# The Materials Flow of Vanadium in the United States
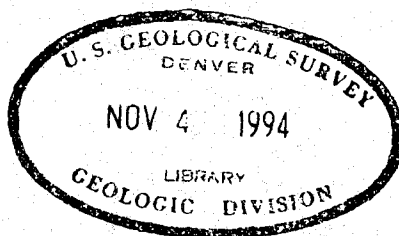
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Information Circular 9409

# The Materials Flow of Vanadium in the United States

By Henry E. Hilliard

UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary

BUREAU OF MINES

# PREFACE

This materials flow study has been prepared to provide reliable information regarding the nature, magnitude, and extent of the flow and emissions of vanadium in the United States for the year 1991. Background on the basic structure of the vanadium industry has been included. Brief process descriptions and simplified flowsheets are given. Where possible, the areas related to existing or potential losses of vanadium to the environment are pointed out. Another objective of this study was to establish a baseline of information on vanadium's overall resource use, and environmental loadings, and lay the ground work for a complete life-cycle inventory assessment.
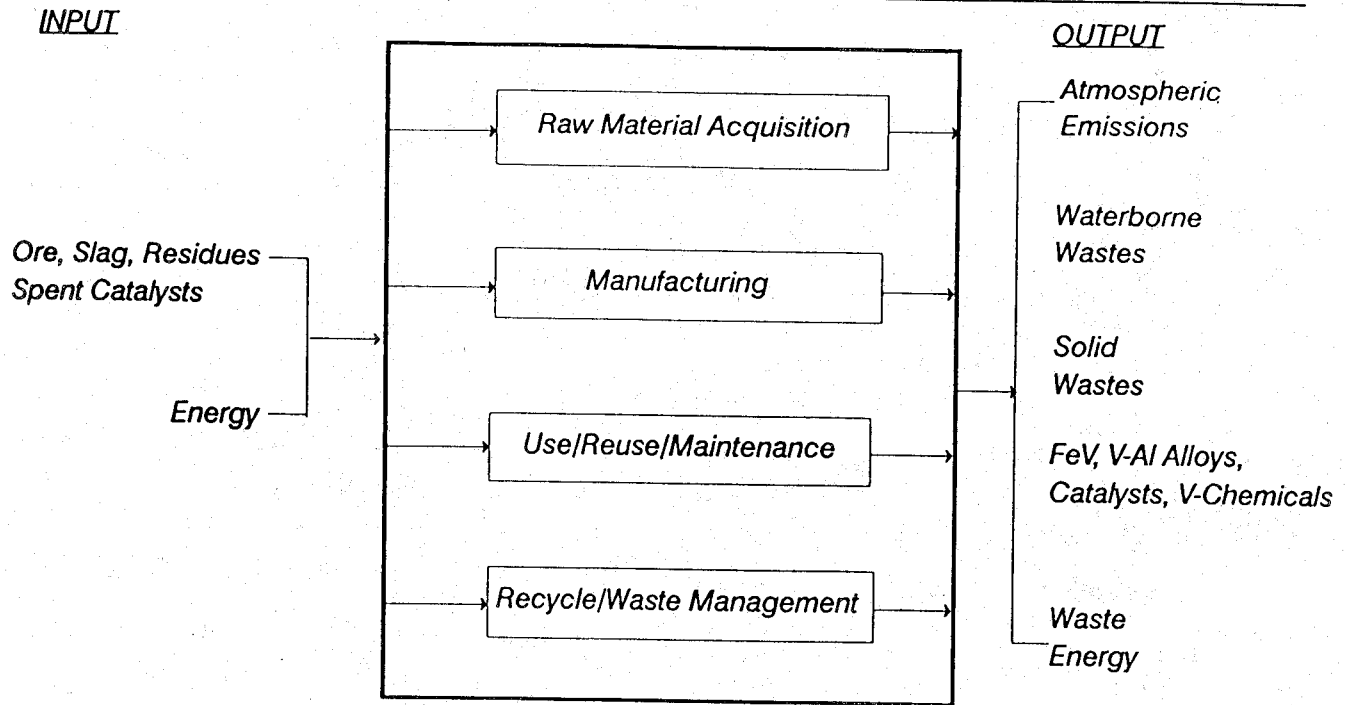
The Society of Environmental Toxicology and Chemistry (SETAC) has defined life-cycle assessment (LCA) as the process of holistically assessing the environmental burdens of products, processes and other managed human activities.* This process, according to SETAC, involves evaluating the environmental effects associated with a given activity from the initial gathering of raw materials from the earth until the point at which all residuals are returned to earth. An alternative terminology used for this process is "cradle to grave" analysis. SETAC reports that some of the most promising applications of life-cycle assessment are for internal use by corporations and regulatory agencies. By developing and using information regarding environmental effects that are both "upstream" and "downstream" of the particular activity under scrutiny, a new paradigm is created for basing decisions in both corporate management and regulatory policy-making. Life cycle assessment may be used as a technical tool to identify and evaluate opportunities to reduce the environmental effects associated with a specific product, production process, package, material, or activity. It can also be used to evaluate the effects of resource management options designed to create sustainable systems. Practitioners and developers of LCA methodology agree that a complete assessment is composed of three parts.** In the first part, an inventory of the raw materials and energy resources put in the product, process, or activity, and the accompanying release of wastes, both matter and energy, to air, water, and soil, is compiled. Next, the stresses that these raw materials and energy use and waste releases placed on the environment are analyzed. This is followed by an improvement phase, where changes in the product, process, or activity are evaluated to minimize the associated environmental stresses. In each of the processes described in figure 1 there may be one or more operations. Each of these has inputs of raw materials and energy and outputs of material wastes, various forms of waste energy, and commercial products. Once boundary conditions for the study have been set, the mass of material inputs, including fuels, into each operation should equal the mass of outputs of products and material wastes from the operation.

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*Perlson, Bruce D. "Life-Cycle Assessment: An Environmental Decision-Making Tool?" Pres. at 203d ACS Nat. Meet., Chem. Marketing and Econ. Div. San Francisco, CA. Apr. 5-10, 1992.

**A Technical Framework for Life-Cycle Assessments. Fava, J. S., R. Denison, B. Jones, M. A. Curran, B. Vigon, S. Selke, and J. Barnum, ed. Soc. of Environ. Toxicology and Chem. and SETAC Foundation for Environ. Inf., Jan. 1991, 134 pp.

