VI. DEVELOPMENT OF STANDARD

Basis for Previous Standards

In 1954, the American Conference of Governmental Industrial Hygienists (ACGIH) proposed threshold limit values (TLV) of 0.5 mg/cu m for vanadium pentoxide dust and 0.1 mg/cu m for vanadium pentoxide fume [109]. These TLV's were adopted in 1956 [18], and they referred to TWA concentrations for an 8-hour work shift. Although no justification for the limit values was given at the time of publication, the information used to derive the values was provided in the 1962 edition of Documentation of Threshold Limit Values [66]. Roshchin [41,68] had earlier recommended limits for vanadium pentoxide dust and fume of 0.5 and 0.1 mg/cu m, respectively, based on limited animal experiments. The Documentation [66] stated that these recommended values were later substantiated by Stokinger in more extensive animal studies. Another study cited was that by Lewis [25], who found no toxic effects in humans exposed to vanadium dusts, including vanadium pentoxide, at concentrations of 0.1-0.3 mg/cu m. The ACGIH recommended a lower TLV for vanadium pentoxide fume than for the dust because of "the recognizedly greater toxicity of fume compared with dusts of larger size and smaller surface area."

The 1963 TLV for vanadium pentoxide dust was designated a ceiling limit not to be exceeded [110], and the TLV for vanadium pentoxide fume was designated a ceiling limit in 1964 [111], although the numerical values did not change. The 1971 edition of Documentation of Threshold Limit Values [112] cited a 1967 study by Zenz and Berg [32] that noted severe upper respiratory tract irritation in five humans exposed to vanadium pentoxide dust at a concentration of 0.2 mg/cu m for a single 8-hour period. They also found upper respiratory tract irritation, though not as severe, in two humans exposed to vanadium pentoxide dust at a concentration of 0.1 mg/cu m. Zenz and Berg [32] concluded that the TLV of 0.5 mg/cu m for vanadium pentoxide dust should be lowered. The Documentation also stated that Hudson [34] considered the standard for vanadium pentoxide dust too high because he found adverse effects in workers exposed at 0.25 mg/cu m. The ACGIH did not lower the TLV for vanadium pentoxide dust. However, in 1972 [113], the vanadium pentoxide fume ceiling limit was reduced to 0.05 mg/cu m, based on the papers cited in the 1971 Documentation. The ceiling limit designation was removed from the TLV for vanadium pentoxide dust, making it again a TWA concentration limit. A notation that vanadium pentoxide was to be expressed as vanadium was also added. No justification was given for these changes.

For ferrovanadium, the ACGIH proposed a TLV of 1.0 mg/cu m as a TWA concentration in 1954 [109] and adopted this value in 1956 [18]. The justification for this limit, provided in the 1962 edition of <u>Documentation of Threshold Limit Values</u> [66], stated that the only published information on which a limit could be based was from the USSR on exposed workers and on animal experiments. The Documentation cited the work of Roshchin [41,68] who found pathologic changes only in animals exposed to ferrovanadium dust at concentrations of 1,000-2,000 mg/cu m for 2 months. Chronic bronchitis and inflammation of the lungs were the pulmonary changes observed. Animals exposed at a concentration of 10,000 mg/cu m showed no acute intoxication. Roshchin recommended a limit for ferrovanadium of 1 mg/cu m. The ACGIH agreed that this value would provide a large margin of safety and adopted it as a TLV.

The report of the Sixth Session of the Joint ILO/WHO Committee on Occupational Health [114] listed maximum allowable concentrations of 0.5 and 0.1 mg/cu m for vanadium pentoxide dust and fume, respectively, for Finland (1962), Rumania (1966), USSR (1963), Yugoslavia (1964), and the Federal Republic of Germany (1966). The standards listed for vanadium pentoxide dust and fume for Hungary (1965) were TWA concentrations of 0.5 and 0.1 mg/cu m, respectively. Rumania (1966), USSR (1963), and the Federal Republic of Germany (1966) listed a maximum allowable concentration of 1.0 mg/cu m for ferrovanadium. In addition to these standards, the ILO/WHO Committee reported maximum allowable concentrations of 0.5 mg/cu m for vanadium trioxide (sesquioxide) dust in the USSR (1963) and 0.1 mg/cu m for vanadium in Poland (1967). The bases for these were not described by the ILO/WHO Committee except for a statement that the limits for the Federal Republic of Germany were based on the 1966 edition of Documentation of Threshold Limit Values [115].

