

AIR POLLUTION ASPECTS
OF
VANADIUM AND ITS COMPOUNDS

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FOREWORD

As the concern for air quality grows, so does the concern over the less ubiquitous but potentially harmful contaminants that are in our atmosphere. Thirty such pollutants have been identified, and available information has been summarized in a series of reports describing their sources, distribution, effects, and control technology for their abatement.

A total of 27 reports have been prepared covering the 30 pollutants. These reports were developed under contract for the National Air Pollution Control Administration (NAPCA) by Litton Systems, Inc. The complete listing is as follows:

Aeroallergens (pollens)	Ethylene
Aldehydes (includes acrolein and formaldehyde)	Hydrochloric Acid
Ammonia	Hydrogen Sulfide
Arsenic and Its Compounds	Iron and Its Compounds
Asbestos	Manganese and Its Compounds
Barium and Its Compounds	Mercury and Its Compounds
Beryllium and Its Compounds	Nickel and Its Compounds
Biological Aerosols (microorganisms)	Odorous Compounds
Boron and Its Compounds	Organic Carcinogens
Cadmium and Its Compounds	Pesticides
Chlorine Gas	Phosphorus and Its Compounds
Chromium and Its Compounds (includes chromic acid)	Radioactive Substances
	Selenium and Its Compounds
	Vanadium and Its Compounds
	Zinc and Its Compounds

These reports represent current state-of-the-art literature reviews supplemented by discussions with selected knowledgeable individuals both within and outside the Federal Government. They do not however presume to be a synthesis of available information but rather a summary without an attempt to interpret or reconcile conflicting data. The reports are

necessarily limited in their discussion of health effects for some pollutants to descriptions of occupational health exposures and animal laboratory studies since only a few epidemiologic studies were available.

Initially these reports were generally intended as internal documents within NAPCA to provide a basis for sound decision-making on program guidance for future research activities and to allow ranking of future activities relating to the development of criteria and control technology documents. However, it is apparent that these reports may also be of significant value to many others in air pollution control, such as State or local air pollution control officials, as a library of information on which to base informed decisions on pollutants to be controlled in their geographic areas. Additionally, these reports may stimulate scientific investigators to pursue research in needed areas. They also provide for the interested citizen readily available information about a given pollutant. Therefore, they are being given wide distribution with the assumption that they will be used with full knowledge of their value and limitations.

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ABSTRACT

Vanadium is toxic to humans and animals, especially in its pentavalent form. Human exposure through inhalation of relatively low concentrations (less than $1,000 \mu\text{g}/\text{m}^3$) has resulted in inhibition of cholesterol synthesis, and chronic exposure to environmental air containing vanadium has been statistically related to mortality rates from heart diseases and certain cancers. Exposure to high concentrations (greater than $1,000 \mu\text{g}/\text{m}^3$) results in physiologically observable effects of varying severity on the gastrointestinal and respiratory tracts. In general, very little research has been done on the toxicity of environmental concentrations of vanadium.

No information has been found on the effects of vanadium air pollution on commercial or domestic animals or plants. Only one reference was found on the effects on materials: vanadium in fuels was found to be corrosive to heating plants.

The major sources of vanadium air pollution are the vanadium refining industries, alloy industries, and power plants and utilities using vanadium-rich residual oils.

The concentration of vanadium in the atmosphere is monitored by the National Air Sampling Network. The average levels noted ranged from below detection ($0.003 \mu\text{g}/\text{m}^3$) to 0.30 (1964), 0.39 (1966), and 0.90 (1967) $\mu\text{g}/\text{m}^3$.

No information has been found on economic losses resulting from vanadium air pollution, and little information exists on the costs of abatement. One report on abatement indicated that an economic gain resulted from extracting vanadium from steam generators using vanadium-rich fuel. No other information was found on abatement procedures specifically intended to control vanadium emissions; normal particulate control methods are suitable.

The methods of quantitative analysis of vanadium in the atmosphere that are available—including colorimetric, atomic absorption spectroscopy, emission spectrography, and polarography—provide sensitivities in the $0.001 \mu\text{g}/\text{m}^3$ range.

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1. INTRODUCTION

Vanadium is moderately toxic to humans and animals. Exposure to vanadium or its compounds at low concentrations through inhalation has produced observable adverse effects on the human organism. Chronic exposure to environmental air concentrations has been statistically associated with the incidence of cardiovascular disease and certain types of cancer.

Vanadium is emitted into the atmosphere from such sources as the industries producing the metal, its chemical compounds, alloys, and other products, as well as power plants and utilities consuming residual and crude oils and coals containing vanadium. The present concentrations of vanadium in the atmosphere of the United States are on the order of a few micrograms per cubic meter; however, the fast-increasing production and use of vanadium and its compounds, added to the growing consumption of vanadium-bearing oils and coals, will significantly augment the potential for air pollution by vanadium.

2. EFFECTS

Vanadium appears to be a trace metal essential for the human body—and for mammals in general—but the final proof of its essentiality is still lacking. In spectrographic analysis of organs and muscle tissues of Americans, vanadium has been detected only in lung and intestine: most positive samples showed 0.01 μg or less of vanadium per gram of tissue. Vanadium appears to be stored mostly in fat and serum. Studies of the fate of vanadium in man point to the existence of a vanadium homeostasis, but the exact mechanism is presently not known.⁷⁶

Increasing knowledge of the role of essential and non-essential trace metals in metabolic processes at cellular and molecular levels has stimulated research on the biochemical effects of vanadium. Vanadium has been found to inhibit the synthesis of cholesterol,^{8,14,21,23,24,39,43,61,65,84,92,100} phospholipids, and other lipids.^{12,27,61,82} Vanadium's inhibitory role has been also studied with respect to amino acids^{31,44} in general and theotic acid⁵⁰ and uric acid⁹³ in particular, as well as the enzymatic activities of tyrosinase,^{7,63} xanthine reductase,⁶² cystine,^{10,59,60} and nitrate reductase.⁶⁴ Studies have also been made of the adverse bioeffects of vanadium on tissue oxidation.¹¹ inhibition of sulfhydryl activity;⁸² blood lecithin content;³⁹ excretion of corticosteroids;^{13,40} acetylcholine metabolism;⁴⁵ liver acetylation process;

inhibition of the activities of coenzymes A, Q, and I;^{6,49,50} inhibition of adenosene triphosphatases;⁶⁹ and precipitation of serum proteins.³⁰

The most-studied effect is the inhibition of cholesterol synthesis. Vanadium has been found to interfere with the formation and utilization of mevalonic acid, one of the intermediate substances in the process of cholesterol synthesis from acetyl groups. Furthermore, vanadium has been shown to inhibit the metabolic activities of coenzymes A and Q, which are involved in the early stages of cholesterol synthesis. These coenzymes form various acetyl-coenzymes, which, in turn, produce the necessary condensation of acetyl groups to form mevalonic acid. There is also evidence that vanadium contributes to depletion of cholesterol stored in the tissues and reduces dietary cholesterol retention.

The interrelationship of the various metabolic processes mentioned above is shown in Figure 1. The chain of cause-and-effect relationships that link inhibition of cholinesterase and other activities to a number of diseases is discussed in the following paragraphs.

The role of cholinesterase consists of splitting acetylcholine into choline and acetic acid. Choline is an essential nutrient that protects the tissues (mainly the liver) from excess fat accumulation by converting fats into phospholipids. Choline deficiency is also associated with fatty infiltration

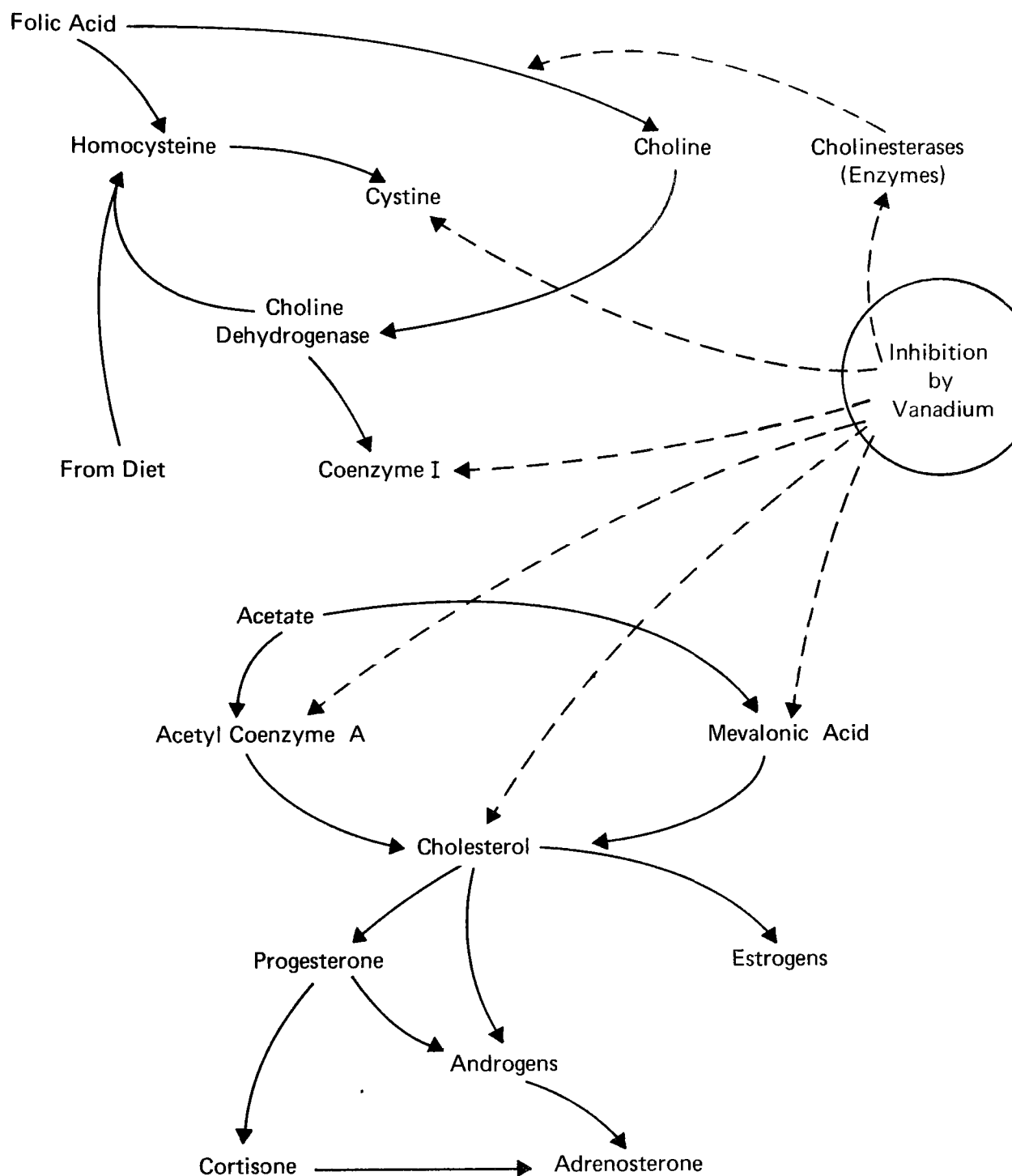


FIGURE 1

The Complex of Bioprocesses Inhibited by Vanadium

of the myocardium which can ultimately cause an infarct. Sclerosis (Monckeberg type) has also been observed, with more or less calcified lipid deposits in the aorta and coronary vessels. Deficiency of choline causes a decrease in serum albumin and an increase of phospholipids and the alpha-and beta-globulins. Finally, choline is known to have a favorable effect on growth, reproduction, and pregnancy in both lower and higher organisms.

Experimentally determined indications of choline deficiency include growth retardation, anemia, high infant mortality, kidney atrophy, fatty degeneration and cirrhosis of the liver, necrosis of the kidney tubules, creatinuria, progressive muscular dystrophy, and even death.

Since the role of vanadium as an inhibitor of cholinesterase activity is well established, it is possible that the above physiological effects are at least partially correlated with the presence of vanadium. As will be shown in the following sections, a positive correlation to some of these effects has been established.

The importance of vanadium's indirect inhibitory effects on the adrenocortical hormones may be assessed on the basis of the following considerations. Cholesterol, as the name indicates, is a member of the sterol group that belongs to the larger group known as steroids, which are widely distributed in nature and include many important hormones. Cholesterol,

a cell constituent of most warm-blooded animals, is relatively concentrated in the adrenal cortex, where it is a precursor of the all-important adrenocortical hormones (see Figure 1). The latter affect a great number of metabolic processes, including salt, water, mineral, and carbohydrate metabolism. It has been established that cholesterol can give rise to all the corticosteroids (hormones, glucogenic steroids, and androgens). Inhibition of the majority of these metabolic processes is known to result in a great number of physiological alterations.

The next most-studied aspect of vanadium is its role as an inhibitor of cystine, cysteine, and methionine—the three basic sulfur-containing amino acids. Cysteine forms and is formed by cystine, and its decarboxylation results in the formation of part of coenzyme A. Cystine is the sulfur-containing constituent of skin, hair, and nails. Methionine has a sulfur-bound methyl group which through enzymatic activity is used in the production of adrenaline, choline, and creatine.

Vanadium has been shown to interfere with tissue respiration at the stage of dehydrogenation which is catalyzed by coenzyme I. Inhibition of this coenzyme's activity by vanadium results in reduced incorporation of iron in the related porphyrins which, in turn, inhibits hemoglobin synthesis. The nonutilized portion of iron has been observed to accumulate in the reticuloendothelial tissues after experimental exposure

to vanadium. The metal's action is supported by its potential inhibition of the activity of monoamineoxidase, which catalyzes the oxidation of serotonin to 5-hydroxyindolacetic acid. The urine content of this acid has been found to fall as a result of experimental exposure to vanadium. Thus, inhibition of monoamineoxidase may result in the accumulation of serotonin in the central nervous system.

On the other hand, it has been found that the activity of monoamineoxidase was considerably enhanced by 1.0 millimole of vanadium(III) and vanadium(IV), but not vanadium(V). In this respect, it has been suggested that vanadium is a co-factor in tissue monoamineoxidase.⁷⁶

The conflicting evidence regarding the role of vanadium in monoamineoxidase activity may be explained by the fact that many trace metals can either inhibit or enhance a given metabolic activity, depending on their level of concentration and other relevant variables or parameters. Among 18 metals tested, vanadium was found to be the major catalyst in the oxidation of 5-hydroxytryptamine (serotonin), adrenaline, and other important catecholamines.⁴⁸ In insulin hypercalcemia, the adrenaline level can rise to 10 times the normal and, in patients with catecholamine-producing tumors, noradrenaline levels 100 times greater than normal have been observed. Adrenal hormones can cause high blood pressure and marked reduction in the renal blood circulation, renal plasma circulation, and glomerular filtration rate. They can also increase

oxygen consumption and indirectly, production of corticosteroids.

The exact etiological mechanism linking the above effects to observed physiological changes in tissues and organs is not known. Most of the observed adverse effects of vanadium have occurred after human or animal exposure to relatively high concentrations in relation to normal environmental concentrations of vanadium. Such effects are clinically observable and, in most cases, can be specifically attributed to vanadium. However, chronic exposure to the relatively low concentrations observed in urban atmospheres usually does not produce any clinically observable physiological changes.¹⁰³ The effects of vanadium, if any, on metabolic processes are not felt by the person exposed, and the biochemical changes produced are usually links in a chain of adverse effects that can result from a multitude of pollutants as well as diseases. It is for these reasons that such changes as a 10 percent decrease in normal cholesterol and/or cystine levels become important in considering the possible health effects of environmental concentrations of vanadium.