*Figure 1*



*Life cycle inventory model for vanadium.*

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## ILLUSTRATIONS

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## UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

g/yr        grams per year

$\mu$g/m³    micrograms per cubic meter

ppb         parts per billion

ppm         parts per million

wt %        weight percent

# THE MATERIALS FLOW OF VANADIUM IN THE UNITED STATES

By Henry E. Hilliard[1]

## ABSTRACT

The production, use, and emission of vanadium in the United States has been traced for the year 1991. Consumption was 3,300 tons[2], exports 1,285 tons, and imports 2,013 tons. About 98% of production was used in metallurgy; the remainder was consumed in chemicals, including catalysts. Total emissions to the environment in 1991 were estimated at about 3,100 tons, including emissions due to the combustion of coal and petroleum products. Emissions resulting from the production of ferrovanadium were 130 tons, and emissions from the production of steel about 6 tons. Dissipative losses, defined as losses that occurred during use or as a result of wear, were estimated to be no more than 3 tons. Disposal losses were estimated to be about 4,600 tons. Most of these losses were steel products that contained 0.1% or less vanadium and may or may not have been recycled. When these products are recycled by the steel industry, vanadium ends up in the steelmaking slag and does not return to vanadium use cycle. Worldwide emissions due to anthropogenic and natural sources were briefly reviewed. It was concluded that industrial emissions were about three times greater than emissions from natural sources.

[1]Physical scientist, U.S. Bureau of Mines, Washington, DC.
[2]Metric tons, unless noted.
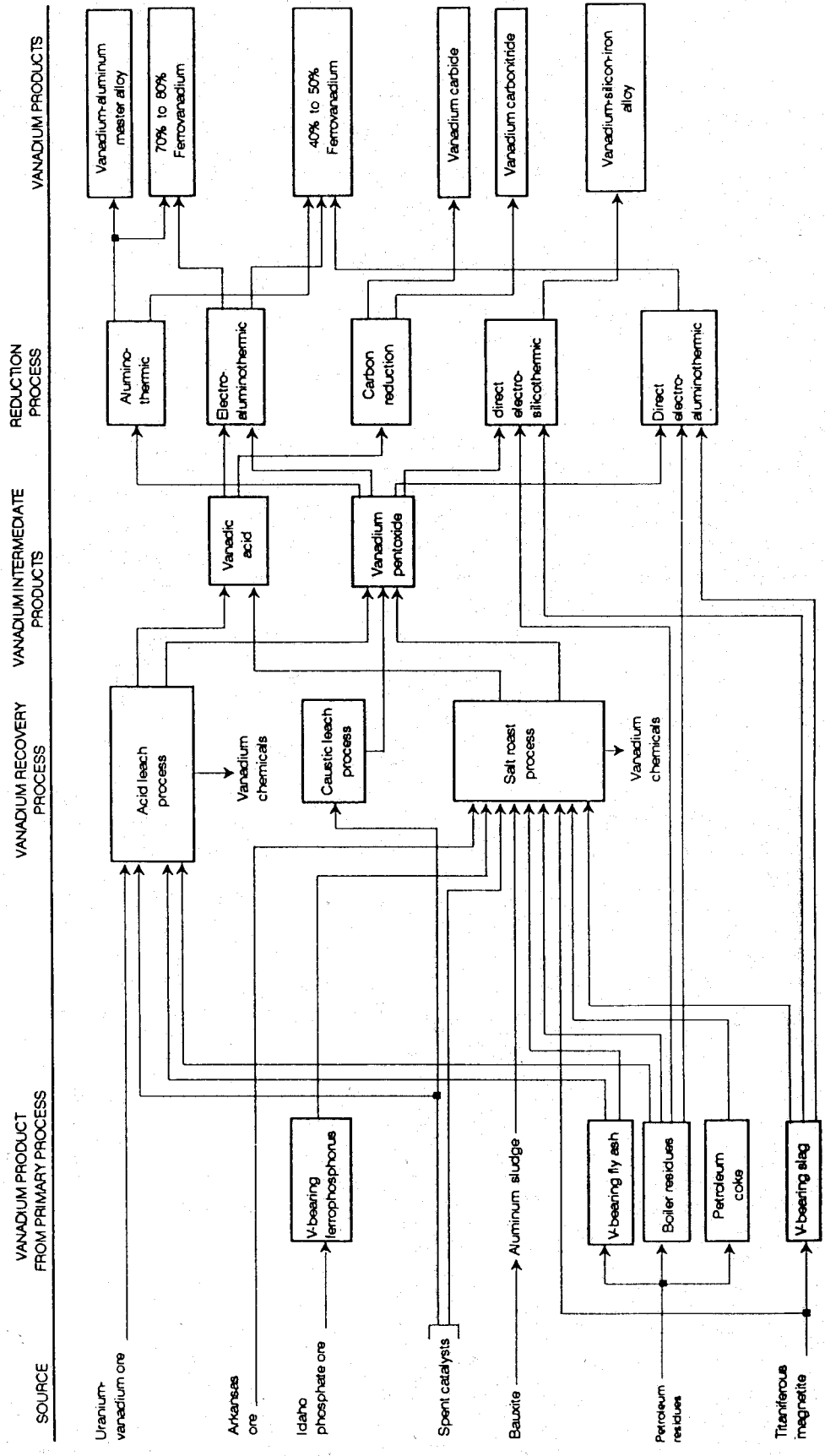
# SOURCES OF VANADIUM

## OCCURRENCES

Vanadium rarely occurs in deposits that can be economically mined for the element alone. This is despite the fact that there are at least 50 distinguishable mineral species and that, in terms of available earth's crust, vanadium is at least as plentiful as zinc and nickel. While a few commercial deposits of carnotite and magnetite contain as much as 3% vanadium pentoxide, most contain 0.1% to 1% . Apart from the vanadium sulfides of Peru, which are no longer in production, commercially exploited vanadium is usually in an oxidized form such as metal vanadates. Invariably, the commercial extraction of vanadium is feasible only as a byproduct or a coproduct of some other valuable mineral. Thus, the carnotite ores can be processed only when the market for uranium is advantageous, and the exploitation of vanadium from titaniferous magnetite is contingent on the market for magnetite concentrates and on transportation. The reason for this is that the concentration of vanadium in its ore is so low that the extraction of vanadium alone is not economical; in other words, the market price of vanadium cannot support the mining and production costs involved in such an operation. When vanadium is recovered as a coproduct, the market price of the main product supports the cost of extraction of vanadium, and the recovery and sale of vanadium, in turn, makes recovery of the main product more attractive economically. There is a sharing of mining and production cost between the main product and coproduct with the main product carrying the larger fraction of the cost burden. An example of this is the UMETCO Mineral Corp. operations in Blanding, UT, where uranium is the main product and vanadium is the coproduct. When vanadium is a byproduct, the situation is the same as when it is a coproduct except that the recovery and sale of byproduct vanadium is not a necessary condition for making the recovery and sale of the main product economically viable. Byproduct vanadium is produced at Kerr McGee Chemical Corp.'s Soda Springs, ID plant, from ferrophosphorus slag generated by Monsanto's elemental phosphorus and phosphoric acid operations. (See figure 2.)