The present federal standard (29 CFR 1910.1000) for workplace exposure to vanadium pentoxide dust is a ceiling limit of 0.5 mg/cu m, based on the ACGIH TLV of 1968. The federal standard (29 CFR 1910.1000) for vanadium pentoxide fume is a ceiling limit of 0.1 mg/cu m, based on the ACGIH TLV of 1968, and not on the lower standard adopted by the ACGIH in 1972. The present federal standard (29 CFR 1910.1000) for workplace exposure to ferrovanadium is a TWA concentration of 1 mg/cu m for an 8-hour work shift based on the 1968 ACGIH TLV.

Basis for the Recommended Standard

(a) Permissible Exposure Limits

Occupational exposure to vanadium, especially vanadium pentoxide, produces mainly irritation of the eyes and of the upper respiratory tract, often accompanied by productive cough, wheezing, rales, chest pains, difficulty in breathing, bronchitis, questionable pneumonia, and rhinitis [17,19,24-26,39,47,64,65,67]. There have been occurrences of green-to-black discoloration of the tongue, metallic taste, nausea, and diarrhea [24,25,67]. Six studies reported skin irritation [19,26,30,36,37,62]. Similar effects on the skin and respiratory tract have been described in workers exposed to vanadium-containing byproducts of residual oil or crude oil combustion, gasification of fuel oil, and gas-turbine combustion [23,28,30,37,38,45,50,51]. General fatigue, weakness, headache, and tremors of the hands have been reported [22,24,26,39,67] but their relationship to vanadium exposure has not been demonstrated. Earlier investigations [15,24] that suggested systemic poisoning effects from vanadium have not been confirmed by later and more detailed studies [25,26,36,65,67].

Examination of the literature has revealed that vanadium compounds such as the oxides and vanadates cause respiratory tract irritation, with possible eye and skin irritation. While there is no information on halides, it is reasonable to interpret, in part because they decompose to halide acids and vanadium oxides, that they will cause similar effects. Other forms of vanadium, eg, ferrovanadium, other alloys of vanadium, vanadium metal, and vanadium carbide are much less active toxicologically and cause lesser effects. Therefore, two categories of vanadium are proposed on which two standards should be recommended. Substances in each category produce essentially the same type of reaction, though the chemical form changes. Effects are typically of an acute or subacute rather than a chronic nature. There is some evidence of sensitization on repeated exposure [19,35]. Slight irritant effects were noted in two resting subjects exposed to vanadium pentoxide at a concentration of 0.06 mg V/cu m [32]. Since mild irritant effects followed exposure at 0.06 mg V/cu m for 8 hours, a finding at least consistent with observations from several workplaces where exposures were approximated if not accurately estimated, it is evident that the environmental limit for vanadium pentoxide and some other compounds (vanadates, sulfates, halides, and other salts) should be lower. Experimental or epidemiologic data to demonstrate how much lower this limit should be are not available. A ceiling limit of 0.05 mg/cu m based on 15-minute sampling periods is proposed as a permissible limit pending the development of more definitive data that would justify a higher or lower value. A ceiling of 0.05 mg/cu m is probably equivalent in actual plant practice to a significantly lower TWA concentration, perhaps 0.01-0.03 mg/cu m. As a consequence, the TWA corresponding to the ceiling is from one-sixth to one-half the 8-hour TWA concentration causing mild irritant effects in the subjects studied by Zenz and Berg [32]. This seems a reasonable factor to apply inasmuch as the adverse effects being considered are mild or slight. Inasmuch as the toxic actions of vanadium compounds are expressed largely, if not entirely, by irritant effects on the respiratory tract, it is likely that a ceiling concentration limit would be more appropriate as a control measure than a TWA concentration limit. This is based on the belief that irritant effects are usually proportional to exposure concentration, rather than to exposure dose (as approximated by a TWA concentration), or, in other words, are concentration-limiting rather than dose-limiting.

