent on the demand for the latter two metals.

According to the Bureau of Mines (RA Markle, written communication, September 1978), there has been no domestic mine production of cobalt for several years, and there is only one refinery that processes cobalt in the United States. Most of the cobalt imported, nearly 77%, comes from Zaire and Zambia. Imports were up 6%, to 17.5 million pounds, in 1977. Cobalt consumption in the United States for 1977 was about 16.6 million pounds, up 0.6% from 1976. Much of that increase was due to demand in the aircraft industry.

About 70% of the cobalt used in the United States goes into the alloy and hard metal industries, mostly to produce magnetic and super-hard alloys [250]. The aluminum-nickel-iron-cobalt alloys are widely used in permanent magnets [39]. Vanadium-iron-cobalt alloys are used for ductile permanent telephone diaphragms. Vitallium, an alloy of cobalt, chromium, nickel, and molybdenum, has been used for prostheses in bone replacement surgery [39,250]. Cobalt is used extensively in the tungsten carbide or hard metal industry as a binder of ingredients in these heat- and wear-resistant metals [39,250-252]. Cobalt-bearing high-speed steel and cemented carbides have excellent cutting properties. Major uses include various chemical, cutting tool, and hard facing applications. Cobalt alloyed with chromium and nickel is used in heat-resistant gas turbine blades and jet engine parts. Hard metal is found in high-speed cutting tools, armaments, masonry drills and cutters, high-speed dental drills, and tire studs.

Cobalt compounds have important uses as catalysts [39,250,253-255]. Cobalt naphthenate, octanoate, oleate, resinates, tallate, and linoleate are used as drying agents for oil-based paints, varnishes, and printing inks. The cobalt compounds act as oxidizing catalysts for the polymerization of unsaturated glycerides. Cobalt is an important catalyst in oxidation and in desulfurization, a process used in refining crude oils. Cobalt acetate is used in the manufacture of dimethyl terephthalate and terephthalic acid. Cobalt catalysts are also used in the production of several primary alcohols and aldehydes.

Cobalt salts have a variety of uses [39,250,255]. Cobalt sulfate and chloride are used in electroplating. Cobalt carbonate, chloride, and sulfate are incorporated as additives in animal feeds. Cobalt chloride is a desiccant indicator, the hydrated form being pink and the anhydrous form blue. This property also leads to its somewhat unusual use as "invisible" ink. Cobalt pigments are very important in the ceramic and pottery industry. A wide variety of pigments in differing shades and colors contain cobalt, often as mixtures with other metal salts. Black cobalt oxide paint is of particular value because of its heat and wear resistance. A mixture of cobalt oxide and cobalt aluminate forms a blue color. Cobalt blue is sometimes added to glass to detint the yellowish color that occurs if iron is present. Small amounts of cobalt salts are also used as boiler water scavengers, in magnetic tapes, and in steel-belted tires.

Table III-1 lists some occupations in which there is potential exposure to cobalt compounds [256]. The amount of exposure to cobalt that workers actually receive in these occupations probably varies widely. Large amounts of cobalt are used in some industries, such as cobalt salts manufacturing, the cemented carbide industry, and the manufacture of cobalt-containing alloys. Many users of these products handle extremely small quantities of cobalt. Others perform cutting, grinding, or welding operations on products, and the potential for worker exposure to cobalt is significant. Exposure of painters to cobalt driers is probably minimal; exposure of spray painters to cobalt pigments is not.

Environmental Data

Cobalt is present in low concentrations in ambient air. Dams et al [257] found mean concentrations of 2.6 ng/cu m (1 mg = 10 exp +6 ng) in an urban area (East Chicago, Indiana) and 0.95 ng/cu m in a rural area (Niles, Michigan). Rancitelli et al [258] reported cobalt concentrations in North and South America ranging from 0.07 ng/cu m (Thule, Greenland) to 3.6 ng/cu m (Santiago, Chile). Hewitt [259] found a concentration of 5 ng/cu m in urban air in England. Also, Janssens et al [260] reported that air samples collected in Belgium, apparently near a cobalt-manufacturing plant, showed levels of 0.4-7.3 ng/cu m (mean, 2.8). All of these levels in ambient air are far below the Federal standard of 0.1 mg/cu m for cobalt metal fume and dust.

TABLE III-1

OCCUPATIONS WITH POTENTIAL EXPOSURE TO COBALT

Acetic acid makers	Gasoline blenders
Alloy makers	Glass colorers
Alnico magnet makers	Glaze workers
Ammonia mask makers	High-speed tool steel workers
Barometer makers	Hygrometer makers
Bright platers	Ink makers
Catalyst workers	Iron-cobalt platers
Cement makers	Lamp filament makers
Cemented carbide workers	Magnet steel workers
Ceramic workers	Metal smelters
Cermet makers	Nickel byproduct workers
Cobalt soapmakers	Paint drier makers
Cosmetic makers	Painters
Dye workers	Porcelain workers
Drug makers	Protective-coating makers
Electroplaters	Refractory brick makers
Enamellers	Rubber makers
Ethyl acrylate makers	Silicate paint makers
Fertilizer workers	Stone preserver makers
Frit workers	Weatherproof cement makers
Gas mask makers	Welders

Adapted from reference [256]

Much of the data on occupational exposure to cobalt have come from the tungsten carbide industry. McDermott [261], in 1971, found the average concentration of cobalt in 40 general air samples of seven tungsten carbide facilities to be below 0.1 mg/cu m (range, 0.005-0.15). About 70% of the 133 breathing zone samples were also less than 0.1 mg/cu m. Based on the data provided, however, mean concentrations in breathing zones of press operators and machine tool operators averaged 0.16 and 0.21 mg/cu m, respectively.