The only domestic deposit (vanadiferous clays) mined exclusively for vanadium is operated by the U. S. Vanadium Corp. at Wilson Springs, AR. Vanadium also occurs in small amounts in fossil fuels. Fly-ash derivatives and boiler residues from combustion have recently become important sources of vanadium. Three U.S. companies recover vanadium from spent hydroprocessing catalyst and/or oxidation catalysts used in the production of sulfuric acid and other chemicals.

Comminuted vanadium raw materials awaiting extractive treatment are often stockpiled in the open where they are subjected to weathering by air and rain. However, the vanadium is locked in a highly oxidized and distributed form. It is not known if surface drainage picks up soluble vanadium, which would then become a water pollutant. It is common in handling vanadium-bearing minerals to convert the vanadium to water soluble salts. The conversion process involves salt roasting, in which the vanadium-bearing material is mixed with sodium chloride and heated (roasted) to about 850 °C. Under these conditions, oxidized vanadium is converted to sodium metavanadate ($NaVO_3$), which is water soluble. The hot water leaching process is about 95% efficient. Sodium metavanadate is precipitated from the pregnant liquor by adjusting the pH to 1-3 with sulfuric acid. When dried and fused, the product is sold as commercially pure vanadium pentoxide. For this study, plants producing vanadium pentoxide were estimated to be 91% efficient. Solid residues from leaching operations will contain some water-soluble materials. In the case of magnetite pellets, this presents no problem, since these are later fed to the blast furnace, where the vanadium emerges in insoluble oxidized form in slag or, perhaps, as refractory carbide in the pig iron. In any event, further dispersion does not occur. The salt roasting of ferrophosphorus slag from phosphate-rock smelting should be similarly safe, in that the residue from the leaching operation is returned via a smelting operation that locks the residual vanadium into inert form. The residues from roasting and leaching carnotite ores, vanadiferous clays, vanadium slags, and petroleum residues are likely to be heaped on the ground or landfilled, and will be subject to rain and groundwater drainage. Wind blown dispersion is minimized by keeping the heaped material wet at all times. Emissions to the atmosphere are thought to be negligible. The treatment of spent catalysts may not always result in solid residues that require special handling.

3



*Figure 2*

*Generalized flowsheet for processing of vanadiferous raw materials.*

Source: Reference 6.

4

# BIOLOGIC EFFECTS OF VANADIUM

Vanadium is found in air, even in areas where there is no known anthropological contamination (1).[3] This vanadium can be attributed to volcanic activity and seasalt spray. Vanadium concentrations in air are higher in winter than summer, most likely due to increased combustion of coal and heating oil.

Vanadium enters the body of humans and animals mainly through the respiratory system. In a 1964 study, Tipton and Shafer found vanadium in more than half the human lung samples studied, with the highest levels in people over 60 years of age or older (2). The mode of entry of vanadium compounds commonly seen in industrial exposures is limited to areas where vanadium pentoxide is produced, in steel mills where ferrovanadium is used, and in cleaning boilers fired by oil containing vanadium.

Vanadium compounds are irritants chiefly of the conjunctiva and respiratory tract. Prolonged exposure may lead to respiratory irritation with mucus discharge and lower respiratory tract irritation with bronchitis and chest pains (3). Other noted effects of vanadium and its compounds have included contact dermatitis, conjunctivitis, and (green) discoloration of the tongue. The reported toxic effects of exposure to vanadium compounds have been acute, never chronic.

The adopted threshold limit value for time-weighted averages for airborne vanadium, including oxide and metal dust of vanadium, is 0.5 milligram per cubic meter per 8-hour workday/40-hour workweek exposure; the short term exposure limit is 1.5 milligrams per cubic meter for dust (4).

# MINING AND ASSOCIATED LOSSES

The flow of vanadium in the United States begins with the mining of ore. The supply also includes imported and domestic fly-ash, vanadium-bearing slag, petroleum residues, and spent catalysts. A complete flow chart, through usage, is shown as figure 3. Whatever the source, the first objective is production of a vanadium oxide concentrate. Mining and general processing methods for vanadium ores and concentrates are readily available. Records of vanadium emissions are not available, but estimates based on toxic release data (5) indicated that average atmospheric emissions were about 5 kilograms of vanadium per ton of vanadium processed.

In 1991, about 4,000 tons of vanadium raw materials were handled in the United States. Estimating 5 kg of vanadium emissions for each ton of vanadium handled calculates to about 20 tons total vanadium emissions for this segment of the vanadium industry.
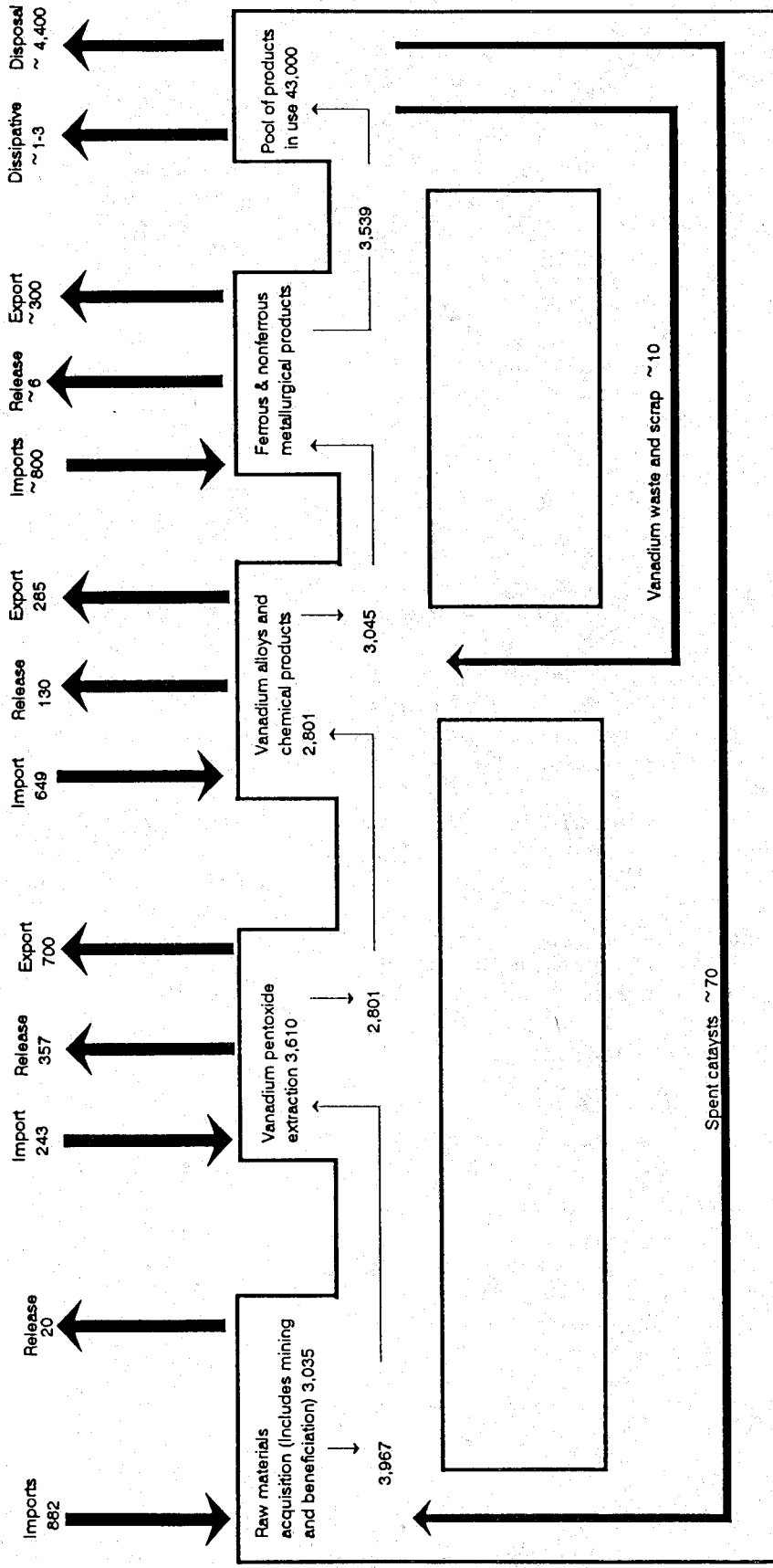
## URANIUM-VANADIUM ORES