2.1 Effects on Humans

2.1.1 Exposure to Low Concentrations

Very few studies have been made on the effects of human exposure to low concentrations of vanadium in the environmental air. In one of these studies, lower-than-normal plasma

cholesterol levels were usually found among vanadium processing workers in Colorado who had been exposed to vanadium levels of from 100 to 300 $\mu\text{g}/\text{m}^3$.^{44,96}

In an experiment with two volunteers, exposure to vanadium pentoxide (V_2O_5) at a concentration of 1,000 $\mu\text{g}/\text{m}^3$ resulted in coughing which persisted for 8 weeks. Another five volunteers were exposed to an average concentration of 200 $\mu\text{g}/\text{m}^3$ (± 60 standard deviation) for about 8 hours. All of them developed loose coughing the following day. Urinalysis showed a maximum concentration of 130 $\mu\text{g}/\text{liter}$ three days after the exposure, while maximum fecal concentration was 3,000 $\mu\text{g}/\text{kg}$.¹⁰⁴

In another instance, when 24 workers were exposed to vanadium pentoxide at concentrations of from 18 to 925 $\mu\text{g}/\text{m}^3$, it was found that serum cholesterol levels were approximately 10 percent below normal.⁴³

In a statistical study by Hickey et al.,³⁵ concentrations of vanadium and nine other metals in the environmental air of 25 communities in the United States were correlated to mortality indices (1962 to 1963) of eight categories of prevailing diseases. Various techniques of correlation analysis were used, including canonical analysis. In the matrix of computed correlation co-efficients the following values were obtained with respect to vanadium's association with some of the diseases and pollutants:

Vanadium—"diseases of the heart"	= 0.50	(fourth highest value after those found for cadmium, zinc, and tin)
Vanadium—nephritis	= 0.47	(third highest after tin and nickel)
Vanadium—"arteriosclerotic heart"	= 0.47	(fourth highest after cadmium, zinc, and tin)
Vanadium—nickel	= 0.94	(highest coefficient of intercorrelation among any two of the ten metals)

Thus, vanadium (together with cadmium, zinc, and tin) was found to correlate significantly with the above diseases and highly with nickel. In subsequent canonical analysis, it was found that the strongest relationship existed between vanadium and "diseases of heart." Moreover, tests of statistical significance of various combinations showed that the addition of vanadium to cadmium produced a more than 10 percent reduction (the highest) in the error of variance.³⁵ The very high intercorrelation between vanadium and nickel was not explained in this study. As shown in the section devoted to sources, the two metals together are major contaminants of crude and residual oils, as well as constituents of the fly ash from their industrial emission sources.

In another statistical study by Stocks,⁸⁹ mortality from lung cancer was found to correlate significantly with the concentration of particulates in many areas in Great Britain.

Concentrations of 13 trace elements were correlated with lung cancer mortality rates in 23 localities. The findings of the study were as follows:

(1) Vanadium, together with arsenic and zinc, showed weak associations with lung cancer.

(2) Vanadium showed a strong association--second only to beryllium and arsenic--with bronchitis in males.

(3) Vanadium and beryllium were found to be associated with pneumonia.

(4) Vanadium, beryllium, and molybdenum showed correlations with other cancers, but only in males.

Thus vanadium ambient air concentrations showed statistical correlations with bronchitis, pneumonia, lung cancer, and other cancers. The estimated correlation coefficients were the following:

Bronchitis, males = 0.620

Pneumonia, males = 0.805 (highest among 11 metals)

Pneumonia, females = 0.711 (second highest after beryllium)

Lung cancer, males = 0.770 (second highest after beryllium)

Other cancer,
except of
stomach, males = 0.556 (highest)

Both the above-mentioned studies represent efforts to test statistically for significant correlations between environmental concentrations of a number of trace elements and mortality rates related to various diseases in urban centers. The study by Hickey³⁵ used more sophisticated techniques

of statistical analysis. His study employed canonical rank correlation to test for the combination of variables that would maximize the correlation between pollutants and diseases; it also tested for and found significant intercorrelations, thus reducing the validity of conclusions based on the estimated numerical values of the correlation coefficients. On the other hand, the study by Stocks⁸⁹ considered diseases which are more well-defined than the majority of those considered in the study by Hickey.³⁵ Further, it considered such important parameters as population density, sex, and age.

However, the two studies cannot be compared, since the correlations were run for different diseases (except for lung cancer) and the sets of pollutants considered were not exactly the same. Nevertheless, it is interesting to note the differences in findings with respect to the relationship between lung cancer mortality and vanadium concentrations. The correlation coefficients estimated by the two studies are 0.320 (Hickey)³⁵ and 0.770 (Stocks).⁸⁹

Hickey³⁵ found that when vanadium was considered together with cadmium the multiple correlation coefficient was 0.767. He points out that in addition to cadmium, vanadium in the ambient air may contribute to diseases of the heart.

Both studies were handicapped by the lack of long-term data (time series), the omissions of important pollutants (e.g., organic compounds) that are known to be causally related to some of the considered diseases and that cannot be

assumed to be constant; the unsatisfactory definition of diseases; and the known and unknown intercorrelations (positive and/or negative) among the pollutants as well as the diseases considered.^{35,89}

Statistical correlation studies are useful mostly in cases of relatively high average levels of atmospheric pollution in cities and towns where the meteorological conditions include fairly prolonged temperature inversions.^{35,89}

2.1.2 Exposure to High Concentrations

Practically all of the studies on high concentrations of vanadium center on occupational exposures, mostly to vanadium pentoxide (V_2O_5).

In one study, exposure to inhalation of V_2O_5 dust by 18 workers engaged in pelletizing pure V_2O_5 resulted in acute illness of all those involved.¹⁰³

In other research, a normal young male was injected intramuscularly with a sodium salt of vanadium ($Na_2V_4O_{11}$). The first dose was 5,600 μg of vanadium, followed by doses of 11,200 μg on the third and fourth days. The following effects were subsequently observed: (1) increased levels of urea and purine nitrogen, but relatively small increases in total nitrogen; (2) an increased level of neutral sulfate in the urine, but relatively small increases in total neutral sulfate; and (3) a significant increase in fecal phosphorus (27 percent,) but very small increase in total phosphorus.⁹¹

Occupational vanadium poisoning was first studied in 1911 among workers exposed to vanadium dust and fumes from Peruvian ores. The effects described included paroxysmal cough leading to hemoptysis. In more severe cases, tuberculosis developed, which sometimes led to death. Among other symptoms were irritation of throat, eyes, and nose; anorexia, tremors, hysteria, and melancholia; and anemia, accompanied by reductions in hemoglobin and in the number of erythrocytes. At tissue levels, the poisoned workers showed destruction of the alveolar epithelium in the lungs and hemorrhagic nephritis. Similar symptoms have since been reported by other investigators in various countries but at lower levels of intensity since industrial precautions are increasing in number. The effects described by various studies during the 1940's and 1950's included bronchitis, pneumonia, conjunctivitis, rhinitis, pharyngitis, laryngitis, and bronchopneumonia. The systemic poisoning effect suggested by earlier investigations^{29,101} has not been confirmed by later and more detailed studies.

During the 1940's and 1950's similar effects were described in cases of exposure to vanadium pentoxide and vanadium trioxide contained in by-products of residual or crude oil combustion.^{36,51,78-80,94} In practically all the cases showing marked effects on the respiratory system, exposures ranged from 1,000 to about 50,000 μg of vanadium per cubic meter. The average particle size was found to be

less than 5 μ^* and sometimes less than 1 μ , mostly in vanadium pentoxide in slag from residual oil combustion.⁹⁸ Actually, the intensity and incidence rate of effects have been found to relate directly to the level of concentration and the particle size: the higher the concentration, the greater the intensity and the incidence rate of the observed effects.

Since concentrations in the above-stated range of values are highly unlikely to occur in urban atmospheres, the type of acute physiological effects described are limited to occupational exposures.

In a recent study, the effects of vanadium on a biochemical level were investigated in 13 workers who had been engaged in the production of vanadium pentoxide for a period of from 1 to 3 years and exposed to 480 to 2,650 μg of vanadium per cubic meter. Clinical findings, shown in Table 1, may suggest that the stated exposure resulted in a derangement of the ascorbic acid metabolism.⁹⁷

2.1.3 Lethal Dose (LD)

The lethal dose of vanadium (through inhalation) for man has been estimated by Stokinger to range from 60,000 to 120,000 μg .⁹¹ The LD for intravenous administration of V_2O_5 (as tetravanadate) to a man of average weight (70 kg) has been estimated as 30,000 μg .⁶⁷ However, doses of 10,000 μg (intravenous) or 20,000 μg (intramuscular or subcutaneous) were found to be tolerated in some instances.

* μ = micron.

The emetic dose for the hexavanadate was estimated as 100,000 to 125,000 $\mu\text{g V}_2\text{O}_5$, while a dose of 60,000 μg by any route was well-tolerated.⁶⁷

It is apparent that the range of values between lethal and nonlethal doses of vanadium, as with other nonessential metals, is very narrow.

TABLE 1

URINARY EXCRETION OF VANADIUM AND ASCORBIC ACID
LEVELS IN WORKERS EXPOSED TO VANADIUM PENTOXIDE FUMES⁹⁷

Urinary Excretion	Max	Avg	Min
<u>Vanadium ($\mu\text{g/liter}$)</u>			
Exposed workers	259.3	92.7	21.0
Controls	11.0	6.9	3.5
Increase factor	23.5	13.4	6.0
<u>Ascorbic Acid ($\mu\text{g/3 hr}$)</u>			
Exposed workers	4,000	1,900	500
Controls	9,700	2,500	700
Percent of decrease	58.8	24.0	28.6

2.1.4 Other Factors Determining Toxicity

Route of Intake. Oral administration of the salt sodium tetravanadate to normal men in 12 daily doses (7,000 μg vanadium) resulted in nearly total excretion, 12 percent through the urine and about 88 percent in the feces. However, when the salt was administered intravenously in six daily doses, (approximately 20,000 μg vanadium) about 90 percent was excreted, of which only 9 percent was recovered in the feces.⁹¹

Synergism. In one case of vanadium intoxication, zinc oxide was found to act synergistically to produce after-effects.⁵⁶

Susceptibility to metabolic disturbances because of a genetic defect (Wilson's disease) has been shown to increase as a result of occupational exposure to vanadium.⁵⁸

It has been reported that organic vanadium dust at extremely low concentrations (1 $\mu\text{g/gm}$ of tissue) may induce disturbances of basic metabolic processes, including reduction of cystine content, which are neither clinically detectable nor felt by the subject.⁹⁰

2.2 Effects on Animals

2.2.1 Commercial and Domestic Animals

No information has been found on the effects of vanadium air pollution on commercial or domestic animals.

2.2.2 Experimental Animals

2.2.2.1 Vanadium Pentoxide (V_2O_5)

Ten rabbits and rats were exposed in gas chambers to inhalation of V_2O_5 aerosol at a concentration of 8,000 to 18,000 $\mu\text{g/m}^3$ for 2 hours daily over a period of 9 to 12 months. The acute and chronic poisoning which developed was characterized by biochemical, functional, and morphological abnormalities similar to those described below for vanadium trioxide (V_2O_5). However, the median lethal concentration

of V_2O_5 was found to be one-third to one-fifth that of V_2O_3 .

In the third month, the test rabbits began to show a considerable decrease in the urine content of 5-hydroxyindolacetic acid, which at the end of the experimental period amounted to about one-third of the normal level.⁷³

2.2.2.2 Vanadium Trioxide (V_2O_3)

Vanadium trioxide is also capable of causing acute or chronic poisoning in experimental animals, depending on the dose or concentration in the air. In another series of experiments, 10 rabbits and rats were exposed in gas chambers to inhalation of vanadium aerosol in concentrations ranging from 40,000 to 70,000 $\mu\text{g}/\text{m}^3$ for 2 hours daily over a period of 9 to 12 months. The observed effects included (1) hypochromic anemia, (2) decrease in the hemoglobin level of from 75 percent to 67 percent of the normal, and (3) a 33 percent decrease in the number of leucocytes in the peripheral blood.

By the end of the second or third month of exposure, chronic poisoning with V_2O_3 dust caused a decrease in albumin and increase in globulin to the extent that the ratio of the former to the latter was reduced by half. By the end of the 11th month, additional effects included (1) an increase in the serum content of aminoacids (cysteine, arginine, histidine), (2) a 10 percent increase in the nucleic acid in the blood, (3) a 29.8 percent decrease in the serum content of sulfhydryl groups, (4) a 50 percent decrease in the blood content of

vitamin C, (5) a considerable increase in the blood content of chloride, and (6) a drastic inhibition of tissue respiration in the liver and brain. Finally, the organs of the respiratory system at the end of the experimental period showed such conditions as (1) suppurative bronchitis, (2) septic bronchopneumonia, (3) pulmonary emphysema, (4) formation of cellular-dust foci with signs of necrobiosis in the phagocytes, and (5) moderate interstitial pulmonary sclerosis.⁷³

2.2.2.3 Vanadium Chloride (VCl_3)

Rabbits and rats exposed to inhalation of VCl_3 showed chronic poisoning effects similar to those described for V_2O_3 , but the effects on tissues were more marked: they were characterized by (1) protein and fatty dystrophies of the cells of liver, kidney, and myocardium; (2) partial necrosis of the tissues of some organs; and (3) reduction in ribonucleic acid (RNA) and deoxyribonucleic acid (DNA) content of the cells of liver, kidney, myocardium, stomach, intestine, and lung. Thus VCl_3 proved to be more toxic than V_2O_3 under the same experimental conditions.⁷³

2.2.2.4 Vanadium Metal (V), Vanadium Carbide (VC), and Ferrovandium (FeV)

The aerosols of vanadium, vanadium carbide, and ferrovanadium are not considered highly toxic. However, they produce certain local and general physiological reactions, such as (1) catarrhal bronchitis; (2) pathological tissue

proliferation; (3) a moderate degree of interstitial pneumono-sclerosis; (4) marked catarrhal gastritis—a local effect occurring after oral administration; and (5) pathohistological alterations in the parenchyma, such as local nephritis, fatty dystrophy of the hepatic cells, sclerosis of hepatic and renal interstitial tissues, and perivascular edema in the myocardium (a typical general toxic effect).

Exposure to iron-vanadium alloy dust was found to cause slight and statistically insignificant changes in the blood such as a decrease in the sulfhydryl groups and nucleic acids, but marked and significant proteinuria. The vanadium of the iron-vanadium alloy was found to be considerably more toxic than free vanadium because of its higher solubility in bio-material. Exposure to vanadium-carbon and vanadium dust was found to produce slight, unstable, and statistically insignificant biochemical changes in the blood.⁷³

2.2.2.5 Sodium Metavanadate (NaVO_3)

The relative toxicities of vanadium, molybdenum, chromium, and tungsten and their sodium salts have been determined in a series of experiments.⁶⁶ Table 2 lists the lethal doses of these substances as administered to cats, based on fatalities occurring within 60 minutes.

2.2.2.6 Other Factors Determining Toxicity

Valence of Vanadium Atoms. Pentavalent compounds, such as V_2O_5 , NH_4VO_3 , NaVO_3 , and $\text{Ca}(\text{VO}_3)_2$, were found to be three

TABLE 2

LETHAL DOSES OF VANADIUM, MOLYBDENUM, CHROMIUM, AND TUNGSTEN METALS AND SALTS, ADMINISTERED INTRAVENOUSLY TO CATS⁶⁶

Metal	Lethal Dose ($\mu\text{g/kg}$ body weight)	Compound	Lethal Dose ($\mu\text{g/kg}$ body weight)
Vanadium	1,880	Sodium metavanadate	7,180
Tungsten	22,600	Sodium tungstate	143,600
Chromium	56,400	Sodium chromate	179,500
Molybdenum	205,000	Sodium molybdenate	972,000

to five times more toxic than trivalent compounds under comparable experimental conditions, as measured by median lethal concentrations.⁷³ This is shown in Table 3.

