

IV. ENVIRONMENTAL DATA

Environmental Concentrations

Workroom studies indicate that vanadium concentrations as low as 0.01 mg/cu m have been detected [25,67] using less effective engineering technology than is available today. Quarterly sampling reports of one vanadium production plant show average vanadium concentrations of 0.04 mg/cu m (range 0.002-0.31 mg/cu m) at 20 locations throughout the plant [80]. Both personal monitors and high-volume samplers were used in this plant, with subsequent analysis by the ferrous ammonium sulfate titration method [81] and flameless atomic absorption spectrophotometry. Precision of vanadium analyses was estimated by the users to be $\pm 5\%$.

Another vanadium pentoxide producer submitted the results of 3 years of area sampling [82]. The first group of samples was taken before the installation of a new dust collection system. The results of these 89 samples averaged 0.12 mg V/cu m. After installation of the new equipment, sampling was resumed and the average of 15 samples was 0.02 mg V/cu m. Air samples were taken from a 12,000-sq ft area, with a high-volume sampler, for 30 minutes at 40 cu ft/minute. Vanadium analysis was performed by the ferrous ammonium sulfate titration method [81]. The producer also reported that, at these vanadium concentrations, there were 8-10 incidents where employees complained of symptoms resembling those of the common cold, but lasting only 2-4 days.

N.E. Whitman reported the results of 30 breathing-zone samples taken in a steel plant [60]. The vanadium concentrations reported ranged from 0.5 to 10.6 μg V/cu m, with one value of 43.6 μg V/cu m. According to N.E.

Whitman (personal communication, August 1977) the samples were analyzed by the method of Talvitie [55].

Table III-2 summarizes some environmental data, together with the effects of exposure at various concentrations and chemical forms of vanadium.

Air Sampling

Several methods have been used to sample airborne vanadium. An ideal method would collect all particles regardless of particle size and would be representative of the worker's actual exposure without restricting normal work activities.

The most frequently used collection devices are filters that may be made of paper, glass, polystyrene, or other polymers such as cellulose ester or polyvinyl chloride. Analytical filter papers such as Whatman 41 have the advantage of low flow resistance, but, depending on face velocity, particles below 0.5 μm may not be completely collected. Filters of glass or polystyrene fibers have higher collection efficiencies and are nonhygroscopic and, therefore, may be preferred over filters of cellulose fiber. Membrane filters, such as the Millipore AA or Nucleopore, are composed of polymers such as cellulose ester or polyvinyl chloride. These filters are usually highly efficient for collection of particles larger than the mean pore size, which can range from 0.01 to 5 μm . Collection of total airborne particulates would require a filter with a small pore size, usually 0.8 μm , which would provide essentially complete collection of particles less than 0.5 μm and of dust particles of larger sizes [83,84]. Membrane filters with larger pore sizes, up to 5.0 μm , may be used, but

possibly with some loss in efficiency. The use of silver membrane filters for collection of vanadium-containing aerosols has not been studied, but they may be of value, provided they do not interfere with procedures involved in analysis. As described by Lippmann [85], they are made by sintering uniform metallic silver particles, and they have a structure similar to that of organic membrane filters.

Air sampling for worker exposure should be performed by personal sampling whenever possible. A personal sample can be taken for up to 8 or 10 hours on a worker by using a battery-operated, belt-worn pump connected by rubber or plastic tubing to a membrane filter holder. Any known flowrate between 0.5 and 3 liters/minute is satisfactory. If both ceiling and TWA concentration exposures are to be assessed, repeated 15-minute samples may be best.

Other sampling devices such as electrostatic precipitators or high-volume area samplers may also be used for collection of airborne vanadium particulates. Electrostatic precipitators have the advantages of being free of filter clogging and problems with flowrate or humidity. These systems are also very efficient in collecting particles of all sizes. When electrostatic precipitators are used, however, special precautions must be taken to guard against electric shock. High-volume sampling is also appropriate for airborne vanadium collection, but the characteristics of the filter medium should be considered so that optimum collection efficiency is obtained. Like electrostatic precipitation, high-volume sampling suffers from the disadvantage that the actual employee exposure may not be estimated as closely as is possible with personal sampling.

Chemical Analysis

Vanadium is readily determined by a number of analytical techniques, most of which are spectrophotometric or titrimetric. Other methods such as polarography [86], emission spectroscopy [87-90], X-ray fluorescence [91-96], and neutron activation analysis [97,98] may also be used, depending on the analyst's requirements for speed, accuracy, sensitivity, and precision. Spectrophotometric procedures are well suited to the determination of vanadium at low concentrations, because these procedures for vanadium are generally quite sensitive and relatively simple.