Vanadium minerals have been recognized in many of the sandstone beds of the Colorado Plateau. Since the discovery of vanadium and uranium, in the sandstones of western Colorado in 1898, and particularly since about 1950, considerable work has been done on the geochemistry and occurrences of vanadium and uranium (6). Much of the literature relating to vanadium deposits in the Colorado Plateau refers to two general types of ore, the roscoelite type and the carnotite type. In general, the roscoelite type of ores occur in relatively clean sandstone beds, while the carnotite type ores are found associated with carbonaceous material.

Open stoping is the principal underground mining method in the Colorado plateau (7). If ore is uniformly distributed within a stratum, the room-and-pillar mining method is usually used. The vanadium content of Colorado Plateau uranium deposits mined by surface mining methods is relatively low, and little vanadium was recovered from this ore. In some instances, uranium-vanadium mineralization is too sparse, or, where it is extensive, too far from milling facilities to be handled in a normal manner at a profit. In such cases, upgrading or beneficiation at the site is given consideration. Sometimes upgrading solely for uranium may not offer an economic advantage but is favorable when vanadium is to be recovered. Beneficiation and upgrading techniques are not limited to use at a remote mine site or to low-grade ore. These techniques may prove advantageous in the treatment of any ore to decrease the total weight of material which must be transported to the mill and which must be handled in the milling operation. (See figure 4.)

Mining and milling operations, which involve grinding, concentrating, and transportation of ores, are potential point sources of vanadium pentoxide emissions. Vertical shafts as deep as 600 feet may be used to reach deposits in the Colorado Plateau. These deep underground mines release little or no vanadium to the atmosphere. However, many mines are near the surface. Blasting, used to loosen ore before it is carried to the surface, could be a source of emissions. At the surface, the ore is loaded onto trucks or trains for transportation to the mill. Dust losses from the milling process are not significant when effective collection systems are used in the areas of sources of dust, and the recovered dust is returned to the process. Airborne dust from crushing and concentrating could be a significant source of emissions if not adequately controlled.

[3]Italic numbers in parentheses refer to items in the list of references preceding the appendix.