A tungsten carbide facility reported that during 1977-78 the concentration of cobalt in worker breathing zones averaged 0.048 mg/cu m in the powder area, 0.033 mg/cu m in the pressing area, 0.019 mg/cu m in grinding, and 0.025 for general maintenance [255]. The highest concentration measured was 0.17 mg/cu m and the lowest was 0.004 mg/cu m.

A study of eight cemented carbide plants in Sweden revealed that exposure to cobalt varies considerably with job classification [262]. Groups handling powder were most exposed, while press operators, shapers, dry grinders, wet grinders, face grinders, and inspection personnel received decreasing levels of exposure to cobalt (in that order). Some workers handling powder probably received short-term exposures in excess of 0.1 mg cobalt/cu m.

At an operation where tungsten carbide tools containing 6.0-8.5% cobalt were sharpened by wet grinding, general air samples were well below 0.1 mg/cu m [40]. Two-thirds of the breathing zone samples, however, were above 0.1 mg/cu m of cobalt (range, 0.04-0.93 mg/cu m). Full-shift TWA exposures were measured on a number of the grinders. Two-thirds of those values were above 0.1 mg/cu m with a range of 0.03-0.56 mg/cu m and a mean of 0.24 mg/cu m.

A US nickel refinery provided cobalt dust exposure data collected in June 1978 (B Roy, written communication, September 1978). Average concentrations of cobalt were generally low, ranging from less than 0.002 to 0.099 mg/cu m, except for two tower cleanup workers whose exposures averaged 0.156 mg/cu m. Within the occupational groups, the concentration ranges were sometimes quite variable; for example, the exposure of one cobalt operator was 0.313 mg/cu m, and for a supervisor it was 0.148 mg/cu m, even though averages for all 13 workers in these groups were substantially lower.

In a plant manufacturing cobalt salts, concentrations of cobalt were measured at work stations where the salts were handled manually [255]. Workers in dusty areas were required to wear respirators. Cobalt concentrations where fine powders were dried were low, ranging from 1 to 2 μ g/cu m. Where the dried cakes were broken into fine powders, cobalt concentrations varied, ranging from not detectable to 0.2 mg/cu m. On the average, the drum-loading operations were the dustiest, but the cobalt concentrations, 0.04-0.5 mg/cu m, varied widely. Other operations in the plant were contained and well ventilated so that the concentration of cobalt in those areas would be expected to be low.

An environmental survey conducted in May 1978 at a US jet aircraft engine assembly plant provided exposure data for three occupational groups (Table III-2) [255]. Workers processed metal alloy parts containing 1-15% cobalt and varying percentages of nickel and chromium. For each location, personal and area samples were collected.

A US manufacturer of cobalt-containing alloys provided data on concentrations of airborne cobalt near the furnaces (most were in the melt shops) and other operations [255]. These data covered 1970 to 1974. Exposures to cobalt on the average were substantially less than 0.1 mg/cu m, but they were quite variable, even for the same areas. For example, exposure to cobalt in the breathing zones of workers in the melt shops were 0.001-1.43 mg/cu m. In the powder products area, six samples ranged from 0.09 to 9.7 mg/cu m. General area samples tended to show a lower cobalt concentration than breathing zone samples.

Almost no published data on exposure to cobalt in welding and thermal cutting operations were found. Hewitt [259] measured cobalt and other metallic contaminants in a number of welding operations in well ventilated areas. Airborne cobalt concentrations were all 0.1-0.4 μ g/cu m. Cobalt-containing welding rods can contain other metals such as nickel or chromium that can also be hazardous if they become airborne.

TABLE III-2
ENVIRONMENTAL DATA FOR COBALT ALLOY OPERATIONS

Occupation, Area	Alloy Composition (% cobalt)	Cobalt Concentration (mg/cu m)
Parts Polisher	1 (maximum)	<0.001
"	"	<0.001
"	15	0.008
Polishing Area	--	<0.001
Bench Operator	1 (maximum)	0.001
"	12-15	0.001
Bench Area	--	<0.001
Cutter-Grinder	5-8	0.006
"	7.75-8.25	0.005
"	7.75-8.25	0.001
Cutting-Grinding Area	--	0.003-0.006

Although small amounts of cobalt driers are commonly added to paints and varnishes, suggesting that worker exposure is minimal, almost no information was found to confirm this suggestion. In a survey of a boat manufacturer, none of 13 lamination workers was exposed to detectable amounts of cobalt [263]. Cobalt naphthenate was present in small amounts in the resin used for lamination.

From July 1972 to January 1978, OSHA collected and measured samples in 79 different workplaces for cobalt dust concentrations; 15 had concentrations exceeding the Federal limit of 0.1 mg/cu m (29 CFR 1910.1000). The majority of inspections were conducted in various metal manufacturing industries, with the remainder in inorganic chemical manufacturing and glass container, abrasive products, ceramics, and other industries [264].

Eight plant site visits were conducted to collect information for this report [255]. The number of production workers ranged from less than 50 to 25,000. The three largest plants (at least 800 production workers) all had formal plans for sampling and inhouse capabilities for analysis. Two other plants sampled for cobalt on an irregular basis, and one other sampled for nuisance dust only. The two plants with less than 50 production workers had no program for air monitoring. These plants had relied on corporate headquarters, insurance carriers, and contractors for air monitoring where in-house capability was unavailable.