The widely used phosphotungstate method relies on the reaction of sodium tungstate with pentavalent vanadium to form a yellow complex which absorbs light at 400-450 nm and can be quantitatively estimated spectrophotometrically [99]. A similar complex, however, may also form between sodium tungstate and other metal ions such as iron, manganese, zirconium, bismuth, antimony and tin [100]. Interfering ions may be removed by mercury cathode electrolysis or by extraction of the sample solution with ethylmethyl ketone [101]. A phosphotungstate method, modified to exclude interference from other ions, has been reported for the determination of vanadium in samples from low-alloy steel [102].

Another spectrophotometric method is based on the measurement of the intensity of the magenta-black color of the complex formed from vanadium and 8-hydroxyquinoline in alcohol-free chloroform medium [55]. This method is especially suited for determination of 1-50 μg of vanadium in samples from biologic materials. Iron must be removed from the same solution, since it is a strong interferent in this procedure. A masking agent such as ethylenediamine tetraacetic acid in the presence of a calcium salt is

usually used for this purpose [55].

Titrimetric procedures have been successfully used for the determination of vanadium in steel and are based on the oxidation or reduction of the vanadium (IV) and vanadium (V) oxidation states. For sample solutions containing no oxidizable element other than vanadium, titrimetric analysis is very simple. An acidic solution of tetravalent vanadium is titrated with a standard permanganate solution. Pentavalent vanadium can also be titrated with a reducing agent, with results that are analogous to those obtained by titrating vanadium (IV) with an oxidizing agent. In principle, vanadium is oxidized to the pentavalent state, excess oxidant is destroyed, and the resulting solution is titrated with a standard solution of ferrous ions. The end points of either of these titrations may be determined visually, spectrophotometrically, potentiometrically, or amperometrically. Visual determinations are probably the least sensitive of these methods.

Excellent results have been obtained by Lingane and Meites [86] after polarographic analysis of a variety of steel and ferroalloy samples supplied by the National Bureau of Standards. Polarographic analysis of steel is possible only after removal of interfering substances such as molybdenum or manganese, either by the addition of phosphoric acid to the sample solution, or by electrolysis using a mercury cathode cell.

Samples obtained from air filters, alloys, and biologic material have been successfully analyzed by emission spectroscopy [87-89]. Excellent sensitivity is realized for this method, which gives a detection limit of 1 fg of vanadium for some biologic samples [90]. The complex spectra of vanadium present many suitable lines for the detection of this element.

Highly skilled personnel may be required to obtain and interpret spectra of high resolution and dispersion.

X-ray fluorescence spectroscopy is a convenient, precise, and relatively simple method for estimation of vanadium in biologic material [91], petroleum [92-94], steel alloys [95], and particulate matter filtered from the air [96]. Using X-ray fluorescence techniques, it is difficult to detect vanadium or any other metal if present in the sample at a concentration less than 100 ppm.

Very accurate and precise determinations of vanadium in particulate samples are possible using neutron activation analysis [97,98]. This type of analysis requires no chemical separations. Interferences, especially by sodium, are common because of simultaneous activation of many elements in the sample. These interferences may be reduced, however, if high resolution detectors are used. Standards are required that contain the same elements as the sample, at similar concentrations, and in the same containment geometry. Once activated, samples must be counted immediately, since even a 20-minute delay will cause a 97.5% reduction in vanadium activity. For air-filtered samples, a detection limit of about 1 ng, corresponding to a concentration limit of 2 ng/cu m, has been achieved [97,98].

Of all the analytical procedures discussed in the literature, atomic absorption spectrophotometry is the most commonly used for trace metal analysis because it is simple, rapid, sensitive, selective, and widely available. There are two main types of atomic absorption analysis: the flame aspiration procedure and the flameless furnace-vaporization technique. Most metals can be determined by either procedure, though

interferences are fewer in the flameless mode. When using flameless atomic absorption for analysis of air-filtered vanadium samples, Quickert et al [103] found that interferences encountered in the conventional flame technique were absent, and that detection limits for vanadium were lowered by two orders of magnitude to the minimum detectable concentration of 0.25 ng/cu m for an air sample of 2,000 cu m. In these analyses of ferrovanadium for vanadium content, they digested the alloy in a mixture of nitric and hydrofluoric acids.