5

*Figure 3*



U.S. *Vanadium materials flow in 1991.*

*Figure 4*



U-V Ore

↓

Crushing

↓

Grinding

↓

Reagents → Flotation → Tailings

↓

Drying

↓
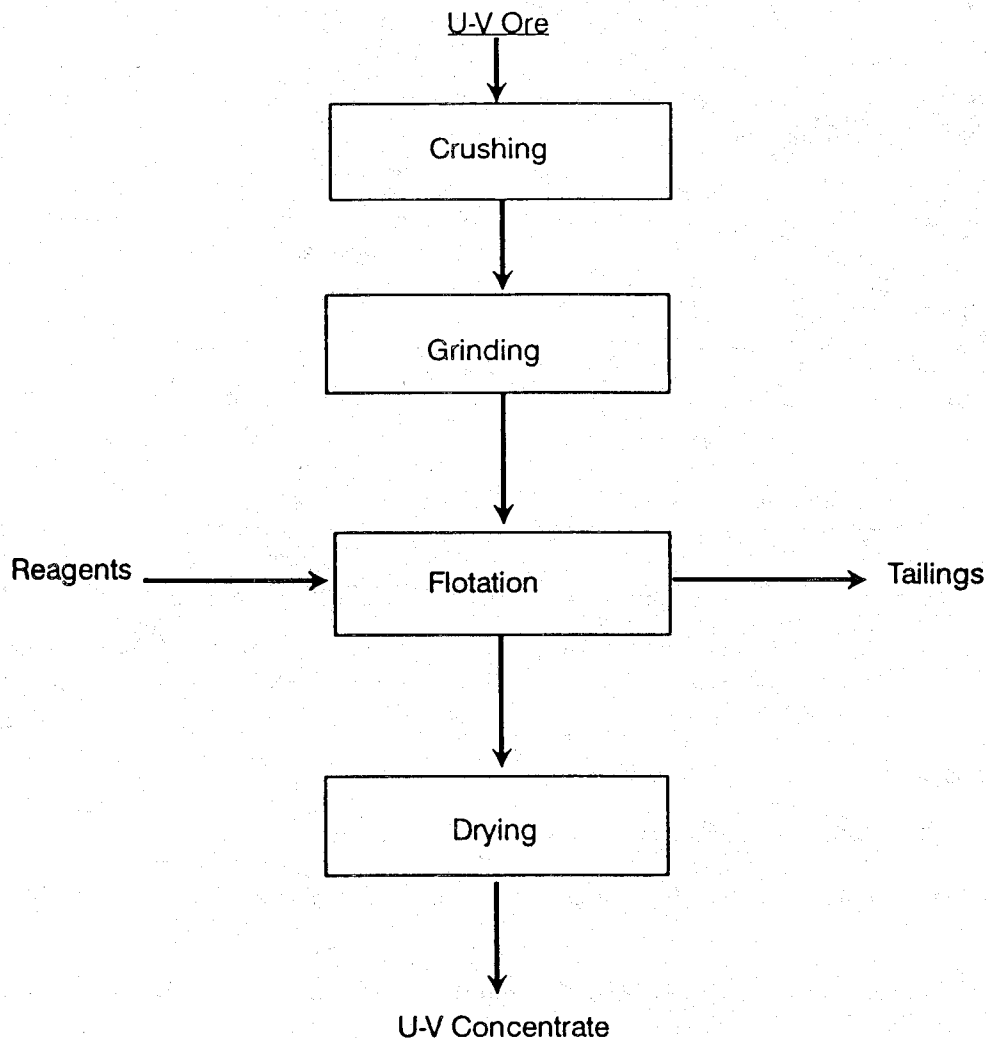
U-V Concentrate

*Simplified flowsheet for producing U-V ore concentrates.*

Prior to 1985, more than one-half of the vanadium mined in the United States was recovered as a coproduct with uranium from sandstones mined in the Colorado Plateau. Companies recovering vanadium from uranium ores were hurt by the downturn in nuclear powerplant construction in the aftermath of the Three Mile Island nuclear reactor accident and the subsequent reduced demand for enriched uranium. Worldwide recession, high interest rates, and the cancellation of powerplant construction in the United States caused the Nuclear Exchange Corp. (Nuexco) exchange value of uranium oxide to decline from $40.00 per pound in 1980 to less than $10.00 per pound in 1991. A direct result of the price decrease was mill closings, decommissionings and personnel cutbacks. At the same time, the price of vanadium pentoxide fell from an average of more than $6.00 per pound in 1990 to about $2.00 per pound in 1992. With these falling prices, coproduct vanadium from uranium-vanadium ores virtually ceased in 1990.

## FERROPHOSPHORUS SLAG

The largest U.S. reserves of vanadium can be found in the phosphate deposits of Idaho. These phosphate deposits occur in the Permian Phosphoria Formation, a stratum of marine origin containing limestones, phosphatic shale, and phosphorite. The Phosphoria Formation covers the adjoining parts of Montana, Wyoming, and

Utah. The vanadium content of the phosphorite beds averages 0.14% vanadium pentoxide (8). The recovery of vanadium from wet phosphoric acid resulting from rock phosphate processing has been accomplished by selective precipitation schemes or solvent extraction techniques. Kerr McGee Chemical Corp., the only company producing vanadium from this source, developed a successful solvent extraction process at its Soda Springs, ID vanadium mill. (See figure 5.)

## VANADIUM-BEARING IRON SLAG

The world's largest known reserves of vanadium ore are contained in the titanomagnetite seams and plugs of the Upper Zone of the Bushveld Complex located in the Republic of South Africa. The main seam has a consistent grade of 1.5% vanadium pentoxide, and averages 4 to 6 feet in thickness. In total, this seam contains more than 200 million tons of proven reserves averaging 1.5% vanadium pentoxide (9). Vanadium from these magnetite ores is extracted as a coproduct with iron, which is converted to steel. Because of the high titanium content of the ore, the iron is produced by a special process involving the pre-reduction of the magnetite with powdered coal in a rotary kiln followed by reduction in a submerged electric arc furnace. The iron from these operations contains about 1% vanadium, which is removed as a slag by low-temperature treatment with oxygen. The slag contains 12% to 24% vanadium pentoxide. China and Russia also produce vanadium-bearing slags that contain between 10% and 20% vanadium pentoxide. A large portion of the slag produced in South Africa is exported to converters in Europe, the United States, and Canada, where it may be directly processed for vanadium extraction without the need of further concentrating.

## PETROLEUM RESIDUES

All crude oils contain vanadium and nickel as impurities, and this has long been known to cause severe corrosion problems in oil-fired boilers using high-vanadium fuels. The concentration of vanadium in crude oil may vary from less than 1 to more than 1,400 ppm, depending on the source of the crude. Vanadium and nickel become concentrated primarily in the petroleum coke byproduct of the oil-refining process (10). Processing of crude oils to reduce their sulfur content coincidently can significantly reduce their vanadium content. This process is a continuous coking-gasification process in which the petroleum vacuum residuals are converted to various gaseous, liquid, and solid products. These residuals are the principal source of the products that are sold as residual fuel oils under such designations as No. 5 and No. 6 or Bunker C fuel oil. Busch noted that many ships burning Venezuelan oils during World War II were equipped to collect the flue dust, which was treated later to recover vanadium. Petroleum coke is the solid product and accounts for only 1 wt% of the residuum feed to the desulfurization process. Most important is the fact that more than 99% of the metals, including vanadium, originally in the residuum feed becomes concentrated in this small amount of solids (11). This solid material has been used as a source of vanadium.

In petroleum refining, the catalysts used for heavy and light petroleum fractions desulfurization usually contain molybdenum trioxide promoted with calcium oxide on alumina as support. During desulfurization, vanadium in the

*Figure 5*
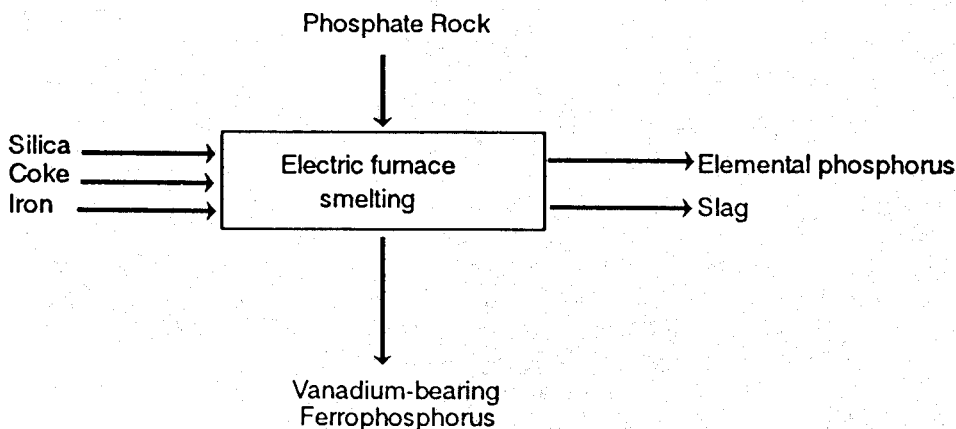


*Simplified flowsheet for producing vanadium-bearing ferrophosphorus slag concentrates.*

crude fractions is deposited on the catalyst. Eventually, because of the deposition of vanadium and other metal impurities, the catalyst becomes poisoned and must be replaced. Vanadium pentoxide concentration on catalysts may reach as high as 21%, and when spent, this material becomes a commercially useful material for vanadium (and molybdenum) extraction. Spent catalysts and petroleum coke may be directly processed for vanadium extraction. Spent chemical process catalyst, e.g., oxidation catalyst used in the production of sulfuric acid, maleic anhydride, and other fine chemicals, can also be processed for the recovery of vanadium. These catalysts are much leaner than spent petroleum refinery catalysts, and may be processed by blending with higher grade materials.