Sampling Methods

Air sampling for particulate cobalt can be performed by methods recommended for metals in general [258,265,266] (see the Appendix). Collecting media include cellulose ester membrane filters, polycarbonate membrane filters [267], cellulose fiber filters [259,260], and polystyrene filters [257]. Cellulose ester membrane filters are widely used and recommended [268,269]. They have high sampling efficiency, relatively low background contamination from cobalt and other trace metals, ease of ashing, and convenience for personal monitoring [40,269,270]. Glass fiber filters, which are widely available, are less suitable for metals because of high and variable background contamination [257] and incompatibility with many routine analytical procedures.

Particle sizing can be performed by using an optical or electron microscope or by light-scattering techniques. Cascade impactors or cyclone separators can be used to separate particles according to size as they are collected [271]. Impaction devices have been used to determine the size distribution of cobalt-containing aerosols [259,270,272]. Since the Federal standard for cobalt requires measurement of total cobalt and not the respirable component, these devices should not be used for compliance purposes. However, they could have use in conducting basic research on the effects of exposure to cobalt.

Electrostatic precipitators were once widely used to sample air for cobalt and other metal aerosols [261], but they have been replaced, for the most part, by some of the more convenient sampling methods discussed above. Electrostatic precipitators have the advantage of being free of filter clogging and problems with flowrate or humidity. They are also effective in collecting particles of all sizes. One disadvantage of electrostatic precipitators is that actual worker exposure may not be estimated as closely as is possible with personal sampling.

Analytical Methods

Many methods have been developed for the analysis of cobalt samples collected from air. Among these, colorimetric procedures can be satisfactory provided that other metals do not interfere with the results. Color reagents that have been used include nitroso R salt (sodium nitroso-2-naphthol-3,6-disulfonate) and sodium thiocyanate [273-275]. Although these methods are tedious and require skill, they can give satisfactory results.

Emission spectrometric methods have been used frequently to analyze airborne particulate material. Because of its sensitivity, the emission spectrograph has been used to measure pollutants in the community atmosphere [276], but this technique is also useful to determine concentrations of airborne cobalt in the workplace. One investigator, using a specialized electrode for air sampling, was able to perform direct analysis of samples using the emission spectrograph [277]. Equipment cost and limited

availability are important factors to consider in recommending the use of the emission spectrograph in routine analysis of samples.

A widespread method used for determination of airborne cobalt levels is analysis by atomic absorption spectrophotometry (AAS) [266,267,278,279]. The advantage of the atomic absorption method is that it can be made both highly specific and sensitive for the detection of cobalt. The NIOSH P&CAM method 173 recommends AAS for detection of cobalt [268]. This method is sufficiently sensitive to detect cobalt in the concentration ranges normally found in the air of plants manufacturing or using cobalt products if sampling is carried out at a flowrate of 1.5 liters per minute for up to 8 hours using a 37-mm cellulose ester filter with a pore size of 0.8 μm . The method will not distinguish between individual cobalt compounds. In a collaborative test of P&CAM 173, the mean cobalt concentration detected by 17 laboratories was 11.9% below a reference value, suggesting some loss of sample. The coefficient of variation was 45.5% for all of the laboratories, but only 2-10% for single laboratories on replicate samples [266]. With the use of graphite electrodes, flameless AAS methods have extended detection limits for cobalt to ambient air levels [267].

Atomic absorption spectrophotometry has been used extensively to analyze biologic samples for cobalt [280-282]. Because of the extremely low concentrations of many metals (including cobalt) normally in such samples, innovative methods to enhance sensitivity have been developed. An example is the formation of an organometallic complex, such as with a dithiocarbamate, which is readily extracted into an organic solvent, eg, methyl isobutyl ketone [283,284]. This procedure increases sensitivity, not only because it concentrates the cobalt in the sample, but also because of enhanced sensitivity of the AAS obtained from the use of an organic solvent. Using ion exchange separation and electrothermal atomic absorption, Alexandersson and Lidums [282] found reasonably good correlation between blood and urine concentrations of cobalt in workers and airborne levels in cemented carbide plants.

Neutron activation analysis (NAA) can analyze a single small sample for a number of trace metals. Dams et al [257], using NAA, reported a detection limit for cobalt of 2 ng. The minimum concentration of cobalt reported to be detectable in a 24-hour sample of urban air was 25 pg/cu m (1 mg = 10^{+9} pg) in the presence of 32 other trace elements that were similarly determined. Although this method is sensitive and does not destroy the sample, the requirements for elaborate equipment, the safety precautions necessary for use of an irradiating beam or radioactive sources, and the relatively small thermal neutron cross section of cobalt make NAA less practical than AAS for routine use.

Another technique for analysis of airborne cobalt use is the x-ray fluorescence method [258,266,272]. The fluorescence method resembles the neutron activation procedure in specificity, sensitivity, and ability to analyze a single sample for a number of elements. It is nondestructive and requires a minimum of sample handling. Results can be obtained quite rapidly for cobalt as well as for a number of other metals [266,272], and the x-ray

fluorescence method can be an acceptable alternative to AAS when analyzing cobalt.

In summary, the collection of air samples on membrane filters and the analysis of those samples by AAS, as described in the NIOSH P&CAM 173, are the methods of choice for monitoring of workers' exposure to cobalt (see the Appendix). Other methods, at least as sensitive and precise, are also acceptable.