The current federal standard for vanadium pentoxide fume is 0.1 mg/cu m. This form of vanadium is believed by many [62,116,117] to be more toxic than the dusts, which have a larger mean particle size. There have been no studies of human reaction to freshly formed vanadium pentoxide fume. Other metals, such as zinc, cadmium, or magnesium, form oxide fumes which, when inhaled, are known to be more toxic than the dusts, producing reactions such as chills, fever, and leukocytosis [118-120]. These reactions have not been reported for vanadium pentoxide when particle sizes are in the respirable range, ie, less than 5 μm. NIOSH recommends, therefore, that the separate federal standard for vandium pentoxide fume be eliminated. NIOSH further recommends that vanadium pentoxide fume be considered a component of the "vanadium compounds."

There have been few quantitative data reported with which to evaluate the reactions of humans to air concentrations of ferrovanadium and vanadium-containing alloys. These metallic compounds appear to be almost toxicologically inert, though some slight acute respiratory irritation may occur if they are inhaled in sufficient quantity. Roberts [20] observed that exposure to vanadium metal, ferrovanadium, vanadium-aluminum alloys, and vanadium carbide, at unknown concentrations and particle sizes less than 200 mesh (about 75 μm [21]), resulted in slight nose, throat, and respiratory irritation. Roshchin [41,68] noted that rats exposed to ferrovanadium dust at concentrations of 1,000-2,000 mg/cu m showed no signs of acute effects. Microscopic examination of the lungs after 2 months of exposure indicated development of peribronchitis and perialveolitis and, in some animals, chronic inflammation of the lungs. He also reported that rabbits and rats exposed for 2 months to ferrovanadium and for 9 months to vanadium carbide at concentrations of 40-80 mg/cu m showed no signs and symptoms of acute intoxication, but did show signs of bronchitis and interstitial sclerosis. The existing federal limit of 1 mg/cu m was originally based on studies [41,68] which are limited and of uncertain validity. It seems evident, however, that metallic forms like ferrovanadium, alloys, and vanadium carbide have greater toxicity than would be expected from an inert dust. Thus, a limit lower than the inert dust limit of 15 mg/cu m is obviously needed, but not a limit as low as that proposed for vanadium compounds, ie, 0.05 mg/cu m. The existing federal limit of 1 mg/cu m may be lower than is needed, but for worker protection it is proposed not to recommend a higher value until valid data are obtained. Thus, it is proposed to maintain the existing federal standard as a TWA concentration limit for up to 10 hours/day, for a workweek not exceeding 40 hours.

Vanadium compounds and metallic vanadium, when absorbed, are rapidly excreted and exhibit low degrees of toxicity, as indicated by minor irritation and lack of systemic effects. The action level is therefore defined as equal to the recommended environmental limit for each of the two proposed categories of vanadium.

(b) Sampling and Analysis

Personal sampling with a cellulose ester membrane filter is recommended, since most of the vanadium in the industrial environment exists as solid particulates and can be collected with 100% efficiency with this method [121]. Because there is no clear correlation between respiratory tract irritation and the particle size of vanadium that causes this effect, ie, both large and small particle sizes produce similar effects, total mass sampling is recommended instead of a respirable sampling method. It is not evident whether this sampling method will collect volatile vanadium compounds such as vanadium oxytrichloride. However, since they decompose in air to form vanadium oxide particulates, then much of the vanadium will be collected by the recommended procedure and, if the decomposition of the airborne halides is quantitative, all should be collected.

Flameless atomic absorption spectrophotometry is recommended for the analysis of vanadium, so that the necessary sensitivity and specificity can be attained. This method is free of interferences, fast, highly sensitive, and relatively simple.

(c) Medical Surveillance

Employees should be given preplacement medical examinations if a potential for occupational exposure to vanadium exists. Special emphasis should be directed to evidence of chronic eye or skin disorders and respiratory conditions or allergies, since exposure to vanadium may aggravate these or independently cause such effects. Because of cases of bronchial asthma and bronchitis in worker population exposed to vanadium compounds, periodic testing of pulmonary function is recommended. While the evidence that vanadium causes emphysema (reviewed in Chapter III) is not persuasive, neither can it be disregarded; periodic spirometry should detect chronic changes possibly leading to emphysema if this is a consequence of exposure to vanadium. The pulmonary or spirometric tests recommended are forced expiratory volume during the 1st second (FEV 1) and forced vital capacity (FVC). For similar reasons, roentgenograms are recommended. However, it is proposed that, except at preplacement examination, X-rays need not be performed routinely but at the discretion of the responsible physician based on his knowledge of work exposure and clinical findings.