# VANADIUM PENTOXIDE EXTRACTION AND LOSSES

Most of the vanadium produced in the United States in 1991 was recovered as vanadium pentoxide. Extraction processes are more art than science, and each producer has developed proprietary procedures that are most efficient for the material being processed. The extraction process usually involves salt-roasting, in which the finely comminuted vanadium-bearing material is mixed with sodium chloride and roasted. Vanadium in the material is converted to a water soluble salt that is leached and precipitated as sodium metavanadate. When dried and fused, the product is sold as vanadium pentoxide flake. Based on U.S. Bureau of Mines data, the average extraction processes in current use are about 91% efficient. Total U.S. losses (releases) from the production of vanadium pentoxide in 1991 are estimated at 357 tons.
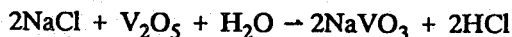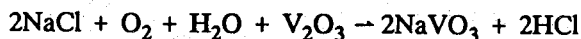
## VANADIUM-URANIUM ORES

Conventional treatment of vanadium-uranium ores begins with crushing and grinding to produce sized ore suitable for leaching. Uranium is extracted from its ores by a variety of processes, which depend upon the uranium minerals present, the associated minerals and gangue, the value of the ore, and the size and location of the ore body. Pretreatment by roasting has been important in the processing of vanadium-uranium ores as a means of improving vanadium extraction. Roasting of carnotite ores with common salt has played an important role in the processing of these ores since the 1930's. It is primarily used to produce a water soluble vanadium product and to effect a separation between vanadium and uranium.

The salt roasting process consists of mixing ground ore at about minus 10-mesh size with 6% to 10% sodium chloride (NaCl) and then heating (roast) at about 850 °C for 1 to 2 hours in a multiple hearth roaster. Oxidizing conditions are necessary to insure that vanadium is in the penta-valent ($V^{5+}$) state and uranium is as highly oxidized as possible. When roasting is complete, the calcine is cooled rapidly. If water is used at this point to extract water-soluble vanadium, the residue from the water leach may then be further treated with dilute acid to extract uranium and additional acid-soluble vanadium. Alternatively, a carbonate-bicarbonate solution may be used as the quenching and leaching solution, and the dissolved vanadium and uranium then separated in subsequent treatment steps. From 85% to 95% percent of the vanadium can be recovered with proper roasting conditions (12).

Vanadium is often present in the reduced state, typically tetravalent or trivalent, in some ores. For this reason, both oxidation and reduction is required to produce a water-soluble pentavalent vanadate.

$$2NaCl + O_2 + H_2O + V_2O_3 \rightarrow 2NaVO_3 + 2HCl$$

$$2NaCl + V_2O_5 + H_2O \rightarrow 2NaVO_3 + 2HCl$$

The sodium vanadate formed by reaction of the NaCl and $V_2O_5$ reacts with uranium compounds to form sodium uranyl vanadates. Because this reaction is reversible, the roasted ore must be quenched as rapidly as possible to prevent reversion of the sodium uranyl vanadate to the sodium vanadate and an insoluble uranium complex.

## SPENT CATALYST

A simplified flowsheet for the recovery of vanadium from spent catalyst is shown in figure 6. As with most procedures for extracting vanadium, the process begins with salt roasting followed by leaching with water or acid. Vanadium, nickel, cobalt, and molybdenum may be recovered from spent petroleum process catalysts. An exception to the roast-leach process was developed by AMAX Metals Recovery Corp. at its Braithwaite, LA, plant. In addition to metals, the AMAX process also recovers alumina. The process produces no solid wastes, only water, which can be discharged to the sewer. (See figure 7.)

## PETROLEUM RESIDUES

The process for treating boiler residues, fly-ash, and petroleum coke is similar to the process used to treat spent catalyst. However, some of this material may contain high concentrations of carbon that must be removed at some stage of the operation. In many instances, roasting at about 800 °C is sufficient, or the carbon content can be reduced to an acceptable level by floatation techniques using kerosene as a collector and pine oil and Dowfroth 250 as frothers (13). (See figure 8.)

Petroleum residues (spent catalysts, fly ash, and boiler residues) are processed by plants located in Arkansas, Idaho, Louisiana, and Texas. In 1991, 2,250 tons of vanadium was recovered from petroleum residues.

*Figure 6*



Vanadium concentrate
(Carnotite ores)

NaCl ——→ Salt Roasting
Heat ——→

Sodium carbonate ——→ Carbonate
solution                        Leach

Sulfuric acid ——→ Acid Leach ——→ Tailings

Leach liquor

Quaternary ——→ Solvent          ←— Recycle
amine                 extraction

Loaded                          Vanadium free
organic phase                   organic phase

Sodium carbonate ——→ Stripping
solution

Alkaline
strip liquor

Ammonium chloride ——→ Vanadium
                                     precipitation

AMV

Ammonium metavanadate          Fusion, flaking,
direct to market               packaging

                               Vanadium pentoxide flake
                               to market

Source: Adapted from U.S. Bureau of Mines OFR 117-76. Energy Use Patterns in Metallurgical and Nonmetallurgical Mineral Processing (Phase 6--Energy Data and Flowsheets, Low-Priority Commodities). Prepared for USBM by Battelle Columbus Laboratories, OH.

*Simplified flowsheet for leaching salt roasted vanadium-uranium ore concentrates.*

10

*Figure 7*



Spent Catalyst

Generalized Process

AMAX Process

Roast ← Soda ash ← Heat

NaOH → Ball mill

Quench, Grind, Leach ← Water ← Sulfuric acid

Autoclave

Filtration → Residue

Solids ← Filter

AMV precipitation ← NH₄Cl

NaOH → Autoclave

V-Mo liquor

Molybdenum precipitation ⇢ Mo recovery

Filtration — Filtrate →

Centrifuge

V-liquor

AMV

Precipitation

Vanadium precipitation

Fusion, flaking packaging

Alumina solution

Dry, oxidize, granulate, packaging

Vanadium pentoxide flake to market

MoO₃ recovery

Al₂O₃ recovery

Ni-Co residue

Granular vanadium pentoxide to market

*Source: Adapted from source cited in figure 6.*

*Simplified flowsheet for processing spent catalysts.*

*Figure 8*

Fly Ash, Boiler Residue,
Petroleum Coke

Carbon adjustment — Optional

H₂SO₄ →
SO₂ → Leach

SO₂ →
Lime Stone → Precipitation → Jarosite

*V-solution*

V-recovery
(Solvent extraction)