Engineering Controls

Engineering design for operations and processes involving vanadium and vanadium compounds should be oriented toward controlling inhalation exposures and minimizing skin and eye contact with the dust. Properly designed and maintained ventilation systems should prevent dispersal of vanadium into the workroom atmosphere and its accumulation on surfaces, thus reducing chances of resuspension. These goals can be accomplished by the use of properly constructed and maintained closed systems operated under negative pressure. Where closed systems cannot be adequately designed or effectively used, local exhaust systems with collection hoods at potential contamination sources should be provided to direct airflow away from the employees' breathing zones into the exhaust system. These systems should be designed to remove dust in as concentrated a form as possible, with proper allowance for makeup air. Guidance for design can be found in Industrial Ventilation--A Manual of Recommended Practice [104], in Fundamentals Governing the Design and Operation of Local Exhaust Systems

(ANSI Z9.2-1971) [105], and in NIOSH's Recommended Industrial Ventilation Guidelines [106].

Since dust clouds of some metallic vanadium are potentially explosive, construction materials must be nonsparking and ignition sources must be eliminated. According to the National Fire Protection Association, the minimum explosive concentration of these dusts is 200 g/cu m with an autoignition temperature of 500 C [107].

Ventilation systems require regularly scheduled inspection and maintenance to ensure effective operation. These inspections should include measurements of system function, such as airflow measurements at collection hoods, static pressure at branch ducts, or pressure drop across filters and fans. Whenever consecutive measurements show a trend toward deterioration, equipment maintenance is indicated. Evaluation of the effectiveness of the dust control system, by measurement of general workroom air, operators' breathing zone air, and potential contamination sources, should be performed whenever changes are made in the ventilation system or in the work operations or processes.

V. WORK PRACTICES

In the production and use of vanadium, good work practices, in concert with engineering controls, should aid in reducing concentrations of airborne vanadium dusts, fumes, and vapors. These measures should further aid in preventing ingestion of and skin and eye contact with vanadium.

(a) Storage, Handling, and Use

Special precautions should be taken when using, storing, or shipping vanadium oxytrichloride. Vanadium oxytrichloride is a light-yellow liquid that decomposes to vanadium pentoxide and hydrochloric acid when exposed to moisture. The hydrochloric acid byproduct should be controlled so that exposures do not exceed the limit expressed in 29 CFR 1910.1000. Vanadium oxytrichloride should be stored in tightly closed, moistureproof containers in dry, well-ventilated areas away from heat or direct sunlight, and should be shipped in an inert atmosphere. Dry powder and carbon dioxide extinguishers should be used to put out fires that may occur near containers of vanadium oxytrichloride.

While vanadium does not pose a fire hazard, except for bulk quantities of finely ground metallic forms, and, so far as is known, is not a significant hazard when ingested, it is good practice to separate rest areas, eating facilities, and smoking areas from the work areas.

Vanadium carbide, vanadium-aluminum alloys, and vanadium metal itself, when ground smaller than 100 mesh (150 μm [21]) are considered by Roberts [20], on the basis of his 15 years' experience at a ferroalloy-production plant, to be combustible. This is also true of ferrovandium ground smaller than 200 mesh (75 μm [21]). When present in bulk

quantities, care should be taken to ensure that these finely ground products are kept dry and away from heat, sparks, or open flame.

Warning labels indicating skin, eye, and respiratory irritation hazards and urging use of adequate ventilation should be on containers used to transport various vanadium compounds, particularly fused flakes and fine granular ammonium metavanadate and vanadium pentoxide, trichloride, oxytrichloride, and tetrachloride. Placards should alert employees to the existence and nature of hazards, indicate the exit locations, and identify areas or situations where respirators or other protective items are needed.

(b) Maintenance of Equipment

The duties of maintenance and repair workers pose special problems with regard to the evaluation of their potential exposure. Often the very circumstances that require the maintenance or repair work and under which work must be done will negate some of the normal control procedures. Because of these factors, very careful supervisory control must be exercised over such activities. These workers should wear the appropriate protective equipment and clothing and should follow the standard operating procedures or directives from special work permits. They should be trained in the recognition and control of hazards to which they may be subjected.

(c) General Housekeeping

Where spills of vanadium dust, liquids, or solutions occur, the area should be posted to prevent entry by other employees and promptly cleaned up by means that will minimize inhalation of, or contact with, the materials. Vacuuming is preferred for spills of dry material along with wet mopping; no dry sweeping or blowing should be permitted. Liquid or wet material spills should be flushed with an abundance of water. The

liquid waste should be channeled into a treatment system or into a holding tank for reclamation or disposal. Process or storage areas where liquid vanadium material is kept in large containers should be diked, and the drainage of this liquid should be channeled into a collection area for reclamation or disposal. Supervisors should emphasize to employees the necessity for prompt cleanup of spills, repair of equipment and leaks, proper storage of materials, proper functioning of dikes, and the prompt collection of vanadium-containing dust. All collected material generated by the processes should be recycled back into the process or disposed of in a manner that meets local, state, and federal regulations.