IV. CONTROL OF EXPOSURE

Over a million workers have some potential for exposure to at least one cobalt-containing compound in the course of their employment. Many receive little exposure because they work with very small amounts of cobalt on an intermittent basis. Others, however, work with large amounts of cobalt regularly. These workers can become exposed through inhalation, dermal contact, or ingestion. In some operations, exposure to cobalt is limited because of the use of extensive engineering controls. Other operations, however, require manual handling of materials containing cobalt. Local exhaust ventilation [261,285] and good work practices can minimize exposure to cobalt in such circumstances. In all cases, ingestion of cobalt is easily prevented by the use of good personal hygiene in combination with the maintenance of a clean worksite. Workers who maintain or repair equipment, enter confined spaces such as tanks or vessels, or are involved in emergencies or other nonroutine situations have an especially high risk of exposure to cobalt. These workers should be trained to recognize hazards, and in some circumstances they may require special protective equipment or clothing to decrease exposure.

Information on typical industrial practices for the control of cobalt came from several site visits to plants manufacturing or using cobalt-containing products. These plants included a refinery, an alloy producer, cemented tungsten carbide producers, and cobalt salt manufacturers. Other sites visited included a welding-rod maker and an aircraft engine manufacturing facility. There is some published information on control of cobalt [261,285], but much of the following information came from plant visits [255].

Engineering Controls

Well-maintained closed systems and the prevention of dust generation, when compatible with the operation involved, are the most effective methods of limiting worker exposure. When a closed system is used, it must prevent or minimize the release of materials. When closed systems are not practical, worker exposure can often be reduced by process equipment modification, the use of control rooms, or local exhaust ventilation.

Properly designed and maintained ventilation systems, including local exhaust systems, can prevent the accumulation of airborne cobalt-containing dusts and fumes. Local exhaust systems were in frequent use in the plants visited. Examples include the use of glove boxes for welding, exhaust hoods provided to individuals using hand-held buffers and grinders, local exhaust on the other grinding machines and on press machines, and dust-collecting hoses for packaging operations [255]. In addition, a ventilation system is desirable as a standby, should a closed system fail. Where exhaust ventilation is required, adequate makeup air, conditioned as necessary for worker comfort, must be provided.

Ventilation requirements for grinding, buffing, and polishing operations were described in a NIOSH research report [286]. Dry grinding equipment was classified as pedestal type, abrasive cutoff tools, surface-type disc grinders, portable grinders and cutoff machines, and other grinding machines according to ventilation system design requirements. Polishing (coated abrasive) equipment was classified as wheel and drum type, disc type, belt polishers, and complex machines. Buffing (loose abrasive) equipment was classified as pedestal type, portable, or multiple buffer machines. For grinding and abrasive polishing, most of the equipment-generated particulate material was thought to be from the workplace. This would be so even for hard metal if a diamond wheel is used. Much more dust was contributed by the abrasive and the abrasive support materials in buffing. The report, in noting that the TLV for cobalt is very much less than for nuisance dust, considered that adequate control of cobalt is not likely to be possible with standard ventilation systems. Totally enclosed ventilation systems and respiratory protection for personnel within the enclosure were recommended. However, many alloys containing only a small percentage of cobalt are used, and restrictions could be less severe in such cases. Engineering controls for most buffing and grinding machines are built to conform to the configuration of the equipment and the materials being handled. Specific guidelines, therefore, are difficult to propose. Figure X-1 shows a diagram of typical local exhaust ventilation for hand held grinders [287]. Workers doing grinding or buffing should be adequately trained to recognize the proper configuration of ventilation equipment for each shape being handled.

Several potentially dusty situations exist in the manufacture or use of cobalt salts, especially if powders rather than crystals are formed. While filter presses are not considered especially dust-producing, they are readily enclosed by local exhaust ventilation as shown in Figure X-2 [288]. Powders formed through filtration, however, present a significant dust problem both in their packaging and in subsequent repackaging and use. The material removed from the filter press is dried, and this dry cake can cause substantial amounts of airborne dust as it is being placed in the pulverizer. One possible type of local exhaust ventilation that would greatly reduce worker exposure is shown in Figure X-3 [288]. Solutions, powders, and crystals of cobalt compounds and fine powders of cobalt metal or mixtures of tungsten carbide and cobalt should be packaged while using local exhaust ventilation. Two typical arrangements are shown in Figure X-4 [288]; many other configurations are also possible. When material is transferred to or from a container to obtain the nominal weight of the package or to use the product, material is often scooped from one container to another. This can be exceedingly dusty, especially with fine powders. Hoods that prevent the powder from dispersing into the work area and do not interfere with the weighing procedure are difficult, but not impossible, to design. Design requirements, however, are quite dependent on the size and shape of the container.

In most of the plants visited, engineering controls in use were generally not specific to cobalt alone, but rather to the entire process [255]. For example, emissions from furnaces preparing specialty steels must be controlled for all the metals in the melt. Cobalt may not be the limiting factor in

control of exposure in such situations. Ball mills used in the cemented carbide industry use solvents, such as acetone, and these emissions must be controlled. Several plants used cobalt in foundry operations where silica and other substances used in the molds dictated many of the control measures used. In milling, hot and cold rolling, and other operations, noise was often a factor in the use of control booths and of other means of control that often helped to lower exposure to cobalt. In buffing, exposure to the abrasive support material must be controlled as must oil mists generated in wet grinding. In manufacture of salts, extensive use of strong acids led to requirements for emission control and cleanup procedures that also limited exposure to cobalt. These overall requirements must be considered in designing engineering controls for cobalt.