TABLE 3

VALENCE OF VANADIUM AND RELATIVE MEDIAN
LETHAL DOSES OF ITS COMPOUNDS⁷³

V Compound	Valence of V Atoms	Relative Value of Median LD
<u>Salts</u>		
NH_4VO_3	5	1 ^a
VCl_3	3	2.3
VI_2	2	6.8
<u>Oxides</u>		
V_2O_5	5	1 ^b
V_2O_3	3	5.6

^a10,000 μg of vanadium per kg body weight.

^b23,000 μg of vanadium per kg body weight.

Diet. Dietary V_2O_5 has been found to be toxic at 100 ppm of vanadium to rats fed a suboptimal (casein) diet, but toxic only at 1,000 ppm of vanadium to rats fed an optimal diet (consisting of Purina chow).⁹¹

Tolerance. It has been shown that some animals develop a certain amount of tolerance to vanadium. Experimental animals may tolerate amounts of vanadium, administered in gradually increasing doses, which would have been lethal if administered in only one or two doses.²⁶

Age. Variations in weight, growth, and ability to survive have been found to relate to age in an experiment with rats fed 100 ppm of vanadium for a lifetime (2 to 5 years).⁹¹

Antagonism and Synergism. At high concentrations, vanadium has been shown to mobilize iron out of the liver and spleen. However, in low concentrations, vanadium has been found to mobilize iron into the liver and to enhance calcium deposition in bone.

2.2.2.7 Absorption, Distribution, and Excretion

After rats had inhaled V_2O_5 dust ($500 \mu\text{g}/\text{m}^3$ of vanadium) 6 hours daily for 6 months, the amounts of vanadium absorbed at the end of this period per gram of tissue were $30 \mu\text{g}$ in the lung, $0.8 \mu\text{g}$ in the kidney, $0.6 \mu\text{g}$ in the spleen, and $0.14 \mu\text{g}$ in the liver. Forty days after the end of the experimental period, the liver was found to retain the highest percent (about 99 percent) of the absorbed amount, followed

by the kidney (60 percent), the spleen (50 percent), and the lung (10 percent). The mean value of urinary excretion of vanadium for pigs was 140 μg of vanadium per liter of urine--28 times higher than for the control animals.⁹¹ Vanadium was excreted mostly through the kidneys when its sodium salt ($\text{NaVO}_3 \cdot \text{H}_2\text{O}$) was administered intraperitoneally or intravenously to experimental animals. When subtoxic single doses were given, renal excretion was found to be rapid, amounting to 60 percent in the first 24 hours. The above percentage was independent of the number of doses administered.²² This fact led to the conjecture that changes in urinary excretion of vanadium reflected changes in its retention. About 10 percent was excreted through the intestines and an approximately equal percentage was retained in the skeleton, while traces were found in all tissues. Retention of vanadium pentoxide in the tissues of rats was twice that of its sodium salt.⁹¹

2.2.2.8 Comparative Toxicity

The elements can be classified according to their toxicity, as measured by the lethal dose (LD_{50}) for small mammals, as follows:^{13a}

Highly toxic	1,001-10,000 $\mu\text{g}/\text{kg}$ body wt
Moderately toxic	10,001-100,000
Slightly toxic	100,001-1,000,000
Relatively harmless	>1,000,000

These classes can then be subdivided according to the mode of intake. The comparative toxicity of vanadium and 12 other metals is shown in Table 4 and Table 21 in the Appendix.

TABLE 4

CLASSIFICATION OF VANADIUM AND OTHER METALS BY TOXICITY^{13a}

Metal	Highly Toxic		Moderately Toxic		Slightly Toxic	
	Oral	Intravenous	Oral	Intravenous	Oral	Intravenous
Arsenic (As^{+3})	x					
Boron					x	x
Cadmium		x	x			
Cobalt			x			
Chromium (Cr^{+6})	x					x(Cr^{+3})
Iron					x	
Fluorine				x		
Mercury	x		x			
Manganese				x		
Nickel				x		
Selenium (Se^{+4})	x					
Vanadium (V^{+5})	x		x			
Zinc				x		

The relative LD₅₀ values for nine of the above metals are given in Table 5.

TABLE 5

LETHAL DOSES OF NINE METALS ORALLY ADMINISTERED
TO RATTUS NORVEGICUS (0.3 kg)^{15,20,25,55,57,83,86}
(Weight of Dry Diet=10 g Metal per Day)

Element	Lethal Dose ($\mu\text{g/day}$)
Vanadium (V^{+5})	1,500
Selenium (Se^{+4})	1,000-2,000
Arsenic (As^{+3})	1,300-5,000
Mercury (Hg^{+2})	8,000
Cadmium (Cd^{+2})	16,000
Fluorine (F^-)	30,000
Iron (Fe^{+2} or Fe^{+3})	>60,000
Zinc (Zn^{+2})	150,000
Boron (Borate)	130,000-270,000

2.3 Effects on Plants

No information was found on adverse effects of vanadium on vegetation.

2.4 Effects on Materials

In boilers fired on residual oils, the accumulation of ash on the external surfaces of superheater tubes causes a loss of thermal efficiency and associated corrosion which at high metal temperatures may result in premature failure of the steam-raising equipment. Vanadium and sodium are considered the most harmful of the ash-forming elements, and their inorganic complexes (naphthanates) form a major part of the superheater deposits. Furthermore, the corrosive action of sodium-vanadium complexes at high temperatures is increased by the oxides of sulfur produced during the combustion process.⁹⁹

2.5 Environmental Air Standards

The 1967 American Conference of Governmental Industrial Hygienists adopted the following values for those occupationally exposed:

Vanadium pentoxide (V_2O_5), dust	500 $\mu\text{g}/\text{m}^3$
---------------------------------------	------------------------------

Vanadium pentoxide (V_2O_5), fume	100 $\mu\text{g}/\text{m}^3$
---------------------------------------	------------------------------

In the U.S.S.R., the following maximum allowable concentrations (MAC) have been adopted⁷³ for occupational exposure to industrial aerosols of vanadium compounds:

Vanadium pentoxide—condensation aerosol	100 $\mu\text{g}/\text{m}^3$
Vanadium pentoxide—comminution aerosol	500 $\mu\text{g}/\text{m}^3$
Vanadates and vanadium chlorides	500 $\mu\text{g}/\text{m}^3$ *
Ferrovanadium and vanadium-aluminum alloys	1,000 $\mu\text{g}/\text{m}^3$
Vanadium carbide	4,000 $\mu\text{g}/\text{m}^3$

*In terms of vanadium pentoxide.

3. SOURCES

3.1 Natural Occurrence

3.1.1 Mineral Ores

More than 65 vanadium-bearing minerals have been identified. The most important of these are (1) patronite ($V_2S_5^{+S}$), found only in Peru, and also containing iron, nickel, molybdenum, phosphorus, and carbon; (2) bravoite ($(FeNi)S_2$), also found in Peru; (3) sylvanite ($3Cu_2S \cdot V_2S_5$), found in Utah and Southern Australia; (4) davidite, a titanium-iron ore found in Southern Australia; and (5) roscoelite ($CaO \cdot 3V_2S_5 \cdot 9H_2O$), found in Colorado and Utah. The last is a vanadium-bearing mica existing as a mineral in a number of rich gold-bearing veins. It occurs in important quantities as a secondary mineral in the sandstones of Colorado and Utah. Vanadium is also found in these two States in such uranium-bearing sandstones as carnotite ($K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$), uravanite ($2UO_3 \cdot 3V_2O_5 \cdot 15H_2O$), tyuyamunite ($CaO \cdot 2UO_3 \cdot 2V_2O_5 \cdot 4H_2O$), and hewettite ($2K_2O \cdot 2Al_2O_3(Mg,Fe)O \cdot 3V_2$). Recent reduction in domestic uranium output and continuing increases in vanadium consumption have made it necessary to seek other sources of vanadium, such as ferrophosphorus, obtained from Idaho and Montana phosphate rock deposits and titaniferous magnetite ores bearing vanadium.

The concentration of vanadium in ores varies widely, from 5 to 25 percent. In roscoelite, V_2O_5 accounts for 20 percent of the total ore. In most of the vanadium-bearing titanium

ores, V_2O_5 accounts for less than 1 percent (0.1 to 0.3 percent) and is removed as an impurity. The phosphate rocks of Idaho and Montana contain from 0.11 to 0.45 percent V_2O_5 .

3.1.2 Coal

As early as 1892, V_2O_5 was found to constitute 0.24 percent of a lignite deposit in Argentina (38.22 percent of the ash obtained). Similar concentrations were also found in Peru and in certain Australian coals. The vanadium is usually bound to the organic matter in the coal.¹ Measurements of vanadium concentrations in domestic coals are shown in Table 6.

TABLE 6
CONCENTRATIONS OF VANADIUM IN DOMESTIC COALS¹

Coal Source	Vanadium in Ash (%)	Vanadium in Coal (ppm)
Northern Great Plains	0.001-0.058	16
Eastern Interior Region		35
Appalachian Region		21
Texas, Colorado, North Dakota, South Dakota	0.01-0.1	
West Virginia	0.018-0.039	
Pennsylvania (anthracite)	0.01-0.02	
Buck Mountain Bed	0.11	176
Diamond Bed	0.09	92

It has been also found that in West Virginia coals the concentration of vanadium is reasonably constant in the main body of the coal but frequently high in thin sections of the

coal between shale partings.¹

3.1.3 Oil

Vanadium compounds are major organometallic constituents of crude oils. Concentrations vary from 0.01 percent in mid-continental crude oil to 0.06 percent V_2O_5 in Venezuelan crude oil.^{16,73}

Ash from combustion of residual oil (grade 6) varies from 0.002 to 0.3 percent (by weight), and its V_2O_5 content varies from 2.7 percent in Texas crude to 63.2 percent (of total ash).¹⁶ Comparative analysis of three typical residual oils is shown in Table 7.

TABLE 7

COMPARATIVE CONCENTRATIONS OF VANADIUM PENTOXIDE AND SULFUR DIOXIDE IN THREE TYPICAL RESIDUAL OILS¹⁶

Content	Percent of Total Ash				
	California		Texas		Venezuela
	Low	High	Low	High	High
Vanadium Pentoxide	7.6	29.9	2.7	21.00	63.2
Sulfur Dioxide	35.6	20.9	45.5	33.00	13.9

Average concentrations of vanadium pentoxide and sulfur dioxide in petroleum from various areas—determined after laboratory combustion—are shown in Table 8.⁷³

TABLE 8

CONCENTRATIONS OF VANADIUM PENTOXIDE AND SULFUR DIOXIDE
IN PETROLEUM FROM VARIOUS REGIONS⁷³

Place of Origin	Percent of Total Ash	
	V ₂ O ₅	SO ₂
California	5.1	15.0
Texas	1.4	1.4
Kansas	0.4	36.4
Iran I	14.0	2.6
Iran II	38.5	7.0
Sahara I	—	0.04
Sahara II	—	0.30

3.1.4 Distribution of Deposits

The geographical distribution of ores and deposits by type and size is given in Figures 3 and 4 of the Appendix, respectively. During the second half of the past decade, practically all of the domestic vanadium output came from the deposits in southeastern Utah and northeastern Arizona.¹⁷ This area is shown in Figure 5 of the Appendix.

3.2 Production Sources

3.2.1 Recovery of Vanadium Oxide from Vanadium-Bearing Ores

Vanadium extraction methods include ion exchange and solvent extraction, which separate both uranium and vanadium from combined extraction circuits in domestic mills. During the 1950's several new methods developed for the recovery of uranium from carnotite and roscoelite were also used for separate recovery of vanadium. Recovery of vanadium by solvent

extraction was started in 1956 (by the Climax Uranium Co. in Colorado), resulting in a vanadium recovery rate of 30 percent.

At some plants making chromium compounds, vanadium has been recovered from chromite ore by an acid precipitation method.

Vanadium has also been recovered by the Anaconda Company from phosphate rock by a leach roasting process.

Experimental methods have been patented and developed for recovering vanadium from titaniferous magnetites, ferrophosphorus ores, and crude oils.

In addition, methods have been developed in other countries for recovering vanadium from (1) the complex ore wulfenite, which also contains molybdenum, gold, silver, and lead; (2) bauxites (Great Britain); (3) lead-zinc ores (Northern Rhodesia); and (4) steel plant slag (Germany).

Flow sheets showing the processes and materials involved in domestically used extraction methods are given in Figures 6 to 9 of the Appendix. No emission data could be found, but given the estimated recovery rates (30 to 75 percent of the vanadium) and the metal's low vaporization temperature, one may form an idea of the corresponding rates of losses in the air.

Slag from processing vanadium-bearing ores contains considerable amounts of vanadium oxides. Crushing of this slag produces aerosols containing lower oxides of vanadium as

well as silica, calcium, iron, chromium, manganese, etc. Furthermore, when calcines are produced from these slags, dust forms which contains soluble vanadates at concentrations as high as $5,000 \mu\text{g}/\text{m}^3$ in the working environment. Vanadium pentoxide, derived from calcium vanadate, is melted before it is used in alloying.⁷²

3.2.2 Production of Vanadium Metal

The output from processing vanadium-bearing ores is an oxide concentrate commercially known as vanadium pentoxide (V_2O_5), containing at least 80 percent V_2O_5 ; most of the remaining part is sodium monoxide and/or calcium oxide. Thus, commercial vanadium pentoxide is actually a sodium and/or calcium hexavanadate. From this compound, high purity V_2O_5 is obtained that is suitable for reduction to vanadium metal.

While recovery of vanadium from ferrophosphorus has been increasing during the 1960's, the greater part of domestic production continues to come from Western vanadium and uranium-vanadium ores. Production and consumption data are given in Tables 14 and 15 of the Appendix.

The long-term trend in vanadium consumption can be best seen in Figure 2 showing the domestic production of vanadium pentoxide. During the 20-year period from 1946 to 1966, production jumped from about 2 thousand to approximately 12 thousand short tons. Domestic mine production of vanadium during the last 35 years displays a continued growth.

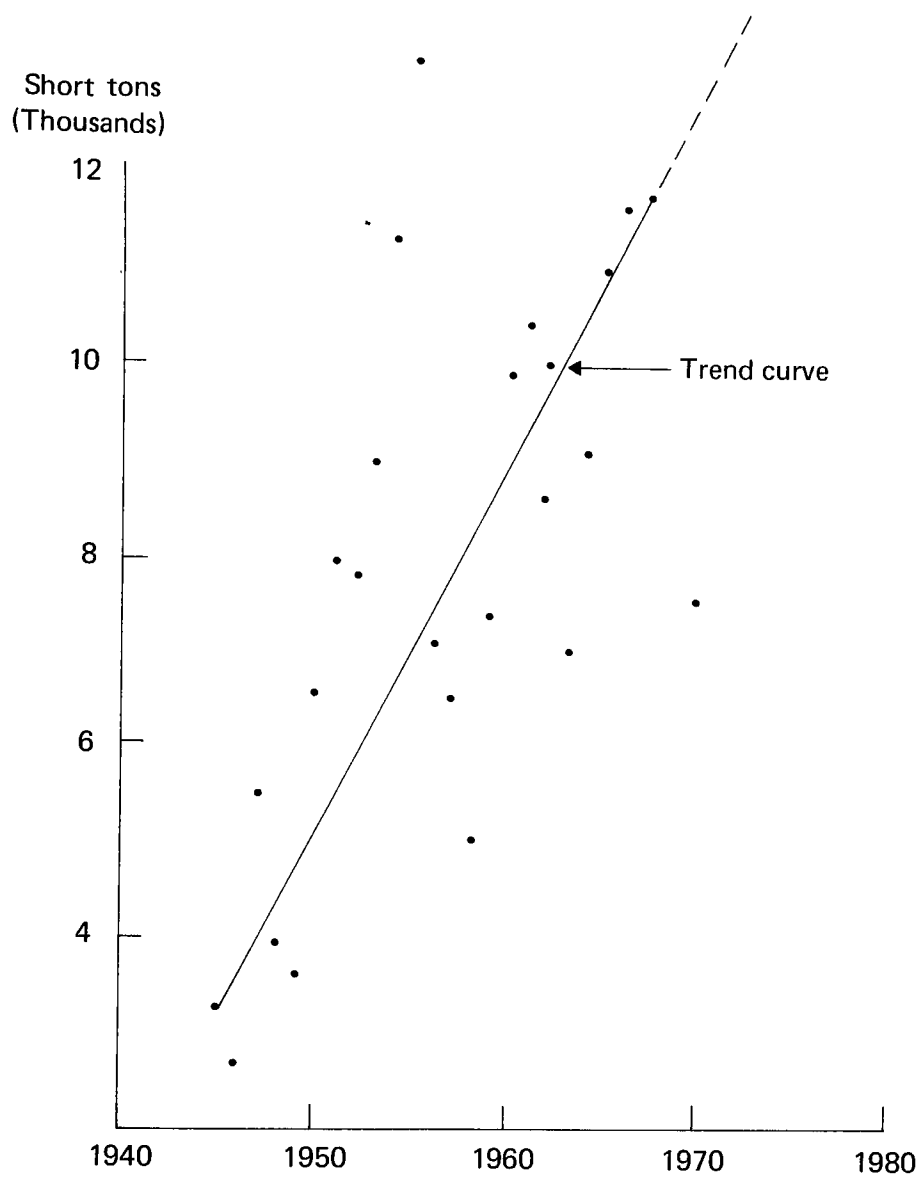


FIGURE 2

Production of Vanadium Pentoxide in the United States⁵⁴

As sources less rich in vanadium are increasingly used, the limitations imposed by the scarcity of the original sources are removed. This plus the fact that improved recovery methods are continuously being developed may maintain the upward trend in vanadium production.