(d) Emergency Procedures

Safety showers and eyewash fountains should be located in or near areas where gross exposures to vanadium compounds are likely to occur and should be properly maintained. If vanadium compounds, especially the halide or oxyhalide liquids, come in contact with the skin, the affected area should be flushed promptly with water. The eyes, if splashed or otherwise contaminated with these reactive halides, should be flushed immediately and thoroughly with water at low pressure. The employee should then be taken promptly to the nearest medical facility to determine the need for further treatment. All employees should be fully informed of the need for carefully observing these procedures.

Although emergency procedures specific to hazards of vanadium and its compounds are not required, general emergency procedures should be developed. Training sessions should be held and complete written procedures for emergencies should be revised and updated periodically. They should include provisions for transportation of injured personnel to

hospitals and the location, use, and maintenance of first-aid or firefighting equipment, emergency showers, and eyewash fountains. Emergency drills should be held at least once a year. All emergency plans should be designed to minimize personal injury, property damage, and process interruption.

(e) Respiratory Protection

Some industrial processes may produce simultaneous exposure to particulate vanadium and to vapors of such volatile liquids as some vanadium halides. In these areas, the employee should wear the recommended type of respirator that will provide protection against both particulate and vapor, and the employee should observe the practices of an established respiratory protective devices program. Cleanliness and maintenance of respirators should be emphasized. Contamination of the interior of the facepiece should be prevented. Detailed information concerning respirators is given in the Respiratory Protective Devices Manual, ANSI Z88.2-1969 [108], and in the current federal standard, 29 CFR 1910.134. The proper respirators for protection against vanadium exposure are described in the Respirator Selection Guide in Tables I-1 and I-2.

(f) Skin and Eye Protection

Safety glasses with side shields and gloves should be issued to, and worn by, employees occupationally exposed to vanadium. Coveralls (which can be of the disposable type) should be worn to minimize the possibility of skin irritation. Rubber aprons or rubber suits and rubber gloves should also be worn in liquid vanadium compound areas, especially where there is production or use of vanadium oxytrichloride and tetrachloride, both of which are very irritating to the eyes, skin, and respiratory tract in

either liquid or vapor form. While data demonstrating this irritation have not been found, it is reasonable to conclude that compounds so reactive with water and other materials, that thereby release heat and irritant materials such as hydrogen chloride, would necessarily be irritating to exposed tissue. Other personal protective equipment should be provided, used, and maintained as specified in 29 CFR 1910.132-137. The proper use of protective clothing requires snug, but comfortable, fit around the neck, wrists, and ankles whenever the wearer is in an exposure area. The protective equipment and clothing must be maintained in good hygienic and uncontaminated condition and should be cleaned or replaced on a regular schedule. Employees should keep such equipment in suitable, designated containers or lockers provided by the employer when the equipment is not in use.

Boiler cleaners should wear acid-resistant boiler suits that fit snugly at the wrists and ankles, rubber gauntlet gloves, and knee-length rubber boots. Eyes should be shielded by goggles, and a suitable respirator should be worn; both goggles and respirator can be incorporated in a full-face mask which gives good protection. This should be worn with a suit with a hood to cover the neck and head. Alternatively, an air-fed hood to cover the head and shoulders may be used. Before entering, fire chambers must be purged with clean air and hosed down with water. Soot should be vacuumed, rather than flushed with compressed air jet, so that displaced soot is collected directly by a dust control system.

(g) Sanitation and Personal Hygiene

The employer should provide locker and change facilities for work and street clothes. Work clothing should not be worn outside the workplace to

limit the possibility of exposure to the workshift, and so that family and friends are not potentially exposed. As a good practice, it is recommended that shower facilities, supplied with soap, be provided for the employees and that they be advised to shower before leaving the workplace at the end of the workday. Contaminated clothing should be removed and discarded or cleaned before reuse. Clothing to be reused should be stored in a container that is impervious to the compound. Personnel cleaning the clothing should also be alerted to the hazards of vanadium.

Good personal hygiene is important for the prevention of dermatitis, eye and respiratory irritation, and gastrointestinal problems from vanadium. It involves washing thoroughly before eating, smoking, drinking, or using toilet facilities.