To ensure effective operation of ventilation systems, trained personnel should conduct a regular monitoring program. Routine inspection should include face velocity measurements of the collecting hood, examination of the air mover and collection or dispersion system, and measurements of atmospheric concentrations of cobalt in the work environment. Where appropriate, the use of continuous airflow indicators, such as water or oil manometers properly mounted at strategic locations and marked to indicate acceptable air flow, should be considered. Any changes in the work operation, process, or equipment that may affect the ventilation system must be evaluated promptly to ensure that control measures adequately protect workers. All exhaust emissions from ventilation systems should be passed through a system designed to minimize the release or recirculation of raw materials, cobalt, and wastes into the occupational and community environments.

Work Practices

Ultimately, any program of worker protection must consider the prevention of pulmonary fibrosis, which has been clearly demonstrated to result from excessive exposure to cobalt metal and oxides. Dermatitis and an occasional case of extreme pulmonary hypersensitivity to cobalt, however, are much more frequently encountered problems in the day-to-day operation of health care for cobalt workers. These problems cannot be neglected in establishing an effective program for worker protection.

Employers should institute programs that emphasize good personal hygiene to prevent skin and respiratory irritation caused by cobalt-containing dusts. After working with cobalt products, workers should thoroughly wash their hands and face before drinking, eating, or smoking. If skin contact with cobalt solutions occurs, the worker should wash the affected skin promptly. The employer should provide showers if workers have substantial contact with cobalt. These workers should be encouraged to wash or shower after each workshift. Employers should prohibit smoking or carrying of tobacco products in work areas because of possible cobalt contamination. For the same reason, employers should prohibit eating, food handling, or food storage within the work area.

To maintain a safe workplace, employers must identify the many physical hazards involved in handling cobalt and take measures to eliminate them. In particular, several potentially hazardous situations were observed in plant site visits [255]. These included sharp edges on some rolled alloys and rolled-alloy scraps, the need to lift heavy containers of cobalt, and press operators who placed their fingers under moving machinery to remove parts. Rolled alloy workers can avoid finger cuts by wearing gloves. Trained workers who follow proper lifting techniques could avoid back injuries when they lift dense material such as cobalt metal. Protective clothing must not increase the potential for injury of workers who handle cobalt when working with machinery with moving parts.

In storage, cleanup of spills, and emergencies involving fires, employers must be aware of the properties of individual cobalt compounds to ensure proper planning. Finely divided cobalt will ignite, but its fire and explosion hazard is very weak [289]. Certain cobalt compounds used in paints, including cobalt linoleinate, cobalt tallate, and cobalt 2-ethyl hexanoate, are often mixed with kerosene or mineral spirits as solvents. These materials present a moderate fire hazard when exposed to heat or flame [255]. Cobaltous acetylacetonate and cobaltous nitrate are incompatible with easily oxidized material. Cobaltous nitrate can react to cause ignition, violent combustion, or explosion. Cobaltous acetylacetonate flashes at its sublimation point. Other substances can emit highly toxic or acrid fumes when heated to decomposition; these substances include cobaltous nitrate, cobalt benzoate, and cobaltous phosphate.

General plant maintenance must be conducted regularly to prevent cobalt-containing dusts from accumulating in work areas. Cleaning should be performed with vacuum pickup or wet mopping to minimize the amount of dust dispersed into the air. A decontamination room should be available for cleaning equipment that is to receive major overhaul or maintenance. Spills of cobalt-containing material should be promptly cleaned up to minimize inhalation or dermal contact. Liquid material spills can be copiously flushed with water and channeled to a treatment system or holding tank for reclamation or proper disposal. Spills of dry material can be removed by vacuuming or wet mopping. Some spills can be removed by hosing, first with a mist of water to dampen the spilled material and then with a more forceful stream that flushes it into a holding tank or other facility for handling contaminated water. Work surfaces or contaminated clothing should never be cleaned by dry sweeping or blowing with pressurized hoses. Recovery systems used to reclaim waste metals should comply with Federal, state, and local regulations. All waste material generated in the handling of cobalt-containing substances should be disposed of in compliance with Federal, state, and local regulations.

Maintenance and repair workers face special problems regarding their potential exposure. The very circumstances that require the maintenance or repair work and dictate the work conditions will often preclude use of some control procedures. Consequently, very careful supervisory control must be exercised over such activities. These workers must wear appropriate protective equipment and clothing, and they must be trained to recognize and control the hazards they face.

Special precautions are necessary when workers must enter tanks or vessels, such as reaction vessels containing cobalt catalysts or vessels used to prepare cobalt salts [290]. Before any worker enters a vessel, all sources for transferring cobalt and other materials into or out of the vessel must be blanked to prevent their entry. The vessel interior must then be washed with water and purged with air. After purging the vessel's interior, trained personnel should test the vessel's atmosphere with suitable instruments to ensure that no hazards from fire, explosion, oxygen deficiency, or dust inhalation exist. No one should enter a tank or vessel without first being equipped with an appropriate respirator and a secured lifeline or harness. Mechanical ventilation should be provided continuously when workers are inside the tank. At least one other worker similarly equipped with respiratory protection, lifeline, and harness should watch at all times from outside the vessel. Workers inside the tank must be able to communicate with those persons outside. Other workers must be available to assist in an emergency. Flame- or spark-generating operations, such as welding or cutting, should be performed only when an authorized representative of the employer has signed a permit based on a finding that all necessary safety precautions have been taken.