As mentioned earlier, vanadium pentoxide is melted before its use in alloying. During the smelting process, vapor of the pentoxide is produced that condenses into a highly dispersed aerosol. Prior to alloying, the molten pentoxide is reduced in electric furnaces to vanadium metal. The reduction process is slow and proceeds from pentoxide to tetroxide, trioxide, oxide, and finally the metal itself. The volatility of the pentoxide is high, especially at temperatures above 3,000°F, as used in alloying processes. Melting of ferrovanadium has been shown to result in concentrations of the pentoxide in the air of the working environment as high as 68,000 $\mu\text{g}/\text{m}^3$, and concentrations of lower oxides up to 450 $\mu\text{g}/\text{m}^3$.⁷¹

3.2.3 Vanadium-Bearing Alloys

No information on vanadium emissions in the industries producing vanadium-bearing alloys has been found. Since the major alloys are ferrovanadium, vanadium-aluminum and vanadium-carbide, such a study should concentrate on the iron-, steel-, and aluminum-alloy industries.

3.2.4 Vanadium Chemicals

The chemical industry is producing a great number of

vanadium chemicals, the major ones of which are listed in Table 16 of the Appendix. The geographical distribution is given in Table 9 below and Table 20 in the Appendix.

TABLE 9
DISTRIBUTION BY STATE OF 119 INDUSTRIAL UNITS
PRODUCING MAJOR VANADIUM CHEMICALS²⁸

State	Number of units	% of total number
New Jersey	24	20
New York	21	18
Pennsylvania	10	8
California	10	8
Ohio	8	7
Illinois	7	6
Texas	7	6
Other (six states)	21	17
Total	119	100

No study has been made of the chemical industry as a source of vanadium emissions. Nevertheless, the fact that New York and New Jersey rank first and second (see Table 9) with respect to vanadium concentration in the environmental air may be partially explained by the high concentration of industrial units producing vanadium chemicals.

3.2.5 Other Sources

While steam and power plants using residual oil and oil refineries are not production sources of vanadium, they are nevertheless sources of vanadium emissions. Actually, most

of the emission data that has been found relate to these sources.

Vanadium emissions in the environmental air arise from the combustion of vanadium-bearing oils in plants refining crude oil and in plants using residual oils to generate heat and power. In such cases, vanadium is a major component of the particulate emissions, and its concentration in the air is often used as an evidence of the presence of fly ash from oil-fired units. Ranges reported for percentage of combustibles in the fly ash are 50 to 75 and 30 to 40, but in 31 tests in one plant, the observed range of values was 61.1 to 95.2 percent. In a plant using residual oil, vanadium (as V_2O_5) was found to constitute 2.5 percent of the total solids in particulate emissions—collected in an electrostatic precipitator—at 230°F from burning PS400 oil. When Grade 4 API oil was used and particulates were collected in a glass filter sock at 300°F, the concentration of vanadium was 4.7 percent.⁸¹

In a study of the economics of crude oil desulfurization, it was found that residual oil contained, in the usual process, 500 ppm of metals, the major ones being vanadium and nickel. How much vanadium is lost to the air during the refining and desulfurization processes is not known. Yet an idea can be formed by considering the amounts of crude oil refined per year and the fact that residual oil content varies from 23 to 500 ppm of vanadium, depending on the origin of the crude oil

used and the type of desulfurization process.

With respect to the total emission of vanadium from industrial and power plants, it must be noted that until World War II nearly all of these plants were using coal. Since World War II and especially during the last 15 years, coal has been replaced by residual oil, mainly for economy. Nevertheless, during the 1960's increasing recovery of gasoline and light fuel oils from the crude oil resulted in lower quality and higher cost of residual oils lower quality meaning higher concentration in the oil of organometallic compounds in general and of vanadium in particular.¹⁶ The Venezuelan crude, which amounts to a large portion of the oil consumed on the East Coast, is noted for its high vanadium content. In 1966, 33 percent of the total imported crude oil and 52 percent of the total imported residual oil, came from Venezuela; together they amounted to 342,000 barrels.

Stack emissions of particulates from fuel oil combustion (at 32°F, 1 atm) vary with the size of the combustion source. For large sources the extreme range is from 0.005 to 0.205 g/scf* of stack gas or 0.15 to 6.3 lb/1,000 lb oil. The usual range is 0.025 to 0.060 g/scf or 0.82 to 1.8 lb/1,000 lb oil, and the average value recommended in emission surveys is 0.033 g/scf of stack gas or 1 lb/1,000 lb oil. For small sources (less than 2,500 lb/hr of oil) the extreme range is from 0.000 to 0.330 g/scf or 0.00 to 10.0 lb/1,000 lb oil.

*scf: standard cubic feet.

The usual range is from 0.033 to 0.13 g/scf or 1.00 to 4.0 lb/1,000 lb oil, and the value recommended for emission surveys is 0.049 g/scf or 1.5 lb/1,000 lb oil.⁸¹

After calcining, the total mineral spinel of some Bessemer, Thomas, and open-hearth slags formed in pig iron processing was found to contain up to 67 percent vanadium (as V_2O_3). During sintering, the mineral spinel oxidizes to hematite and releases pentavalent vanadium.⁷¹

3.2.6 Distribution

The Rifle Mine of Union Carbide Corporation started production in February 1965 and is still the only mine producing vanadium as its principal product. The other major mills that recover vanadium from uranium-vanadium and vanadium-uranium ores were (1965) operated by the following companies:⁵⁴

- (1) American Metal Climax, Inc., Grand Junction, Colo.
- (2) Mines Development, Inc., Edgement, S. Dak.
- (3) Union Carbide Corp., Rifle, Colo.
- (4) Vanadium Corporation of America, Shiprock, N. Mex.

In 1965, the following companies recovered vanadium from ferrophosphorus, a by-product in the production of elemental phosphorus from Idaho phosphate rock:⁵⁴

- (1) Kerr-McGee Corp., Soda Springs, Idaho
- (2) Vitro Chemical Co., Salt Lake City, Utah

3.3 Product Sources

The major single use of vanadium is in alloying, particularly in the production of ferrovanadium, which consumes more

than two-thirds of the vanadium produced. The next major uses are in the production of chemicals and as a catalyst in industrial processes. The distribution among the various major uses of the total quantity consumed is shown in Table 10.

TABLE 10

VANADIUM CONSUMED IN THE UNITED STATES IN 1966, BY USES⁵⁴

Use	Vanadium Content (percent)	Short Tons	Percent of Total Consumption
Steel	0.1-4		
High-speed		501	9.1
Hot-work tool		99	1.8
Other tool		173	3.1
Stainless		38	0.7
Other alloy ^a		2,950	53.9
Carbon		818	14.9
Total steel		4,579	83.5
Gray and malleable castings	0.1-0.15	40	0.7
Nonferrous alloys ^b	2.5-85	594	10.9
Chemicals		183	3.3
Other ^c		85	1.6
Grand Total		5,481	100.0

^aIncludes some vanadium used in nonspecified high-speed tool steels.

^bPrincipally titanium-base alloys.

^cPrincipally high-temperature alloys, welding rods, and cutting and wear-resistant materials.

Various vanadium compounds have been used as driers in paints and varnishes and in making luster for pottery, porcelain, and glass.

Vanadium compounds are basically used as catalysts in many important industrial processes,¹⁷ as follows:

- Production of sulfuric acid
- Oxidation of benzene to maleic acid
- Oxidation of naphthalene to phthalic anhydride
- Oxidation of anthracene to anthraquinone
- Oxidation of chlorinated hydrocarbons to maleic and fumaric acid
- Oxidation of acrolein to acrylic acid
- Oxidation of toluene or xylene
- Oxidation of alkenyl and alkyl derivatives of pyridine in presence of ammonia
- Oxidation of amino acids
- Oxidation of cyclohexanal to adipic acid
- Oxidation of naphthalene to 1,4-naphthoquinone
- Ammonia synthesis
- Hydrogenation of carbon monoxide
- Dehydration of organic acid to ketones
- Dehydrocyclization of paraffins to aromatics such as hexane to benzene
- Dehydrogenation of butanes to butenes
- Dehydrogenation of butenes to butadiene
- Oxidizing agent in the formation of aniline dyes
- Catalyst in petroleum cracking

The amount of vanadium used as a catalyst is still minor compared with that presently consumed in metallurgy. However, the number of metallurgical processes using vanadium is increasing rapidly. For example, in 1956 the new plant of the Vanadium Corporation of America at Cambridge, Ohio, began to produce vanadium oxytrichloride for use as a catalyst in producing ethylene-propylene synthetic rubbers.

Vanadium is also used for photography and ceramics, and in atomic reactors.

An important development is the use of vanadium pentoxide, V_2O_5 , as a substitute for platinum (which is much more expensive) in the manufacture of sulfuric acid by the contact process. Probably half the world production of sulfuric acid by this process is now made with vanadium pentoxide as the catalyst, and it appears probably that it will eventually replace platinum for this purpose.

No data have been found on vanadium emissions from industrial units consuming vanadium or vanadium products.

3.4 Environmental Air Concentrations

Measurements of vanadium concentration in the environmental air from 99 sampling stations in the United States for the period 1954 to 1964 are given in Table 17 of the Appendix.²⁻⁴ In 1964, the average ambient air concentrations ranged from below detection ($<0.003 \mu\text{g}/\text{m}^3$) to $0.30 \mu\text{g}/\text{m}^3$, and the maximum value recorded was $0.88 \mu\text{g}/\text{m}^3$.

In 1967, the average vanadium concentrations (quarterly composites) in ambient air ranged from below detection ($<0.003 \mu\text{g}/\text{m}^3$) to $0.90 \mu\text{g}/\text{m}^3$ in 149 communities (Table 18).⁶⁸ Thirty-one of these communities showed concentrations below the detection concentration. The maximum value recorded in 1967 was $1.4 \mu\text{g}/\text{m}^3$. In 1966, the average concentration in 129 communities ranged from below detection to $0.39 \mu\text{g}/\text{m}^3$ (Table 19).⁶⁸ The maximum concentration in 1966 was $0.61 \mu\text{g}/\text{m}^3$. The percent distribution of observed concentration

values is shown for 1966 and 1967 in Table 11. Ranking of the 15 communities with the highest concentration values is shown in Table 12.

TABLE 11

DISTRIBUTION OF MINIMUM, MAXIMUM, AND AVERAGE VALUES OF
VANADIUM CONCENTRATION IN THE ENVIRONMENTAL AIR OF
SOME COMMUNITIES IN THE UNITED STATES
(Quarterly Composite Values)⁶⁸

Concentration Interval (μg)	Percent of Concentration Values in Each Interval ^a					
	1966 ^b			1967 ^c		
	Min	Max	Avg	Min	Max	Avg
$X > 1.0000$	—	—	—	—	2.0	—
$1.0000 \geq X > 0.1000$	4.7	15.5	10.9	6.0	15.4	12.8
$0.1000 \geq X > 0.0100$	24.8	30.2	32.5	26.2	36.9	31.5
$0.0100 \geq X > 0.0010$	31.7	15.5	17.8	45.7	24.9	34.9
$0.0010 \geq X > 0.0001$	—	—	—	1.3	—	—
$X < 0.0001$	38.8	38.8	38.8	20.8	20.8	20.8

^aNumber of concentration values in each interval as percent of the total for each category of values (Max, Min, Avg).

^bIn this year, 129 communities were sampled.

^cIn this year, 149 communities were sampled.

TABLE 12

RANK ORDERING OF THE 15 COMMUNITIES WITH HIGHEST VANADIUM CONCENTRATIONS BASED ON AVERAGE, MAXIMUM, AND MINIMUM VALUES, 1967 (Quarterly Composite Values)⁶⁸

Community	Concentrations ($\mu\text{g}/\text{m}^3$)			Rank		
	Avg	Max	Min	Avg	Max	Min
New York, N.Y.	.905	1.40	.34	1	1	1
Paterson, N.J.	.565	1.20	.14	2	2	2
New Haven, Conn.	.490	0.74	.10	2	6	10
Jersey City, N.J.	.487	1.10	.18	4	3	3
Bayonne, N.J.	.445	0.99	.22	5	4	2
Perth Amboy, N.J.	.390	0.86	.092	6	5	11
Newark, N.J.	.345	0.62	.16	7	7	4
Providence, R.I.	.271	0.35	.076	8	10	12
Philadelphia, Pa.	.264	0.43	.076	9	9	13
Concord, N.H.	.258	0.51	.072	10	8	14
Baltimore, Md.	.200	0.35	.13	11	11	6
Wilmington, Del.	.190	0.24	.13	12	14	7
Washington, D.C.	.165	0.23	.10	13		9
Hartford, Conn.	.160	0.21	.11	14		8
Bayamon, P.R.	.132	0.31		15	13	
Scranton, Pa.		0.32			12	
Marlton, N.J.		0.24			14	
Warminster, Pa.		0.24			15	
East Providence, R.I.			.062			15

4. ABATEMENT

No information has been found on abatement of air pollution by vanadium emitted from its production or product sources.

When additives such as magnesium oxide are used in oil-fired burners, a chain of reactions occurs resulting in the reduction in the amount of fine particulates and amounts of vanadium escaping to the atmosphere. The portion of total particulates in the less than 10 μ range may be reduced from 60 to 40 percent in the case of high-vanadium content oils. This is significant, since particulate-size distribution is an important parameter of abatement efficiency. Centrifugal collectors are preferred over electrostatic precipitators because they reduce the difficulties associated with the acid character of the ash, especially where bag filters and scrubbers are used. However, for any given particle-size distribution, the efficiency of various centrifuges may vary as much as from 50 to 65 percent and from 70 to 85 percent, around the particle size range of 5 μ , and 10 μ , respectively.¹⁶

The use of efficient fly-ash control equipment in modern coal-fired power plants may considerably reduce the emission of particulates containing vanadium. The control equipment most used are cyclones and electrostatic precipitators. When additives are used, which result in the formation of larger ash particles, cyclones are more efficient and economical to use than electrostatic precipitators. The collection efficiency

achieved in two coal-fired power plants using such equipment is shown in Table 13.