(d) Personal Protective Equipment and Clothing

Several investigators [19,26,30,36,37,62] have reported dermal and ocular irritation caused by vanadium compounds. The symptoms of irritation, consisting of itching or burning, were temporary and rarely accompanied by external lesions. Therefore, to minimize the possibility of skin and eye irritation, clothing resistant to the penetration of liquid vanadium compounds or solutions should be available and worn where indicated to prevent gross skin and eye contact. This clothing should include boots, gloves, coveralls, face shields (8-inch minimum) with goggles, and safety glasses. Emergency showers and eyewash fountains should be readily available in the event of accidental gross contact of the face or eyes with vanadium. In areas where engineering controls are not adequate to reduce exposure to limits set forth in this standard, respiratory protective devices should be used as delineated in Section 4(b) of Chapter I.

(e) Informing Employees of Hazards

Since exposure to vanadium can cause respiratory, eye, and skin irritation, employees who may be occupationally exposed to vanadium should be advised of the adverse effects from such exposure, of methods of preventing exposure, and of surveillance procedures (environmental and medical monitoring) in use to detect, and thus to guide the control of, hazards.

(f) Work Practices

To minimize the possibility of respiratory contact with vanadium, engineering controls should be used when needed to control emissions to the work atmosphere. Such controls should include local exhaust ventilation for processes known to produce large amounts of airborne vanadium compounds. All vanadium containers should be closed tightly and stored properly when not in use to prevent breakage, spillage, or contact with moisture. Finely ground vanadium carbide, vanadium-aluminum alloys, vanadium metal, and ferrovanadium may be combustible and, thus, should be kept dry and away from heat, sparks, or flames. Spills or leaks should be attended to promptly. In case of emergencies resulting in gross skin or eye contact with liquid vanadium compounds or solutions, emergency showers or eyewash fountains should be available and used to clean affected areas. All employees, including maintenance and repair personnel, should be informed of all routine and emergency procedures for their specific jobs.

(g) Monitoring and Recordkeeping Requirements

So that airborne vanadium concentrations do not exceed the recommended environmental limits, a personal monitoring program should be instituted to collect airborne samples. Monitoring should be routinely performed every 3 months unless overexposure occurs, in which case, weekly monitoring should be conducted until successful control is achieved. Environmental monitoring and medical records should be retained for 30 years after termination of employment involving exposures to vanadium, in keeping with the requirements of the Toxic Substances Control Act of 1976.

VII. RESEARCH NEEDS

Proper assessment of the toxicity of vanadium and evaluation of its potential hazard to the working population requires extensive human and animal studies. The following are aspects of epidemiologic and toxicologic research that are especially important.

Epidemiologic Studies

Further research is required to assess the effects of long-term occupational exposure to vanadium and its compounds, particularly the halides. Long-term epidemiologic studies should be performed and should consider pulmonary, skin, eye, and metabolic effects of vanadium. As a minimum, these studies should include medical histories, pulmonary function studies, environmental measurements, and other information such as histories of known or suspected exposures to vanadium compounds, including information on the specific compounds involved, and comparisons of morbidity and mortality data with those for a normal population.

Experimental Studies

Both short-term and long-term studies involving exposure to airborne vanadium at low concentrations should be conducted. Additional toxicologic experiments on a variety of species would further serve to characterize, both functionally and microscopically, the nature of any organ changes produced by vanadium, particularly the halides. Studies should use an exposure schedule simulating occupational exposure and should involve routes of exposure that are likely to occur in occupational contact with vanadium (inhalation, ingestion, and skin contact). These results should provide insight into human susceptibility to the effects of vanadium.

Carcinogenic, Mutagenic, Teratogenic, and Reproductive Studies

Studies on experimental animals should also be conducted to investigate the possibility of carcinogenicity, mutagenicity, teratogenicity, and effects on reproduction from absorption of vanadium compounds.

Sampling and Analysis

Sampling and analysis of vanadium halides and oxyhalides should be investigated. Studies of the kinetics of decomposition of these vanadium compounds may be necessary so that the adequacy of sampling and analytical methods may be evaluated.

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