Work Clothing and Protective Equipment

Cobalt causes skin sensitization, and some substances, such as cemented carbides, are abrasive to the skin as well [81]. The use of coveralls or similar work clothes can minimize the possibility of skin irritation, especially if the clothing is changed daily or more promptly in the event of gross contamination from a spill or leak. Workers in flame- or spark-generating operations should, in addition, wear work clothes made of fire-retardant materials. Gloves and protective sleeves should be used in manual transfer operations, together with a face shield (if respiratory protection is not needed) to keep soiled fingers from touching the face. Employers should provide change rooms and dual lockers so workers can remove soiled coveralls during breaks. Work clothing should be worn for only a single day work period, then collected directly into a designated and labeled container, and laundered by a management-selected laundry service. This is encouraged to prevent the spread of contamination into the homes of workers.

Eye irritation has apparently not been a problem for workers handling cobalt products; however, in operations that do scatter fine particles in the air, such as grinding, eye protection must be used that complies with 29 CFR 1910.133. Workers who are especially sensitive to cobalt or who handle solutions of cobalt in such a manner that cobalt can splash on the skin or into the eyes must wear protective suits, or face shields with goggles as appropriate, to prevent appreciable skin and eye contact. Emergency eyewashing facilities, where needed, must be readily available to affected workers. Workers experiencing skin irritation should see a physician promptly.

Respirators are not a substitute for proper engineering controls. Respirators may be needed, however, for nonroutine maintenance work, entry

into confined spaces, pending installation of adequate controls, and in emergencies where the concentration of cobalt could be unknown or excessive. In these situations, employers must provide workers with respirators, and establish a respiratory protective program meeting the requirements of 29 CFR 1910.134. These programs should emphasize the importance of having clean, well-maintained, well-fitted respirators for use in unusual circumstances and emergencies. Workers must be aware of the need to guard against contamination of the interior of the facepiece. Table IV-1 is a respirator selection guide for cobalt developed under the joint NIOSH/OSHA Standards Completion Program [291]. It is based on the Federal standard for cobalt.

Effective Planning

No program to minimize worker exposure to cobalt can be effective unless adequate attention has been given to problems before they arise. When a new facility is to be constructed, persons knowledgeable in occupational safety and health and industrial hygiene engineering should review plans both in the design phase and during construction. They should ensure that working areas and engineering controls are designed so that spills and airborne cobalt will be minimized when the plant is in operation.

For plants already in operation, management should review material-handling operations, maintenance and repair procedures, and process operations periodically. This review should identify areas and job locations where workers might be exposed to cobalt or cobalt-containing waste products, either through inhalation or direct contact with the skin or eyes. If work practices or engineering controls in any area are no longer adequate, management should modify them promptly.

Contingency planning for emergencies, inadvertent release of materials, and breakdown of facilities is vital. These plans should be developed for each department as well as plantwide. They should outline where appropriate equipment and trained personnel are located, and should be written, well understood by workers, and updated as required. Each plant should also be prepared to assess the impact or hazards of a specific spill or release of material should it reach a waterway or create a cloud. Supervisors should have information available, including lists of appropriate names and telephone numbers, for reporting emergencies. In addition to internal reporting procedures, plant management should clearly understand what situations require recordkeeping or external reporting to OSHA, the Environmental Protection Agency (EPA), and any appropriate state agencies.

TABLE IV-1

RESPIRATOR SELECTION GUIDE FOR COBALT

Concentration (mg/cu m, as cobalt)	Respirator Type Approved under Provisions of 30 CFR 11*
Less than or equal to 0.5	(1) Dust and mist respirator, except single-use respirators
Less than or equal to 1.0	(1) Dust and mist respirator, except single-use and quarter-mask respirators (2) Fume or high-efficiency particulate respirator
Less than or equal to 5	(1) High-efficiency particulate respirator with a full facepiece (2) Supplied-air respirator with full facepiece, helmet, or hood (3) Self-contained breathing apparatus with full facepiece
Less than or equal to 20	(1) Powered air-purifying respirator with a high-efficiency filter and a full facepiece** (2) Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode
Escape	(1) High-efficiency particulate respirator with full facepiece (2) Self-contained breathing apparatus

*Respirators specified for use in higher concentrations of cobalt may be used in atmospheres of lower concentrations.

**A high-efficiency filter is defined as one having a penetration of <0.03% when tested against a 0.3- μ m dioctyl phthalate (DOP) or equivalent aerosol.

Worker Education and Monitoring

A fundamental part of any program designed to provide a more healthful workplace involves education and monitoring of workers. Workers who understand the reasons for rules concerning hygiene and work practices are

more likely to help keep their work area clean. For cobalt, medical and environmental monitoring are especially important since the potential effects of exposure are poorly understood. Employers must follow the results of medical examinations and correlate them with exposure measurements to ensure that workers are adequately protected. Workers should understand the importance of the medical and environmental monitoring to ensure that they will cooperate and report any possible adverse reaction to cobalt promptly.