TABLE 13

CONCENTRATIONS OF FLY-ASH AND VANADIUM AT INLETS AND OUTLETS OF FLY-ASH COLLECTORS USED IN TWO COAL-FIRED POWER PLANTS³²

Test No.	Load %	Efficiency %	Ash %	Fly-Ash ($\mu\text{g}/\text{m}^3$)		Vanadium in the fly-ash ($\mu\text{g}/\text{m}^3$)	
				Inlet	Outlet	Inlet	Outlet
UNIT A ^a							
1	100	94.0	15.1	8,500,000	460,000	6,180	230
2	75	92.3	15.8	8,000,000	180,000	5,150	390
UNIT B ^b							
1 ^c	100	82.6	8.8	16,900,000	1,810,000	11,910	1,580
2	100	45.4	8.1	4,600,000	1,150,000	2,290	1,350
3 ^c	100	81.3	8.1	14,000,000	1,760,000	7,100	1,420

^aCorner-fired dry bottom unit rated at 940,000 lb of steam per hour at 1,050°F and using a cyclone-type separator followed by an electrostatic precipitator (in Ohio).

^bHorizontally opposed fired, wet bottom unit rated at 150,000 lb per hour at 835°F and using a cyclone-type separator only (in Illinois).

^cWith fly-ash reinjection.

In this study,³² vanadium and 16 other trace metals were analyzed semiquantitatively by emission spectroscopy, and the achieved accuracy was estimated as ± 50 percent of the measured concentration values.

5. ECONOMICS

Little information has been found on the economic costs of vanadium air pollution or on the costs of its abatement.

One report⁷⁷ discussed measures taken to reduce the stack emissions from an oil-fired steam generator. Finely-ground magnesium oxide is employed as an additive in the fuel oil. The use of this additive, together with operating the plant at low excess air, resulted in a significant reduction in stack emissions plus recovery of boiler pit ash rich in vanadium pentoxide. The residual oil used contained 250 to 1,000 ppm of vanadium pentoxide, and the boiler ash was found to contain 32 to 43 percent V_2O_5 . In 1965, the unit yielded 120 tons of ash at an average value of \$260 per ton. In a second boiler, an improved additive system yielded concentrations of vanadium pentoxide valued at \$450 per ton.

In addition to the recovered vanadium, this emission control system produced increased boiler efficiency and reliability, reduced maintenance costs, and improved community relations.

Data on the production and consumption of vanadium are presented in Section 3 and in the Appendix (Tables 14 and 15).

6. METHODS OF ANALYSIS

6.1 Sampling Methods

At low concentrations of vanadium in air, high volume samplers are used which operate during the 24-hour sampling period 50 cubic feet of air per minute, or 2,200 cubic meters of air. Preweighed glass-fiber filters (about 10 inches in diameter) are used. The filters should be equilibrated at a standard temperature (75° F), or less with relative humidity of 50 percent or less, and then weighed to determine the concentration of particulate matter. Afterwards, an aliquot of the sample is ashed (at 100° C) and then extracted with nitric and hydrochloric acids. For nonurban samples, extracts are made that are up to five times more concentrated than those for urban samples.⁸⁸

Kuz'micheva⁴¹ described the following sampling method for the colorimetric determination of aerosols of vanadium and its compounds in metallurgical plants. Air samples were passed through filters of polyvinyl chloride fabric and then placed in porcelain dishes, treated with 2 ml of a 50 percent HNO₃ solution, and evaporated to dryness. Ashing was done in a muffle furnace at 500° C, and the residue was treated with 2 ml of a 10 percent NaOH solution which dissolved the vanadium, leaving iron in the residue.

Membrane ultrafilters (having a pore width of 0.6 to 0.9 μ) were used in a study by Jerman,³⁷ who used a polarographic method to determine vanadium concentrations in the air of

alloy and chemical plants.

6.2 Quantitative Methods

6.2.1 Colorimetric Methods

A very simple, inexpensive, and specific method for the determination of vanadium in air is the ring oven technique. The relative error is said to be within the range from 5 to 10 percent, which at the microgram level compares well with other more sophisticated methods. The limit of identification is 0.01 μg , and its range 0.01 to 3.0 μg . The wavelength used is 3184⁰A, and the concentration giving 1 percent absorption is 1.5 μg of vanadium per ml.³⁷

Two other colorimetric techniques have been recently described. The first is based on the oxidation of vanadium and its compounds to vanadium pentoxide and its further reaction with hydrogen peroxide in acid medium. This method has a sensitivity of 17.8 μg of vanadium pentoxide or 10 μg of vanadium. The second method is based on the development of a greenish-yellow color when pentavalent vanadium reacts with sodium tungstate in neutral medium. The method is not specific and there is interference from alkalies and mineral acids. Kuz'micheva⁴¹ used a method based on the formation of yellow phosphotungstovanadic acid when vanadium or vanadium compounds react with phosphoric and sodium tungstate. The determination was made on a 5-ml aliquot placed in colorimetric test tubes. The sensitivity was 5 μg of vanadium pentoxide in 5 ml. No interference was observed by aluminum, calcium,

silicon dioxide, or iron. Colored chromium compounds were found to interfere when present in amounts greater than 40 μg .

In general, colorimetric methods are being replaced by more sophisticated and sensitive methods.

6.2.2 Atomic Absorption Spectroscopy

Vanadium in the range of 500 to 1,000 μg per liter can be determined by atomic absorption spectroscopy in an oxyacetylene or nitrous oxide-acetylene flame. For use with oxyacetylene flames, vanadium is extracted as vanadium cupferrate into a mixture of ketone and acid, and the resultant product is aspirated by the flame. For use with the nitrous oxide-acetylene flame, an aqueous solution of vanadium is aspirated directly.⁷⁴

6.2.3 Polarography

Only one paper described a polarographic method for the determination of vanadium in air. The method described was designed to be used for determining vanadium in the air of the working environment in the alloy industry, where vanadium is used as input, and in chemical manufacture, where vanadium is used as a catalyst. Dusts in such environments contain iron, aluminum, and magnesium, but these elements are not expected to interfere with the test. Following mineralization of the sample in 45 percent nitric acid, the polarographic levels of vanadium were recorded from a conductive solution of borax, ammonia, and chelaton III. The method is said to be sensitive to 1.5 $\mu\text{g}/\text{ml}$ of vanadium pentoxide.³⁷

6.2.4 Emission Spectrography

This method is used by the National Air Sampling Network⁵ for the determination of vanadium concentration in aliquots obtained from 24-hour samples after ashing and Extraction. In 1966, improvements in sensitivity made this method accurate enough for the determination of vanadium in many nonurban air samples. The minimum detectable concentration of vanadium by this method is $0.003 \mu\text{g}/\text{m}^3$ for urban samples and $0.0005 \mu\text{g}/\text{m}^3$ for nonurban samples.

6.2.5 Other Methods

Other analytical methods, used mostly for the determination of vanadium in biomaterial, are paper chromatography,^{53,102} neutron radioactivation,^{21,47} electrophoresis,³⁸ low-energy X-ray mass absorption,¹⁸ and autoradiography.⁸⁵

Determinations of vanadium content have been made in erythrocytes,⁹⁵ bones,⁸⁵ organ tissues,⁸⁷ urine,^{70,75} and biomaterial in general.^{18,21,42,47}

7. SUMMARY AND CONCLUSIONS

Vanadium is toxic to humans and animals—especially its pentavalent compounds. Exposure of humans through inhalation of relatively low concentrations (less than $1,000 \mu\text{g}/\text{m}^3$) has been found to result in inhibition of the synthesis of cholesterol and other lipids, cysteine, and other amino acids, and hemoglobin. Low concentrations also act as strong catalysts on serotonin and adrenaline.

Chronic exposure to environmental air concentrations of vanadium has been statistically associated with the incidence of cardiovascular diseases and certain cancers.

Human exposure to high concentrations of vanadium (greater than $1,000 \mu\text{g}/\text{m}^3$) results in a variety of clinically observable adverse effects whose severity increases with increasing concentrations. These effects include irritation of the gastrointestinal and respiratory tracts, anorexia, coughing (from slight to paroxysmal), hemoptysis, destruction of epithelium in the lungs and kidneys, pneumonia, bronchitis and bronchopneumonia, tuberculosis, and effects on the nervous system ranging from melancholia to hysteria.

No information has been found on adverse effects of atmospheric vanadium concentrations on vegetation or on commercial or domestic animals.

What is known about the effects of vanadium on materials related mostly to the corrosive action of vanadium, acting (together with sulfur dioxide) on oil- and coal-fired boilers,

especially those using vanadium-rich residual oils and coals.

The major sources of vanadium emissions are the metallurgical processes producing vanadium metal and concentrates; the alloy industry; the chemical industry; power plants and utilities using vanadium-rich residual oils and; to a lesser extent, the coal and oil refining industries. Vanadium production is concentrated in the states of Colorado, Utah, Idaho, and New Mexico, while the highest concentration of industries producing vanadium chemicals is found in New Jersey and New York. Domestic vanadium consumption has more than doubled since 1960, and the domestic mine production of ores and concentrates increased from 1,482 short tons of vanadium in 1945 to 5,226 short tons in 1965.

In communities in the United States in which vanadium concentrations were measured, the average values (quarterly composites) ranged from below detection ($0.003 \mu\text{g}/\text{m}^3$) to 0.30 (1964), 0.39 (1966), and 0.90 (1967) $\mu\text{g}/\text{m}^3$.

Little information is available on the economic losses due to vanadium air pollution or on the costs of abatement. One report indicated that measures taken to reduce the loss of vanadium to the atmosphere from an oil-fired steam generator resulted in recovery of commercially valuable vanadium pentoxide, thereby producing a profit from air pollution abatement. No other information was noted in the literature on control procedures specifically intended to reduce air

pollution by vanadium. However, customary methods used to control particulate emissions in general are considered suitable to the industrial processes using vanadium or vanadium-containing fuels.

Methods of quantitative analysis of vanadium in the environmental air include colorimetry, atomic absorption spectroscopy, emission spectrography, and recently polarography. The trend is toward more use of spectrographic and spectrophotometric methods, some of which are more sensitive than the other methods and easily automated. Sensitivities on the order of $0.001 \mu\text{g}/\text{m}^3$ are reported.

Based on the material presented in this report, further study is suggested in the following areas:

(1) Determination of the relationships of low concentrations of vanadium in various oxidation states with enzyme inhibition, cardiovascular disease, and cancer.

(2) Determination of the concentration and valence of vanadium near oil and coal burning industries (especially those burning vanadium-rich oil), and the vanadium metallurgical and chemical industries.

(3) Evaluation of the abatement and economics of vanadium air pollution control.

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.

APPENDIX

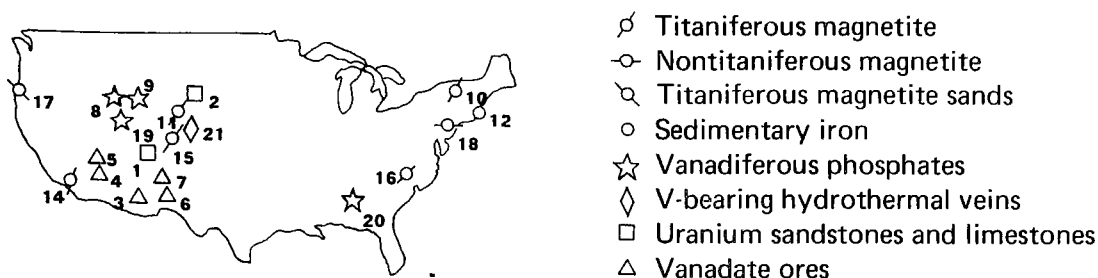
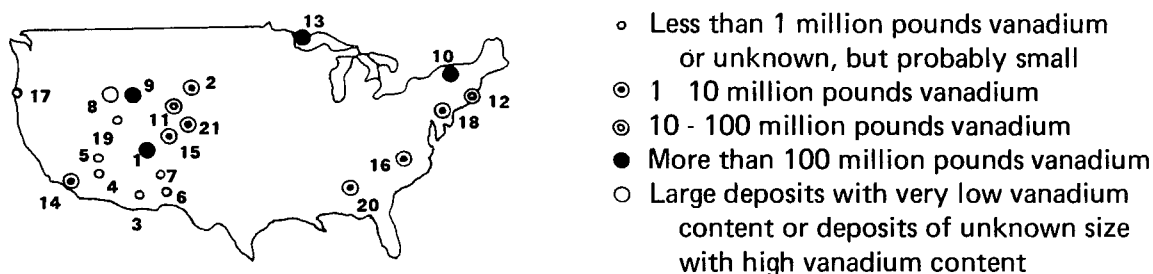


FIGURE 3

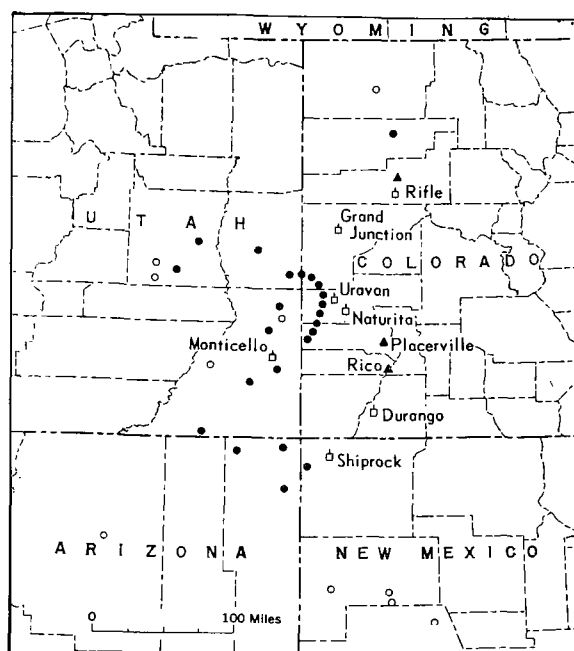
Productive and Potential Vanadium Sources by Type¹⁷



- | | |
|---------------------------------------|--|
| 1 Colorado Plateau | 12 Iron Mine Hill, R.I. |
| 2 Black Hills, S.Dak. and Wyo. | 13 Duluth gabbro deposits, Minn. |
| 3 Mammoth, Ariz. | 14 Los Angeles Co., Calif. |
| 4 San Bernardino Co., Calif. | 15 Colorado, Caribou and Iron Mountain |
| 5 Goodsprings, Nev. | 16 Western North Carolina |
| 6 Cutter, N.Mex. | 17 Curry County, Oreg. |
| 7 Magdalena, N.Mex. | 18 New Jersey deposits |
| 8 Phosphate deposits, Idaho | 19 Camp Floyd district, Utah |
| 9 Vanadiferous shales, Idaho and Wyo. | 20 Alabama flake graphite |
| 10 Lake Sanford, N.Y. | 21 Colorado Front Range |
| 11 Iron Mountain, Wyo. | |

FIGURE 4

Productive and Potential Vanadium Sources by Deposits and Districts¹⁷



- ▲ Vanadium deposits with a little uranium
- Uranium deposits yielding co-product vanadium
- Uranium deposits with little or no vanadium
- ▣ Production units of vanadium concentrates

FIGURE 5

Principal Areas of Vanadium and Uranium Mining and the Seven Major Production Units of Vanadium Concentrates¹⁷