*Red cake*

Fusion

Flaking and
packaging

Vanadium Pentoxide
to market
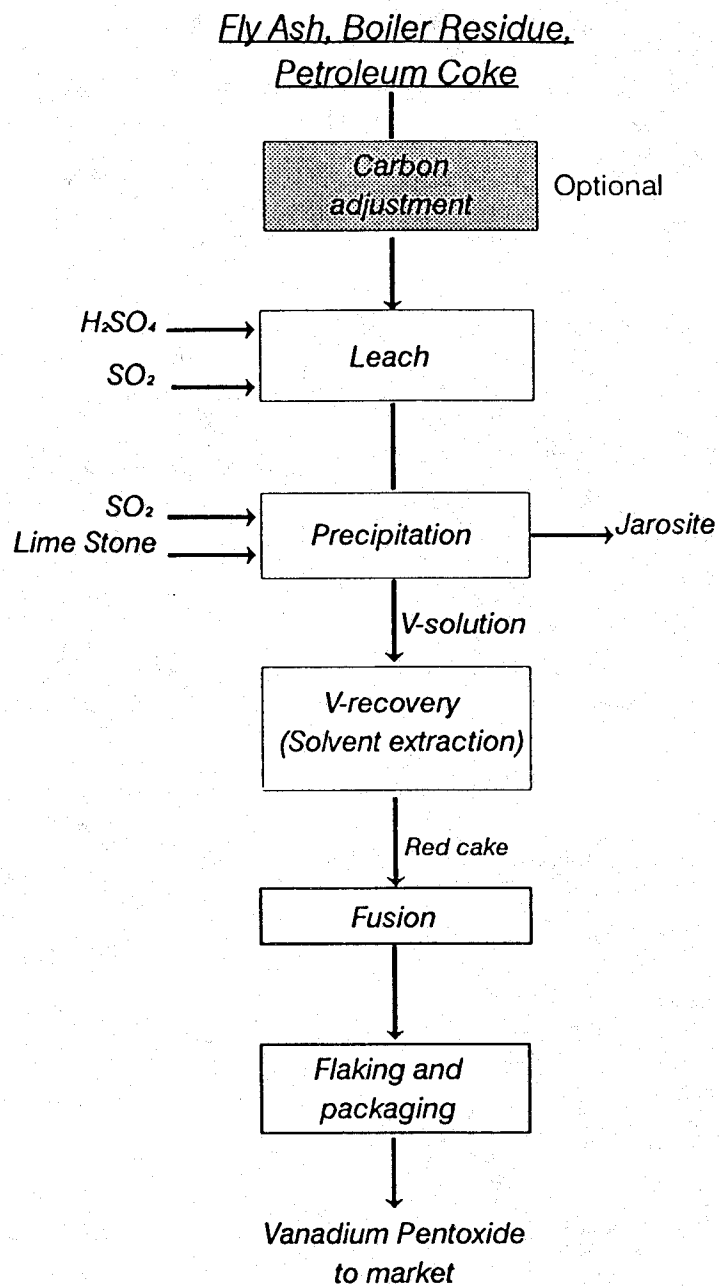
*Source: Reference 10.*

*Simplified flowsheet for processing petroleum residues.*

# FERROVANADIUM, NONFERROUS ALLOYS, AND CHEMICALS - MANUFACTURE, USES, AND LOSSES

## FERROUS AND NONFERROUS ALLOYS

Once vanadium pentoxide has been extracted from its ore or other raw materials, most is converted to FeV. The primary use of FeV is as a means of introducing vanadium into steel, where it gives additional strength and toughness. The use can be subdivided into micro-alloyed or low-alloy steels, which generally contain less than 0.15% vanadium, and higher-alloy steels. Together, these account for about 86% of vanadium usage, the remaining 14% being in light alloys such as Ti-Al-V alloys for the aerospace industry, and a variety of chemicals. Ferrovanadium is available in alloys containing 45% to 50% or 80% vanadium. The 80% grade is mostly produced by the aluminothermic reduction of vanadium pentoxide in the presence of steel scrap or by direct reduction in an electric arc furnace. The 45% to 50% grade is produced from slag and other vanadium-containing materials by the silicon reduction process. Vanadium additions to titanium alloys are made with aluminum-vanadium master alloys which are also produced by the aluminothermic reduction of vanadium pentoxide followed by vacuum refining. (See figures 9 and 10.)
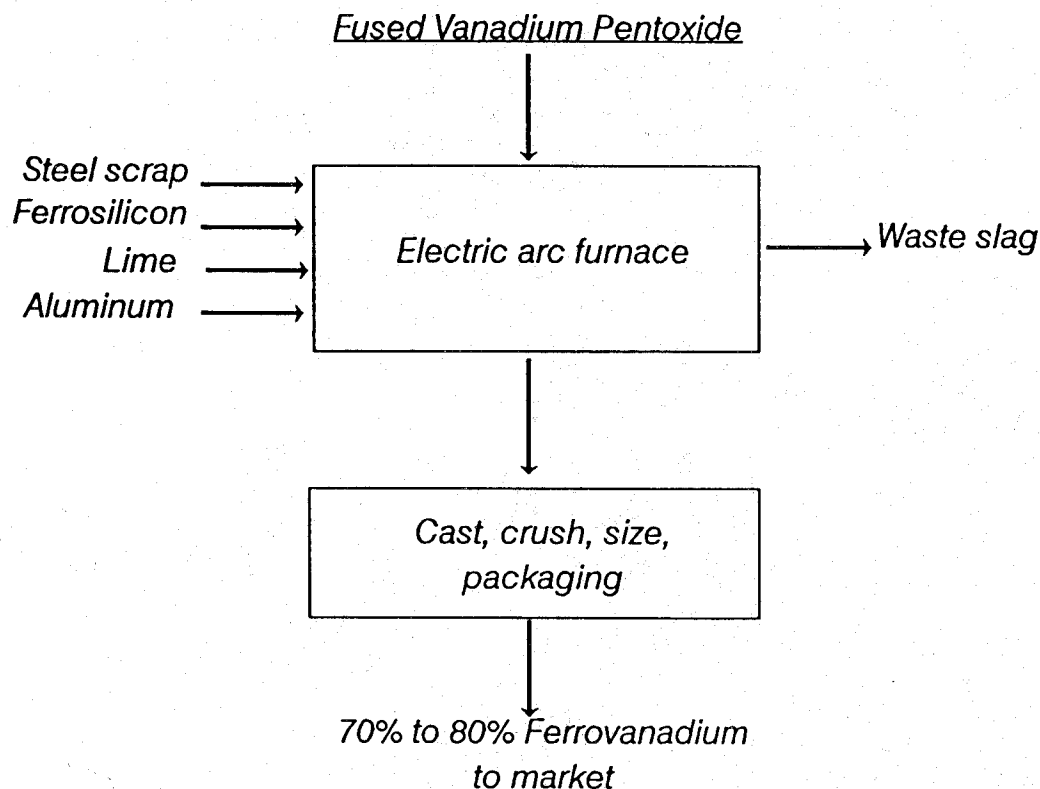
### Ferrovanadium

The most important use of vanadium is as an alloying element in the steel industry, where it is added to improve grain refinement and hardenability in steels. Vanadium steels are used in taps and dies and in cutting tools because of their wear resistance. They are also used in constructional steels, iron and steel castings, automobile parts, and springs and ball-bearings. U.S. Bureau of Mines data indicate that about 86% of vanadium consumed in 1991

*Figure 9*



Source: Work cited in figure 6.