(a) Training Programs

Workers must know how to handle cobalt safely. Instructions concerning proper handling methods, cleanup procedures, personal protective equipment, and emergency procedures should be part of a continuing education program presented in training sessions and in written form. The NIOSH publication An Identification System for Occupationally Hazardous Materials [292] describes the types of information on physical, chemical, and toxicologic properties of materials that should be kept in written form. This information should be readily available to persons who handle cobalt-containing substances, and each cobalt compound used should have a corresponding material safety data sheet.

(b) Workplace Monitoring

Manufacturers of all cobalt compounds and users (unless trivial amounts are involved) should conduct an industrial hygiene survey at each location where cobalt is used to determine where workers are likely to be exposed to cobalt. Surveys should be repeated at least once every 3 years, preferably annually, and as soon as possible after any process change that is likely to increase the concentration of airborne cobalt.

For workers in areas where the concentration of airborne cobalt is likely to exceed 0.05 mg cobalt/cu m (one-half the Federal limit), the employer should establish the following program.

1. Personal monitoring should be conducted to identify and measure, or permit calculation of, the exposure of each worker. Appropriate methods for sampling and analysis are listed in the Appendix.
2. Samples should be representative of the breathing zone air of workers, but source and area monitoring can be a useful supplement for identifying leaks or other sources of emissions.
3. While all workers do not have to be monitored, sufficient samples should be collected to characterize the exposure of all workers. Variations in exposure during different shifts, because of location or job function and of changes in production schedule, should be considered in deciding the number of samples to be collected.
4. If a worker is exposed to cobalt at concentrations exceeding the Federal standard, improved measures to control exposure should be taken immediately. Once the control measures are in effect, exposure monitoring should be repeated. If two consecutive measurements, taken at least 1 week

apart, are below the Federal standard, the worker's exposure may be considered no longer excessive.

Personal monitoring records should be kept for 30 years to ensure compliance with new OSHA regulations concerning worker rights to information about their exposure (29 CFR 1910.20).

(c) Medical Surveillance

NIOSH encourages the provision of medical surveillance programs for workers. Some companies already maintain high-quality programs that allow absorption of hazardous chemicals to be detected at the earliest possible time. This allows early intervention by surveying the workplace and initiating work practice and engineering changes necessary to protect workers.

Medical surveillance programs should ideally include preplacement examinations and periodic reevaluations that will, based on the characteristics of the individual substance or agent, allow detection of absorption before onset of perceptible damage. In most programs, periodic examinations should be carried out on an annual basis. Since cobalt has been implicated to lesser or greater degrees with many effects on the body, these examinations should include not only the points discussed below but also be thorough enough to give reasonable assurance that effects have not occurred elsewhere in the body. The circumstances of each workplace and the types of cobalt compounds present will of course influence the program chosen by the responsible physician.

The most dramatic effect of cobalt is on the lungs, involving development of pulmonary fibrosis. As a result, a medical history is important to determine the presence of factors that would argue against placement in a job requiring exposure to cobalt. The physical examination should give special attention to the chest and lungs. Because pulmonary function studies are sensitive indicators of early changes in lung tissues, NIOSH recommends that they be conducted yearly. The forced expiratory volume in 1 second (FEV 1) and forced vital capacity (FVC) tests are sensitive and easy to administer. Chest x-rays can be useful but are somewhat less able to detect early changes as compared to pulmonary function tests, so 3 years is probably a suitable time between radiologic examinations.

The skin should receive attention because cobalt compounds can cause allergic responses and sensitization. Once sensitized, a worker can probably not tolerate any additional exposure. As a result, any worker with a previous history of allergic skin disease should be carefully counselled and schooled in techniques that will minimize contact with cobalt. In addition, skin protection should be stressed in the workplace to keep the number of new cases of skin sensitization at a minimum.

Cobalt affects the thyroid gland, and results in production of goiter. While the strength of this association is not clear, it seems that palpation of the thyroid for enlargement would be a prudent and simple step to include.

Thyroid function studies do not seem necessary unless enlargement or some other sign or symptom of thyroid dysfunction is present.

Present information suggests the possibility of polycythemia in the blood and electrocardiographic changes in the heart being produced by exposure to cobalt. The information is very unclear and appears to show effects only at a very high dosage. Therefore, no specific tests are suggested for these organ systems unless there is a potential for exposure to high levels of cobalt in the workplace.

The medical surveillance program should be reevaluated frequently and changed to reflect current working conditions and knowledge of health effects.

Medical records should be kept for 30 years after the worker's last exposure to cobalt. This will ensure compliance with OSHA's (29 CFR 1910.20) standard concerning worker's rights to his or her own medical records.

V. BASIS FOR STANDARDS CONCERNING OCCUPATIONAL EXPOSURE TO COBALT

A TLV for workplace exposure to cobalt of 0.5 mg/cu m was proposed by the ACGIH in 1962 [293] and adopted in 1963 [294]. ACGIH's 1966 Documentation of Threshold Limit Values [295] supported the TLV by citing the development of pulmonary changes in workers in the tungsten carbide industry. Reports by Miller et al [23] and Lundgren and Swenssen [296] were mentioned as evidence that cobalt was the etiologic agent involved. Work by Fairhall and colleagues [37,297] was cited as showing the potential for serious and occasionally fatal responses to cobalt at exposure concentrations of 1-2 mg/cu m or less in the tungsten carbide industry. These reports indicated that lung impairment often diminished when workers were removed from the workplace environment and that a hypersensitivity reaction appeared to be involved. A study by Stokinger and Wagner [138] was cited as evidence for the involvement of hypersensitivity in cobalt-exposed animals. A description by Schwartz et al [298] of an allergic dermatitis observed after exposure to cobalt was also noted. Irritation and itching had also been cited by ACGIH in its 1966 documentation [295].