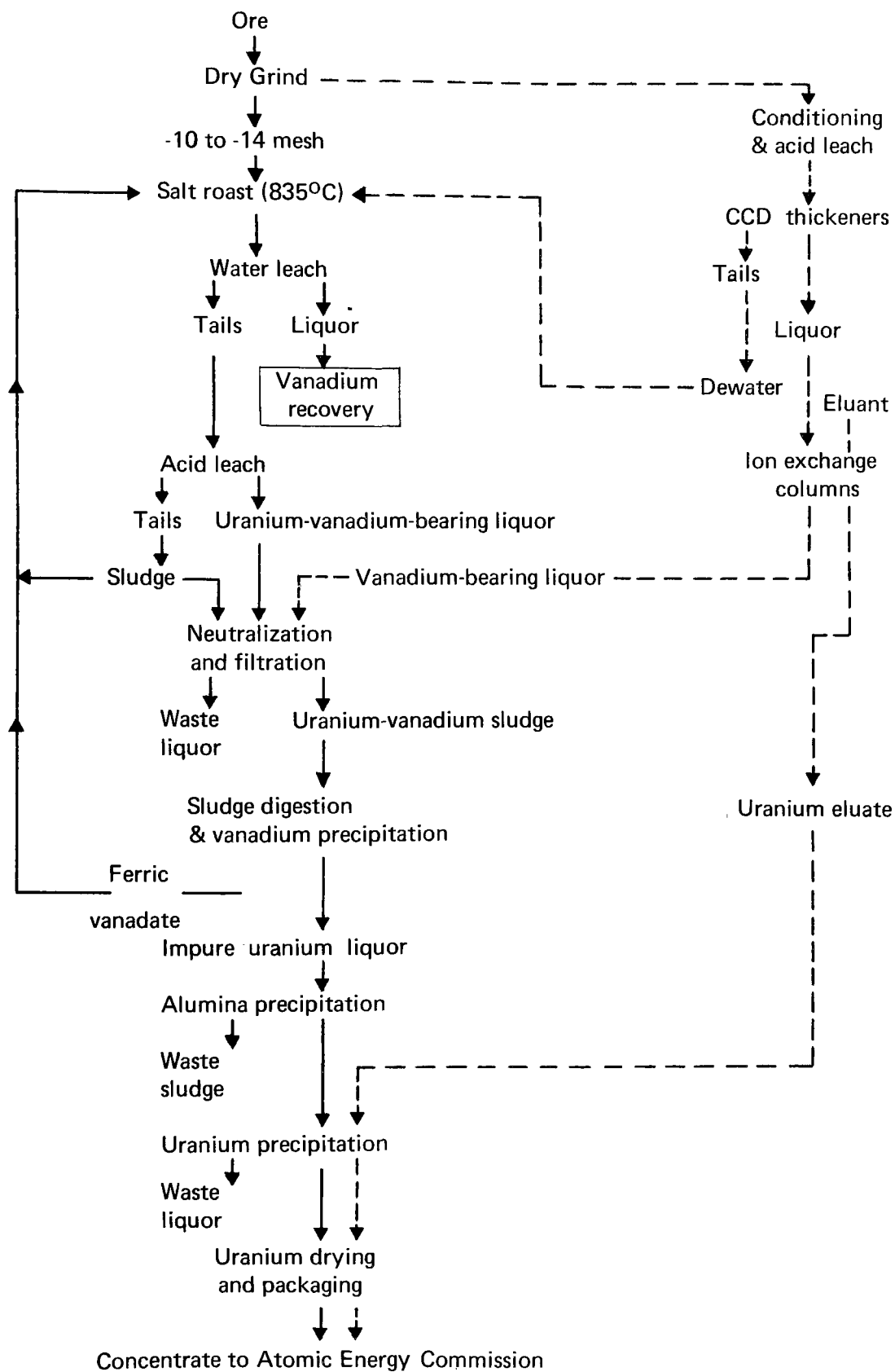


FIGURE 6

Uranium and Vanadium Processing and Ion Exchange Process¹⁷

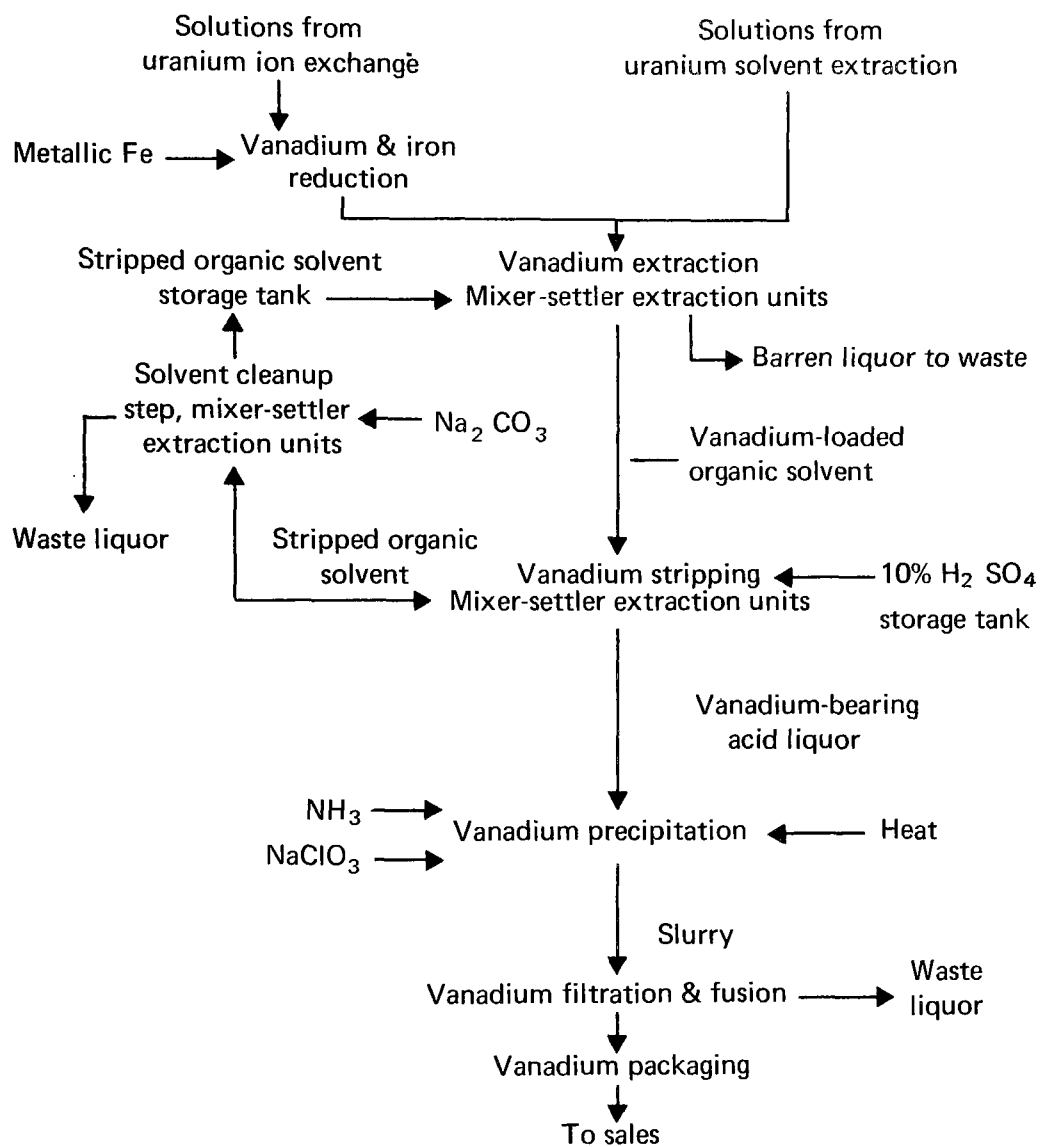


FIGURE 7

Vanadium-Uranium Recovery by Solvent Extraction¹⁷

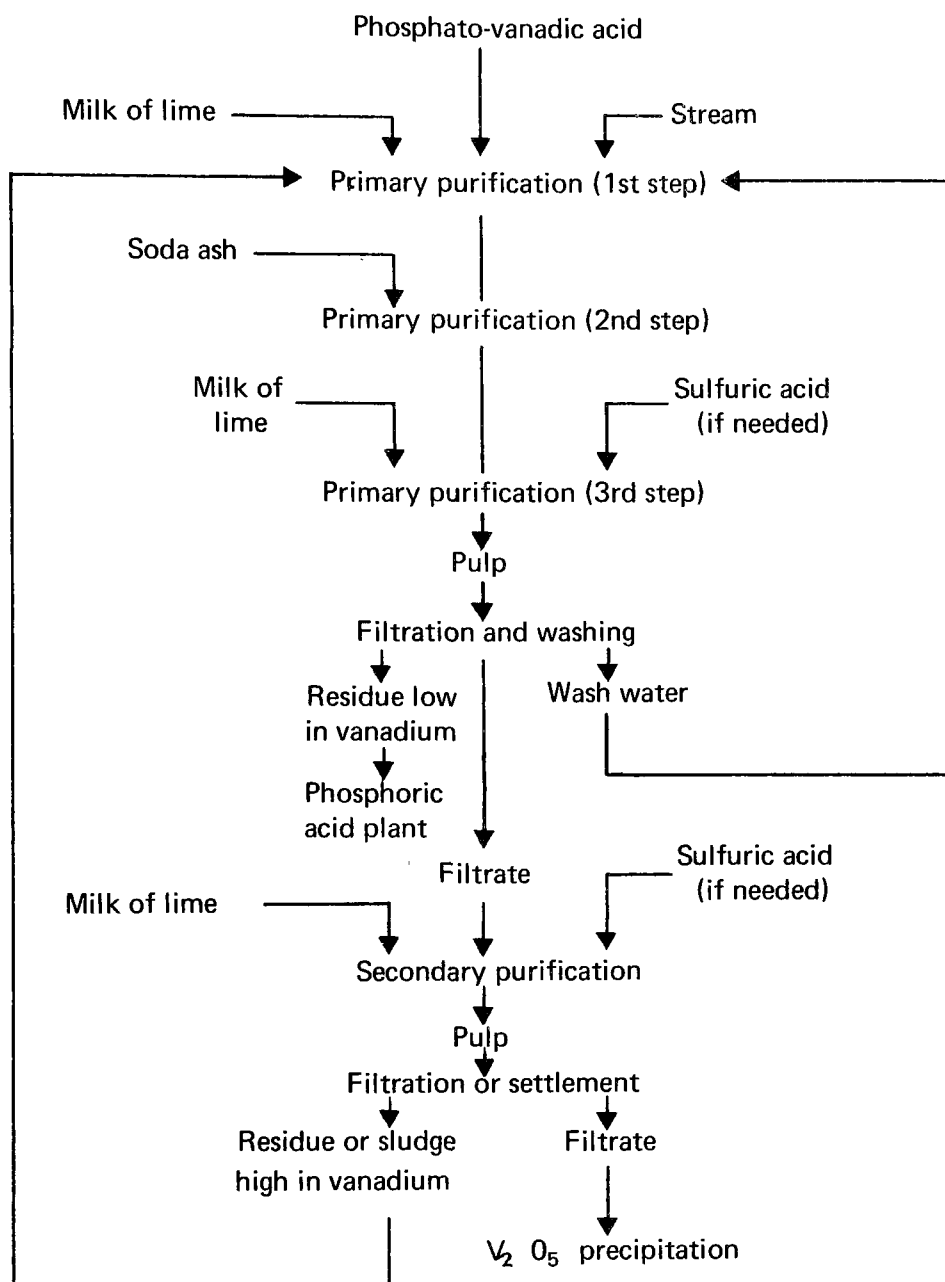


FIGURE 8

Recovery of Vanadium from Phosphate Rock¹⁷

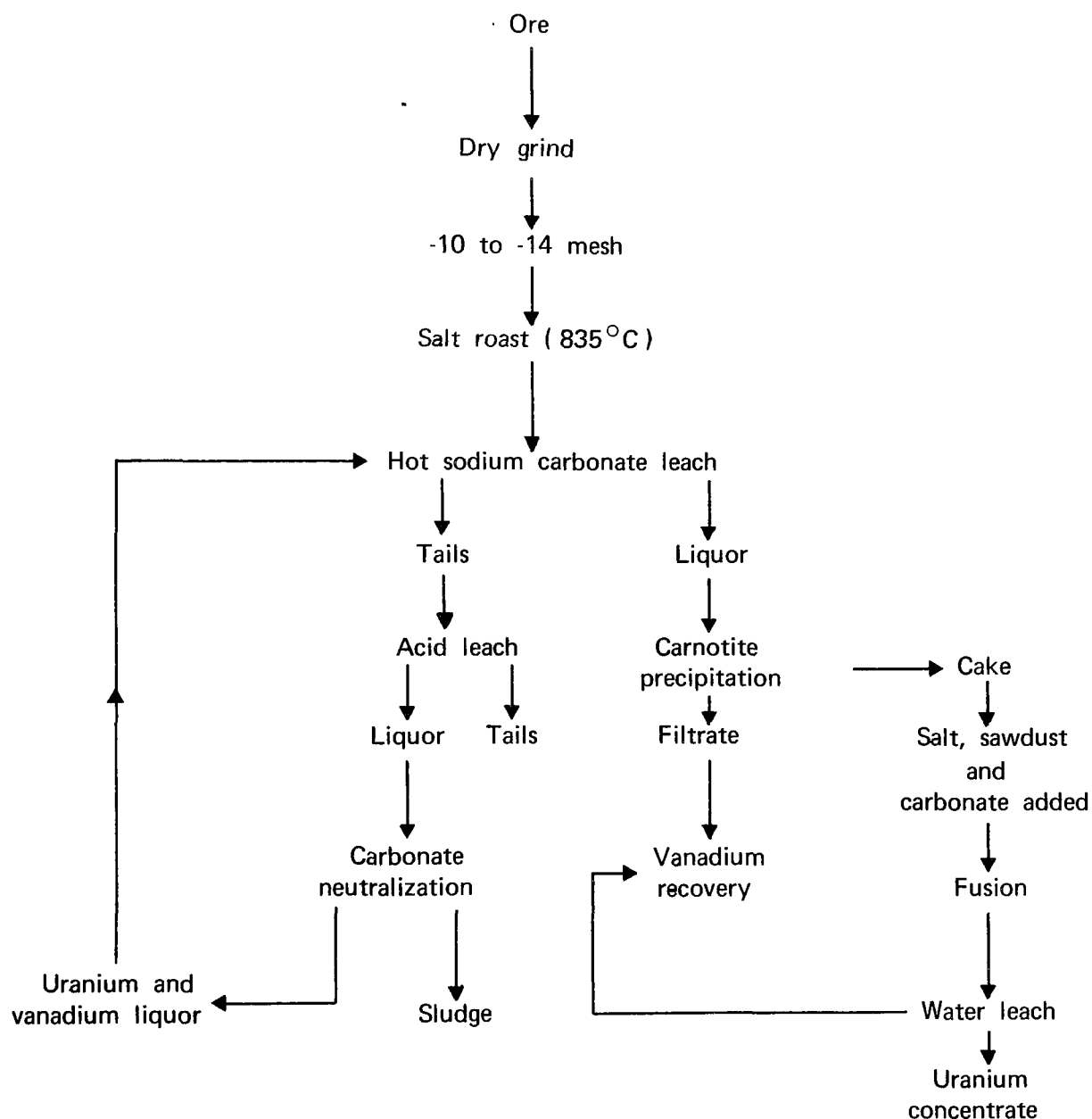


FIGURE 9

Sodium Carbonate and Acid Leach Method
of Vanadium-Uranium Recovery¹⁷

APPENDIX

TABLE 14

VANADIUM AND RECOVERABLE VANADIUM IN ORE AND CONCENTRATE
PRODUCED IN THE UNITED STATES, 1930-1965⁵⁴
(Short Tons of Contained Vanadium)

Year	Ore and Concentrate ^a	Recoverable Vanadium ^b
1930	c	c
1931	c	c
1932	270	c
1933	2	c
1934	6 ^d	c
1935	25 ^d	c
1936	70	c
1937	543	c
1938	807	c
1939	992	c
1940	1,081	c
1941	1,257	c
1942	2,220	c
1943	2,793	c
1944	1,764	c
1945	1,482	c
1946	636	510
1947	1,059	821
1948	894	670
1949	1,580	1,188
1950	2,298	1,598
1951	3,040	2,126
1952	3,588	2,571
1953	4,643	3,057
1954	4,930	3,026
1955	4,983	3,286
1956	5,635	3,868
1957	7,294	3,691
1958	7,266	3,030
1959	7,392	3,719
1960	8,800	4,971
1961	5,343	5,817
1962	5,221	4,750
1963	3,862	3,897
1964	4,362	5,049
1965	5,226	6,160

^aMeasured by receipts at mills.

^bRecoverable vanadium represents the vanadium that can be recovered from ores produced but not necessarily processed and is based upon the general recovery rate for mills producing vanadium pentoxide during a specific year.

^cData not available.

^dCarnotite ores only.

APPENDIX

TABLE 15

VANADIUM CONSUMED IN THE UNITED STATES⁵⁴

<u>Year</u>	<u>Short Tons</u>
1965	4,708
1964	3,550
1963	2,906
1962	2,314
1961	2,015
1960	2,016
1959	1,891
1958	1,259
1957	1,790
1956	1,938
1955 [*]	1,700

*First year data became
available.

APPENDIX

TABLE 16

PRODUCERS OF VANADIUM CHEMICALS¹⁹Vanadium Acetylacetonate

Aceto Chemical Co. Inc., Flushing, N.Y.
 Atomergic Chemetals Co. Div. Gallard-Schlesinger
 Chemical Mfg. Corp, Carle Place, Long Island, N.Y.
 Dynamit Nobel Sales Corp., Hackensack, N.J.
 MacKenzie Chemical Works, Inc., Central Islip, N.Y.
 Shepherd Chemical Co., Cincinnati, Ohio
 Stauffer Chemical Co., Speciality Chemical Div.,
 New York, N.Y.
 Akron, Ohio
 Chicago, Ill.
 Houston, Tex.
 Los Angeles, Calif.
 Wilmington, Del.
 Troy Chemical Corp., Newark, N.J.
 Var-Lac-Oid Chemical Co., Elizabeth, N.J.

Vanadium Carbide

Atlantic Equipment Engineers, Bergenfield, N.J.
 Atomergic Chemetals, Carle Place, Long Island, N.Y.
 Bram Metallurgical Chemical Co., Philadelphia, Pa.
 Cerac, Inc., Butler, Wis.
 Electronic Space Products, Inc., Los Angeles, Calif.
 Var-Lac-Oid Chemical Co., Elizabeth, N.J.

Vanadium Dichloride

Atlantic Equipment Engineers, Bergenfield, N.J.
 Atomergic Chemetals, Carle Place, Long Island, N.Y.
 Foote Mineral Co., Exton, Pa.
 Rocky Mountain Research, Inc., Denver, Colo.
 Var-Lac-Oid Chemical Co., Elizabeth, N.J.

Vanadium (Metal)

Atlantic Equipment Engineers, Bergenfield, N.J.
 Atomergic Chemetals, Carle Place, Long Island, N.Y.
 Belmont Smelting and Refining Works, Inc., Brooklyn, N.Y.
 Bram Metallurgical Chemical Co., Philadelphia, Pa.
 Cerac, Inc., Butler, Wis.
 Electronic Space Products, Inc., Los Angeles, Calif.
 Foote Mineral Co., Exton, Pa.
 Reading Alloys, Inc., Robesonia, Pa.
 Union Carbide, Mining & Metals, Div. Birmingham, Ala.
 Chicago, Ill.
 Cleveland, Ohio
 Detroit, Mich.
 Houston, Tex.
 Los Angeles, Calif.
 Phillipsburg, N.J.
 Pittsburgh, Pa.
 Portland, Oreg.

(continued)

TABLE 16 (Continued)

PRODUCERS OF VANADIUM CHEMICALS

Vanadium (Metal) (cont.)

United Mineral & Chemical Corp., New York, N.Y.

Var-Lac-Oid Chemical Co., Elizabeth, N.J.

Vanadium Oxytrichloride

Alfa Inorganics, Inc., Beverly, Mass.

Atomergic Chemetals, Carle Place, Long Island, N.Y.

Foot Mineral Co., Exton, Pa.

Stauffer Chemical Co.,

Specialty Chemical Div.,

Akron, Ohio

Chicago, Ill.

Houston, Tex.

Los Angeles, Calif.

Wilmington, Del.

Union Carbide, Mining & Metals Div., Birmingham, Ala.

Chicago, Ill.

Cleveland, Ohio

Detroit, Mich.

Houston, Tex.

Los Angeles, Calif.

Phillipsburg, N.J.

Pittsburgh, Pa.

Portland, Oreg.

Var-Lac-Oid Chemical Co., Elizabeth, N.J.

Vanadium Pentoxide (Vanadic Acid Anhydride)

Atlantic Equipment Engineers, Bergenfield, N.J.

Cerac, Inc., Butler, Wis.

Electronic Space Products, Inc., Los Angeles, Calif.

Foot Mineral Co., Exton, Pa.

Union Carbide, Mining & Metals Div., Birmingham, Ala.

Chicago, Ill.

Cleveland, Ohio

Detroit, Mich.

Houston, Tex.

Los Angeles, Calif.

Phillipsburg, N.J.

Pittsburgh, Pa.

Portland, Oreg.

United Mineral & Chemical Corp., New York, N.Y.

Var-Lac-Oil Chemical Co., Elizabeth, N.J.

Vanadium Sulfate (Vanadyl Sulfate)

Atlantic Equipment Engineers, Bergenfield, N.J.

Atomergic Chemetals, Carle Place, Long Island, N.Y.

City Chemical Corp., New York, N.Y.

(continued)

APPENDIX

TABLE 16 (Continued)

PRODUCERS OF VANADIUM CHEMICALS

Vanadium Sulfate (Vanadyl Sulfate) (Cont.)

Stauffer Chemical Co.,
Specialty Chemical Div., Akron, Ohio
Chicago, Ill.
Houston, Tex.
Los Angeles, Calif.
Wilmington, Del.
Var-Lac-Oid Chemical Co., Elizabeth, N.J.

Vanadium Tetrachloride

Atomergic Chemetals, Carle Place, Long Island, N.Y.
Dynamit Nobel Sales Corp., Hackensack, N.J.
Foote Mineral Co., Exton, Pa.
D.F. Goldsmith Chemical & Metal Corp., Evanston, Ill.
Stauffer Chemical Co.,
 Specialty Chemical Div., Akron, Ohio
 Chicago, Ill.
 Houston, Tex.
 Los Angeles, Calif.
 Wilmington, Del.
Union Carbide, Mining & Metals Div.,
 Birmingham, Ala.
 Chicago, Ill.
 Cleveland, Ohio
 Detroit, Mich.
 Houston, Tex.
 Los Angeles, Calif.
 Phillipsburg, N.J.
 Pittsburgh, Pa.
 Portland, Oreg.
Var-Lac-Oid-Chemical Co., Elizabeth, N.J.

Vanadium Tetroxide

Atomergic Chemetals, Carle Place, Long Island, N.Y.
City Chemical Corp., New York, N.Y.
Rocky Mountain Research, Inc., Denver, Colo.
Var-Lac-Oid Chemical Co., Elizabeth, N.J.

Vanadyl Acetate

Atomergic Chemetals, Carle Place, Long Island, N.Y.
City Chemical Corp., New York, N.Y.
Var-Lac-Oid Chemical Co., Elizabeth, N.J.

Vanadyl Acetate

Troy Chemical Corp., Newark, N.J.

Vanadyl Oxalate

Atomergic Chemetals, Carle Place, Long Island, N.Y.
City Chemical Corp., New York, N.Y.
Rocky Mountain Research, Inc., Denver, Colo.
Var-Lac-Oid Chemical Co., Elizabeth, N.J.

(continued)

TABLE 16 (Continued)

PRODUCERS OF VANADIUM CHEMICALS

Vanadyl Sulfate

Atomergic Chemetals, Carle Place, Long Island, N.Y.

Chemical Commerce, Newark, N.J.

Var-Lac-Oid Chemical Co., Elizabeth, N.J.

APPENDIX

TABLE 17

CONCENTRATION OF VANADIUM IN THE AIR²⁻⁴
 (Values of Individual Samples in $\mu\text{g}/\text{m}^3$)

Location	1954-59 ^a		1960		1961		1962		1963		1964	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Alabama												
Birmingham											.01	.00
Alaska												
Anchorage	.63	.06										
Arizona												
Phoenix			.03	.01			.01	.00			.01	.00
Tucson			.01	.00								
California												
Los Angeles	1.1	.10	.13	.02	.10	.02	.13	.03	.05	.01		
Berkeley	.30	.04										
Pasadena	.70	.07										
San Bernadiono									.03	.01		
San Francisco	.20	.03					.08	.01	.08	.01		
San Jose	.14	.03										
San Leandro	.30	.05										
Colorado												
Denver	.07	.03					.02	.00	.04	.00	.00	.00
Connecticut												
Waterbury	3.0	.88										
District of Columbia												
Washington	2.0	.33					.35	.12	.28	.10	.26	.09
Deleware												
Wilmington			2.5	.56								
Florida												
Tampa	.94	.06							.08	.03		
Georgia												
Atlanta	3.8	.22							.04	.00		

(continued)

APPENDIX

TABLE 17 (Continued)

CONCENTRATION OF VANADIUM IN THE AIR
(Values of Individual Samples in $\mu\text{g}/\text{m}^3$)

Location	1954-59 ^a		1960		1961		1962		1963		1964	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Illinois												
Chicago	.90	.09			.54 ^b	.14 ^b			.17	.05	.08	.03
Cicero							.06	.02				
East St. Louis	.07	.02							.02	.01		
Indiana												
East Chicago	1.4	.18			.05 ^b	.02 ^b					.21	.04
Indianapolis							.01				.01	.00
Gary			.21	.07								
Hammond									.08	.02		
Iowa												
Des Moines			.01	.00			.04	.00			.01	.00
Kentucky												
Louisville	.25	.04										
Louisiana												
New Orleans	.08	.01					.05	.02	.04	.01		
Maryland												
Baltimore	4.3	1.3					1.0	.13			.66	.16
Massachusetts												
Boston	3.0	.96									.45	.21
Everett	3.0	.86										
Michigan												
Detroit	2.10	.28					.02	.01	.03	.01	.02	.01
Minnesota												
Minneapolis	.30	.05									.03	.01
Missouri												
St. Louis	.20	.04					.04	.01	.04	.01	.02	.00
Kansas City	.40	.06										
Nebraska												
Omaha					.01	.00						

(continued)

APPENDIX

TABLE 17 (Continued)

CONCENTRATION OF VANADIUM IN THE AIR
(Values of Individual Samples in $\mu\text{g}/\text{m}^3$)

Location	1954-59 ^a		1960		1961		1962		1963		1964	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Nevada												
Las Vegas					.01							
New Jersey												
Camden	1.20	.30										
Elizabeth	1.80	.57										
Jersey City	6.00	.30										
Newark					.98 ^b	.50 ^b	.60	.19			.72	.19
Paulsboro	2.34	.42										
Perth Amboy	1.20	.29										
Trenton	1.20	.33										
New Mexico												
Albuquerque			.03	.01								
New York												
Buffalo							.04	.01				
New York	9.98	2.57			3.60	.67	2.20	.62	1.00	.41	.88	.30
Rochester			.04	.01								
North Carolina												
Charlotte											.03	.01
Winston-Salem							.03	.01				
Ohio												
Akron			.01	.00								
Canton					.02	.01						
Cincinnati	1.54	.02	.03	.01	.01	.00	.02	.00	.01	.00	.01	.00
Cleveland							.01	.01	.01	.00	.01	.00
Columbus					.02	.01	.05	.00				
Youngstown	.16	.07	.02	.00			.01	.00	.01	.00		
Oklahoma												
Oklahoma City					.01	.00						

(continued)

APPENDIX

TABLE 17 (Continued)

CONCENTRATIONS OF VANADIUM IN THE AIR
(Values of Individual Samples in $\mu\text{g}/\text{m}^3$)

Location	1954-59 ^a		1960		1961		1962		1963		1964	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
Oregon												
Eugene					.06	.01						
Medford					.10	.02						
Portland	.80	.16							.04	.01	.06	.02
Pennsylvania												
Allentown					.32 ^b	.10 ^b						
Altoona	.03	.01										
Bristol	.55	.17										
Chester	1.6	.25										
Johnstown									.01	.00		
Philadelphia	4.65	.61	.99	.44	.73	.21	.61	.21	.45	.17	.41	.16
Pittsburgh	.07	.02					.05	.01	.01	.00	.01	.00
Scranton					.75 ^b	.12 ^b						
Williamsport	.10	.04										
Tennessee												
Memphis											.01	.00
Chattanooga	.40	.02			.01	.00					.01	.00
Texas												
Bellaire	.10	.04										
El Paso							.00	.00			.01	.00
Houston	.07	.01										
Lakeworth	.39	.12										
Utah												
Salt Lake City	.40	.06										
Washington												
Seattle	1.30	.47					.08	.03	.05	.02		
Tacoma							.09	.02			.08	.02

(continued)

APPENDIX

TABLE 17 (Continued)

CONCENTRATIONS OF VANADIUM IN AIR
(Values of Individual Samples in $\mu\text{g}/\text{m}^3$)

Location	1954-59 ^a		1960		1961		1962		1963		1964	
	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg
West Virginia Charleston	.60	.08			.09	.03					.05	.01
Wisconsin Milwaukee Racine	.48	.20	.03	.02							.01	.00
Wyoming Cheyenne											.02	.00

^aThe data in this column may include only one year or the average of all measurements made during these years.

^bValues shown in Reference 3. Different values for same city and year, as stated in Reference 4 are shown below.

	<u>Max</u>	<u>Avg</u>
Chicago	.35	.10
Indianapolis	.03	.01
Allentown	.21	.06
Scranton	.22	.07
Newark	.62	.30

APPENDIX

TABLE 18

CONCENTRATIONS OF VANADIUM IN THE AIR
OF 118 COMMUNITIES^a OF THE UNITED STATES, 1967⁶⁸
(Quarterly Composite Values)

Location	Concentration ($\mu\text{g}/\text{m}^3$)			Number of Samples ^b
	Min	Max	Avg	
Alabama				
Montgomery	.0033	.0033	.0033	1
Alaska				
Anchorage	.0027	.011	.0058	4
Fairbanks	.0032	.0071	.0052	3
Arizona				
Phoenix	.0031	.0042	.0037	2
California				
Glendale	.0036	.022	.0095	4
Humboldt County	.0009	.0012	.0010	2
Long Beach	.014	.057	.026	4
Los Angeles	.0077	.034	.0189	4
Oakland	.018	.041	.030	4
San Diego	.013	.034	.021	4
San Francisco	.023	.039	.031	2
Colorado				
Denver	.0034	.0034	.0034	1
Connecticut				
Hartford	.11	.21	.16	2
New Haven	.74	.10	.49	4
Delaware				
Kent County	.014	.035	.029	4
Newark	.027	.070	.046	4
Wilmington	.13	.24	.19	4
District of Columbia				
Washington	.10	.23	.165	4
Georgia				
Atlanta	.0037	.0092	.0056	3
Hawaii				
Honolulu	.018	.026	.021	3
Illinois				
Chicago	.0077	.10	.0589	4
East St. Louis	.0034	.007	.0058	3
Rockford	.0038	.016	.0084	3
Springfield	.0028	.0039	.0033	4

(continued)

APPENDIX

TABLE 18 (Continued)

CONCENTRATIONS OF VANADIUM IN THE AIR
OF 118 COMMUNITIES^a OF THE UNITED STATES, 1967
(Quarterly Composite Values)