A change in the TLV for cobalt from 0.5 to 0.1 mg/cu m as cobalt metal dust and fume was recommended by the ACGIH in 1966 [299] and adopted in 1968 [7]. The 1971 documentation (1976 addendum) [300] supported this lower TLV and cited additional information including a 1955 report by Schepers [55], which showed that intratracheal administration of cobalt metal led to chronic pneumonitis in guinea pigs. The results of surveys in Michigan and Pennsylvania were also cited. These showed that workplace concentrations of cobalt could be reduced to 0.1 mg/cu m or less. A concomitant reduction in cases of pneumonitis or dermatitis was observed in the Michigan survey over 18 years when cobalt levels were reduced from 14.42 mg/cu m to below 0.1 mg/cu m.

A reduction of the TLV from 0.1 to 0.01 mg/cu m was tentatively recommended in 1975 by the ACGIH Committee on Threshold Limits [8]. This recommendation was subsequently revised, and a limit of 0.05 mg/cu m was proposed by the TLV committee in 1976 [9]. The supporting documentation for both recommendations was the same and can be found in the 1974-75 and 1976 supplements to the Documentation of Threshold Limit Values for Substances in Workroom Air [300] or in the Transactions of the 38th Annual ACGIH Meeting [301]. Information cited to support the change included reports by Siegesmund et al [22] and Kerfoot et al [44]. The reason for lowering the TLV from 0.1 mg/cu m was not clear from the documentation, but it probably was based on the finding of Kerfoot et al [44] that swine exposed at 0.1 mg/cu m developed pulmonary changes.

Standards for occupational exposure to cobalt in other countries are listed in Table V-1. Since 1971, a commission of the German Research Association of the Federal Republic of Germany has included cobalt in the form of respirable dusts of metallic cobalt and sparingly soluble cobalt salts on its list of animal carcinogens (D Henschler, written communication, November 1978). Documents considered in this decision included papers on carcinogenicity [169,170,174,177,178,302-304] and other studies [305,306].

The present US limit (29 CFR 1910.1000) for workplace exposure to cobalt metal, fume, and dust measured as cobalt is an 8-hour TWA concentration limit of 0.1 mg/cu m. This standard is based on the TLV adopted by the ACGIH in 1968.

TABLE V-1

OCCUPATIONAL ENVIRONMENTAL LIMITS FOR COBALT IN FOREIGN COUNTRIES

Country	Compound	Concentration (mg/cu m)	Reference No.
Australia	Cobalt and cobaltous oxide	0.1	307
Belgium	"	0.01	307
Bulgaria	"	0.5	307
Czechoslovakia	Cobalt metal, fume, and dust	0.1	308
Finland	Cobalt and cobaltous oxide	0.1	307
Germany (Federal Republic)	Cobalt metal, fume, and dust	0.5	308, 309
Germany (Democratic Republic)	"	0.1	308
Italy	Cobalt and cobaltous oxide	0.1	307
Netherlands	"	0.1	307
Poland	Cobalt	0.5	310
Romania	Cobalt and cobaltous oxide	0.2 (av.) 0.5 (max)	310
Sweden	Cobalt metal, fume, and dust	0.1	308
Switzerland	Cobalt and cobaltous oxide	0.1	307
USSR	Cobalt metal, dust, and fume	0.5	308
Yugoslavia	Cobalt	0.1	310

VI. RESEARCH NEEDS

Much research conducted on cobalt compounds has served a very specific purpose, and the investigations have not examined overall toxicity. Very few reports except for those concerning pulmonary fibrosis in the hard metal industry have examined the effects of cobalt exposure in the workplace. Considerably more research needs to be done on cobalt, but the following is particularly needed.

The possibility that cobalt compounds in general are fibrogenic should be considered. Inhalation studies in animals should include as a minimum a cobalt salt. Workers in industries other than those manufacturing or using cemented carbide should be examined for adverse lung effects. For both animals and humans, an attempt should be made to obtain dose-response data if fibrosis or prefibrotic changes are found.

The possibility that certain specialty steels cannot release cobalt in the lung following inhalation should be examined. Some of these substances are used because of their extreme heat and corrosion resistance. It is possible that their toxic effects are unrelated to their cobalt content.

An effort should be made to determine the prevalence of dermatitis caused by sensitization to cobalt in various US industries. Information should be collected for different types of cobalt and should include cobalt metal, cemented carbide, and cobalt salts. Work practices and types of protective clothing should be considered in order to determine the protection needed by workers to minimize their chances of becoming sensitized.

The issue of the possible carcinogenicity of cobalt is very much unresolved. Inhalation studies need to be conducted in animals, and such studies could be performed in conjunction with examination of possible fibrotic effects. In humans, epidemiologic studies should be conducted. The cemented carbide industry, in particular, should be examined since the process is sufficiently old that an appropriate cohort should be available. Any epidemiologic study should also collect information on heart disease. The possibility that cobalt exposure at fairly low levels over a considerable period of time could lead to heart disease cannot be ruled out from information now available.

Finally, many cobalt compounds in commercial use have not been examined for toxicity, or very little information of limited use is reported. For example, some cobalt pigments and cobalt driers for oil-based paints have widespread use. Compounds such as these should be subjected to thorough testing for toxicity.