Location	Concentration ($\mu\text{g}/\text{m}^3$)			Number of Samples ^b
	Min	Max	Avg	
Indiana				
East Chicago	.026	.10	.0497	4
Hammond	.017	.054	.0345	4
Indianapolis	.0097	.020	.0157	4
Monroe State Forest	.001	.0017	.0013	3
Parke County	.0012	.0012	.0012	2
South Bend	.0031	.11	.0305	4
Terre Haute	.003	.0042	.0036	2
Iowa				
Cedar Rapids	.0042	.011	.0076	2
Des Moines	.0035	.0035	.0035	1
Dubuque	.0062	.0062	.0062	1
Kentucky				
Covington	.0025	.0031	.0028	2
Lexington	.0029	.0033	.0031	2
Louisville	.0025	.032	.0126	3
Louisiana				
New Orleans	.017	.056	.034	4
Maine				
Acadia National Park	.0090	.040	.0295	4
Maryland				
Baltimore	.13	.35	.20	4
Calvert County	.0033	.11	.0443	4
Michigan				
Detroit	.0068	.016	.0114	4
Flint	.0026	.0030	.0028	2
Grand Rapids	.0025	.0025	.0025	1
Minnesota				
Minneapolis	.0027	.018	.0080	3
St. Paul	.0036	.077	.0322	3
Mississippi				
Jackson County	.0031	.0044	.0037	4
Missouri				
Kansas City	.0027	.022	.0192	3
St. Louis	.0042	.025	.0116	3
Shannon County	.0026	.0026	.0026	1
Nebraska				
Omaha	.0041	.0041	.0041	1
Nevada				
Reno	.018	.069	.0365	4

(continued)

APPENDIX

TABLE 18 (Continued)

CONCENTRATIONS OF VANADIUM IN THE AIR
OF 118 COMMUNITIES^a OF THE UNITED STATES, 1967
(Quarterly Composite Values)

Location	Concentration ($\mu\text{g}/\text{m}^3$)			Number of Samples ^b
	Min	Max	Avg	
New Hampshire				
Concord	.072	.51	.2585	4
Coos County	.0045	.012	.0074	4
New Jersey				
Bayonne	.22	.99	.445	4
Marlton	.036	.24	.1125	4
Glassboro	.017	.070	.052	4
Jersey City	.18	1.1	.4875	4
Newark	.16	.62	.345	4
Paterson	.14	1.2	.565	4
Perth Amboy	.092	.86	.3905	4
New Mexico				
Rio Arriba County	.0014	.0014	.0014	1
New York				
Cape Vincent	.011	.014	.012	3
New York	.34	1.4	.905	4
North Carolina				
Charlotte	.0057	.034	.0182	4
Cape Hatteras	.0045	.0063	.0050	4
Ohio				
Akron	.0058	.013	.0063	3
Cincinnati	.0037	.021	.0101	3
Cleveland	.0070	.0074	.0072	2
Columbus	.0056	.0056	.0056	1
Dayton	.0037	.014	.0093	4
Toledo	.0051	.011	.055	3
Youngstown	.0041	.0079	.0061	3
Oregon				
Curry County	.0011	.0011	.0011	1
Eugene	.0043	.013	.0078	3
Medford	.0031	.0033	.0032	2
Portland	.023	.053	.0377	4
Pennsylvania				
Allentown	.027	.12	.0795	4
Altoona	.0039	.012	.0068	3
Bethlehem	.014	.13	.063	4
Clarion County	.0021	.0024	.0025	4
Erie	.0035	.0037	.0036	2
Lancaster	.017	.091	.0415	4
Philadelphia	.076	.43	.264	4

(continued)

APPENDIX

TABLE 18 (Continued)

CONCENTRATIONS OF VANADIUM IN THE AIR
OF 118 COMMUNITIES^a OF THE UNITED STATES, 1967
(Quarterly Composite Values)

Location	Concentration ($\mu\text{g}/\text{m}^3$)			Number of Samples ^b
	Min	Max	Avg	
Pennsylvania (cont.)				
Pittsburgh	.0078	.034	.0164	4
Reading	.019	.21	.0815	4
Scranton	.015	.32	.104	4
Warminster	.030	.24	.0985	4
West Chester	.015	.11	.0575	4
York	.041	.21	.1135	4
Puerto Rico				
Bayamon	.044	.31	.132	4
Guayamilla	.013	.10	.0382	4
Ponce	.0062	.021	.0127	4
San Juan	.020	.10	.056	4
Rhode Island				
East Providence	.062	.18	.1065	4
Providence	.076	.35	.2715	4
Washington County	.035	.064	.0485	4
South Carolina				
Columbia	.0034	.017	.0084	3
Richland County	.0046	.0061	.0052	3
South Dakota				
Black Hills Forest	.011	.011	.011	1
Tennessee				
Chattanooga	.0083	.010	.0091	2
Knoxville	.0078	.0078	.0078	1
Nashville	.0027	.0038	.0032	2
Texas				
Houston	.0043	.0043	.0043	1
Utah				
Salt Lake City	.0034	.010	.0059	3
Vermont				
Orange County	.0094	.10	.0646	4
Virginia				
Hampton	.011	.051	.0282	4
Lynchburg	.0037	.019	.0097	3
Norfolk	.034	.068	.051	4
Shenandoah National Park	.0013	.0052	.0025	4
Portsmouth	.012	.068	.034	4
Richmond	.022	.081	.047	4
Roanoke	.0056	.022	.0113	4

(continued)

APPENDIX

TABLE 18 (Continued)

CONCENTRATIONS OF VANADIUM IN THE AIR
OF 118 COMMUNITIES^a OF THE UNITED STATES, 1967
(Quarterly Composite Values)

Location	Concentration ($\mu\text{g}/\text{m}^3$)			Number of Samples ^b
	Min	Max	Avg	
Washington Seattle	.013	.030	.0225	4
West Virginia Charleston	.0056	.023	.0156	4
Wisconsin Door County	.0010	.0020	.0015	2
Kenosha	.0048	.0061	.0054	2
Milwaukee	.0027	.0075	.0048	4

^aIn 31 communities no value was observed above the detection limit.

^bNumber, out of four measurements, with observed values above the detection limit (four decimal places).

APPENDIX

TABLE 19

CONCENTRATIONS OF VANADIUM IN THE AIR
OF 79 COMMUNITIES^a OF THE UNITED STATES, 1966⁶⁸
(Quarterly Composite Values)

Location	Concentration ($\mu\text{g}/\text{m}^3$)			Number of Samples ^b
	Min	Max	Avg	
Alabama				
Mobile	.012	.017	.013	4
Alaska				
Anchorage	.011	.014	.0124	3
Arizona				
Phoenix	.007	.007	.007	1
California				
Burbank	.011	.039	.0206	3
Los Angeles	.007	.062	.022	4
Oakland	.007	.022	.0147	4
Pasadena	.010	.052	.031	2
San Diego	.007	.030	.0167	4
San Francisco	.029	.038	.0338	2
Connecticut				
Hartford	.034	.320	.1638	4
New Haven	.110	.440	.3275	4
Delaware				
Kent County	.012	.057	.0332	4
Newark	.034	.078	.0532	4
Wilmington	.032	.170	.1155	4
District of Columbia				
Washington	.048	.230	.1182	4
Georgia				
Atlanta	.017	.038	.0275	2
Hawaii				
Honolulu	.013	0.59	.0222	4
Illinois				
Chicago	.008	.091	.0475	4
Indiana				
East Chicago	.014	.092	.0425	4
Hammond	.006	.027	.0175	4
Indianapolis	.008	.016	.0123	3
Monroe State Forest	.002	.002	.002	1
New Albany	.006	.006	.006	1
Parke County	.003	.003	.003	1
South Bend	.008	.160	.0502	4
Kentucky				
Covington	.006	.006	.006	1
Louisville	.007	.007	.007	1
Louisiana				
New Orleans	.006	.016	.095	4

(continued)

APPENDIX

TABLE 19 (Continued)

CONCENTRATIONS OF VANADIUM IN THE AIR
OF 79 COMMUNITIES^a OF THE UNITED STATES, 1966
(Quarterly Composite Values)

Location	Concentration ($\mu\text{g}/\text{m}^3$)			Number of Samples ^b
	Min	Max	Avg	
Maine				
Acadia National Park	.010	.014	.042	4
Maryland				
Baltimore	.110	.350	.255	4
Calvert County	.004	.048	.025	4
Michigan				
Detroit	.006	.007	.066	3
Minnesota				
Minneapolis	.005	.015	.010	2
St. Paul	.006	.014	.010	2
Mississippi				
Jackson County	.003	.005	.0036	3
Missouri				
Kansas City	.013	.013	.013	1
St. Louis	.007	.019	.012	3
New Hampshire				
Concord	.029	.100	.093	4
Coos County	.006	.020	.010	4
New Jersey				
Marlton	.027	.110	.0525	4
Camden	.090	.280	.1675	4
Glassboro	.020	.052	.0377	4
Jersey City	.160	.330	.2625	4
Newark	.150	.340	.2575	4
Perth Amboy	.150	.260	.1525	4
Trenton	.074	.150	.110	4
New York				
Cape Vincent	.004	.011	.0067	4
New York	.250	.610	.3875	4
North Carolina				
Charlotte	.008	.037	.0195	4
Cape Hatteras	.004	.007	.0057	4
Ohio				
Cincinnati	.004	.004	.004	1
Dayton	.003	.004	.0033	3
Toledo	.003	.003	.003	1
Youngstown	.003	.008	.0023	3
Oregon				
Portland	.020	.042	.0305	4

(continued)

APPENDIX

TABLE 19 (Continued)

CONCENTRATIONS OF VANADIUM IN THE AIR
OF 79 COMMUNITIES^a OF THE UNITED STATES, 1966
(Quarterly Composite Values)

Location	Concentration		($\mu\text{g}/\text{m}^3$)	Number of Samples ^b
	Min	Max	Avg	
Pennsylvania				
Clarion County	.002	.002	.002	3
Lancaster	.023	.063	.0442	4
Philadelphia	.088	.200	.1332	4
Reading	.035	.160	.0925	4
Warminster	.024	.280	.0945	4
Puerto Rico				
Bayamon	.030	.094	.0625	4
Guayanilla	.011	.017	.013	3
Ponce	.014	.024	.018	4
San Juan	.032	.130	.0692	4
Rhode Island				
Providence	.055	.290	.3412	4
Washington County	.008	.061	.0317	4
South Carolina				
Columbia	.004	.006	.005	2
Greenville	.003	.036	.015	3
Richland County	.002	.005	.0033	3
Tennessee				
Chattanooga	.008	.008	.008	2
Utah				
Salt Lake City	.003	.005	.004	2
Vermont				
Burlington	.094	.120	.1022	4
Orange County	.005	.038	.024	4
Virginia				
Danville	.006	.015	.0116	3
Norfolk	.016	.050	.0325	4
Shenandoah National Park	.002	.004	.003	2
Washington				
Seattle	.011	.055	.0285	4
West Virginia				
Charleston	.013	.016	.0142	4
Wisconsin				
Milwaukee	.003	.004	.0035	3

^aIn 50 communities no value was observed above the detection limit.

^bNumber, out of four measurements, with observed values above the detection limit (four decimal places).

APPENDIX

TABLE 20

SOME PRODUCERS OF VANADIUM PRODUCTS²⁸

<u>Vanadium Oxides, Salts, Alloys, and Other Derivatives</u>	
Aceto Chemical Co., Inc.	Flushing, N.Y.
City Chemical Corp.	Jersey City, N.J.
Fairmount Chemical Co., Inc.	Newark, N.J.
Foote Mineral Co., Vancoram Operations	Cambridge, Ohio
Kerr-McGee Corp.	Shiprock, N. Mex.
MacKenzie Chemical Works, Inc.	Soda Springs, Idaho
Ozark-Mahoning Co.	Central Islip, N.Y.
Semi-Elements, Inc.	Tulsa, Okla.
The Shepherd Chemical Co.	Saxonbur, Pa.
Stauffer Chemical Co.	Cincinnati, Ohio
Industrial Chemical Div.	Houston, Tex.
Specialty Chemical Div.	Weston, Mich.
Susquehanna-Western, Inc.	Edgemont, S. Dak.
Union Carbide Corp.	
Mining and Metals Div.	Hot Springs, Ark
	Maybell, Colo.
	Niagara Falls, N.Y.
	Rifle, Colo.
	Riverton, Wyo.
	Uravan, Colo.
	Wilson Springs, Ark.
U. S. Borax Research Corp.	Anaheim, Calif.
Vitro Corp. of America	Salt Lake City, Utah

APPENDIX

TABLE 21

PROPERTIES, TOXICITY, AND USES OF VANADIUM AND SOME VANADIUM COMPOUNDS⁵²

Compound	Properties	Toxicity	Uses
Vanadium	Light gray or white lustrous powder or fused hard lumps mp 1,717°C bp 3,000°C Insoluble in water	The pentoxide dust has been reported to be a respiratory irritant and to cause skin pallor, greenish-black tongue, chest pain, cough, dyspnea, palpitation, lung changes. When ingested, causes gastrointestinal disturbances. May also cause a papular skin rash	In manufacture of rust resistant vanadium steel
Vanadium carbonyl $V(CO)_6$	Blue-green powder. Sensitive to air. Should be stored under nitrogen. Decomposes at 60-70°C	May liberate CO. See also Vanadium	
Vanadium pentafluoride VF_5	Liquid, turns yellow on exposure to moist air. mp 19.0°C bp 47.9°C		

(continued)

TABLE 21 (Continued)

PROPERTIES, TOXICITY, AND USES OF VANADIUM AND SOME VANADIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Vanadium pentoxide V_2O_5	Yellow to rust-brown orthorhombic crystals mp $690^{\circ}C$		As a catalyst in the oxidation of SO_2 to SO_3 , alcohol to acetaldehyde, etc.; for the manufacture of yellow glass; as a depolarizer; as developer in photography; in form of ammonium vanadate as mordant in dyeing and printing fabrics and in manufacture of aniline black
Vanadium tetrafluoride VF_4	Brownish powder. Very hygroscopic. Deliquesces. Decomposes above $325^{\circ}C$		
Vanadium trifluoride VF_3	Greenish-yellow powder mp above $800^{\circ}C$ Sublimes at bright red heat		
Vanadium trioxide V_2O_3	Black powder mp $1,940^{\circ}C$ Insoluble in water		As a catalyst, e.g., when making ethanol from ethylene

(continued)

APPENDIX

TABLE 21 (Continued)

PROPERTIES, TOXICITY, AND USES OF VANADIUM AND SOME VANADIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Vanadium trisulfate $V_2(SO_4)_3$	Lemon-yellow powder	See Vanadium	
Vanadium trisulfide V_2S_3	Greenish-black powder Decomposes when heated		
Vanadyl arsenate $VOAsO_4 \cdot 5H_2O$	Yellow, tabular crystals		
Vanadyl dichloride $VOCl_2$	Green, very deliquescent tabular crystals	No specific data. Probably an irritant. See Vanadium	As mordant in printing fabrics
Vanadyl sulfate $VOSO_4 \cdot 2H_2O$	Blue, crystalline powder Soluble in water	See Vanadium	As mordant in dyeing and printing textiles, manufacture of colored glass; for blue and green glazes on pottery

(continued)

APPENDIX

TABLE 21 (Continued)

PROPERTIES, TOXICITY, AND USES OF VANADIUM AND SOME VANADIUM COMPOUNDS

Compound	Properties	Toxicity	Uses
Vanadyl trichloride VOCl_3	Yellow liquid emitting red fumes bp $126-127^\circ\text{C}$	Readily liberates highly irritating HCl . See Vanadium	

The metals: VO^{+2} = vanadyl

VOCl_2 = vanadium oxydichloride (or vanadite)

VOCl_3 = vanadium oxytrichloride (hypovanadate)

NH_4VO_3 = ammonium metavanadate

$\text{Na}_2\text{V}_4\text{O}_9$ = sodium vanadite

Na_3VO_4 = sodium orthovanadate

$\text{Na}_4\text{V}_2\text{O}_7$ = sodium pyrovanadate

$\text{Na}_2\text{V}_4\text{O}_{11}$ = sodium tetravanadate

$\text{Na}_4\text{V}_6\text{O}_{15}$ = sodium hexavanadate

Also a number of complex Vanadium-arsenic and Vanadium-antimony compounds