*Simplified flowsheet for production of 70% to 80% ferrovanadium from fused vanadium pentoxide flake.*

was consumed by the steel industry. This percentage of FeV consumption in ferrous metallurgy has remained essentially constant since 1943, when the Bureau of Mines Minerals Yearbook reported that "more than 80% of vanadium consumption is in the form of ferrovanadium."

Most ferrovanadium is produced by aluminothermic reduction in an electric-arc furnace. The charge consists of steel scrap, fused vanadium pentoxide, and carbon, with aluminum as the reducing agent. Also, Shieldalloy Metallurgical Corp., Cambridge, OH, has produced quantities of 40% to 50% FeV by treating vanadium-bearing iron slag with silicon, flux, and carbon as the reducing agent. With either process, most of the charge becomes molten slag but a substantial amount evolves as fume. The particle size will range from 0.1 to 1 $\mu$m, and the total particulate emission to the atmosphere resulting from the production of FeV in 1991 totaled 130 tons (ref. 15). The emissions are concentrated in the vicinity of FeV producing plants, of which there are three in the United States.

Vanadium carbides, used as alloying agents, are produced in closed systems operating under vacuum. This is a clean operation in that very little vanadium escapes into the atmosphere.

The use of high-strength low-alloy (HSLA) and constructional steels that contain vanadium is substantial and increasing. There are also many tool and die steels that contain vanadium in concentrations up to 4%, but these are produced in relatively small amounts. In each case, vanadium is introduced into the steel as FeV or vanadium carbide (VC) at a stage in steelmaking such that the vanadium is efficiently dissolved in the liquid steel. Economics demands that as little as possible be lost to the slag or furnace refractories. In conventional steelmaking operations, there seems little basis for expecting much loss of vanadium in fume or airborne dust. Ferrovanadium dissolves readily in the molten steel and has negligible vapor pressure. Any vanadium oxides formed dissolves readily in the slag, which is a reasonably inert vitreous substance.

*Figure 10*



Simplified flowsheet for production of aluminum-vanadium master alloys.
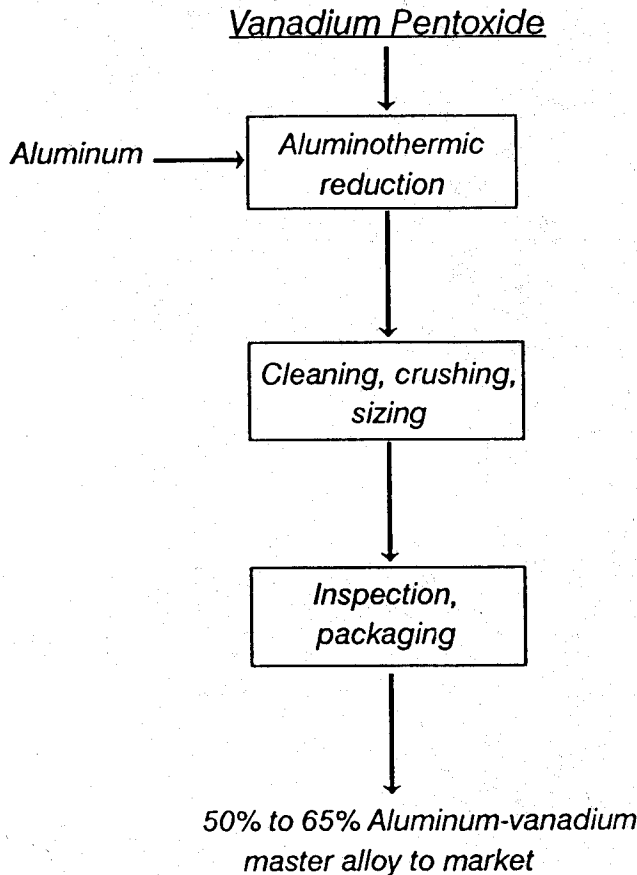
Although the slag may be landfilled and subjected to rain and drainage, there is no evidence that traces of vanadium could exist in any fugitive form.

A large part of all steel finds its way back to steel-making operations as scrap. In the refining stage of such operations, vanadium is oxidized out of the liquid metal as completely as feasible. In the former use of the open-hearth furnace, vanadium from the scrap steel would simply be oxidized into the slag, which would then be skimmed off, granulated, and discarded with reasonable safety. Today, most scrap steel is recycled by the basic-oxygen furnace (BOF), which refines steel with a high pressure stream of oxygen. This process produces enormous clouds of fume that consist primarily of metallic oxides. Most of the fume consists of iron oxides. However, some portion of the vanadium in the scrap charge might be expected to be incorporated in the fume. Clouds of fume discharged form the BOF deposit particles on the surrounding land for many miles. Fume can usually be characterized as a suspension of particles less than 0.01 $\mu$m in diameter. In 1991, steel produced in the BOF was 48 million tons (14). The emissions factor for the BOF has been estimated at 21 kg of particulate matter per ton of steel and the degree of emissions control at 97% (15). Using these figures, one can calculate a total fume emission of about 200 tons of vanadium in 1991, of which 6 tons escaped to the atmosphere. Compared with emissions from other sources, this may seem small, but the intensity of deposition is high because the discharge is highly concentrated and local.

The vanadium that finds its way back to the steelmaking process via steel scrap, and is not lost as fume, is defined as "disposal" vanadium losses for this report. The vanadium content of this scrap, estimated at 0.1% or less, ends up in the steelmaking slag and does not find its way back to the vanadium-use cycle. The Bureau of Mines 1991 Iron and Steel Scrap Annual Report reported that 45.8 million tons of iron and steel scrap was consumed in all types of furnaces in 1991. If this scrap averaged 0.1% vanadium, then there were about 4,400 tons of disposal vanadium losses in 1991.

Steel ingots are processed to finished or semifinished plate, bars, sheet, and forgings. Most metal working is done while the workpiece is hot. At the temperatures used, steel oxidizes superficially, and thick mill scale is formed. Most of the mill scale is recycled to the melting operation. A portion of the mill scale is removed by pickling. In this operation, the workpiece is placed in an acid bath. Spent pickling solutions contain water soluble salts of all alloying elements in the steel, including vanadium.

The high-cost tool and die steels are mostly produced in vacuum-induction and vacuum arc-melting systems, which are closed and do not vent to the atmosphere.

## Nonferrous Alloys

Bureau of Mines data show that about 12% of U.S. consumption of vanadium in 1991 was in non-ferrous alloys. The principal application of vanadium in non-ferrous alloys was in the titanium 6Al-4V alloy, which is important in supersonic aircraft and other aerospace applications. Vanadium imparts high temperature strength to the titanium alloy, an important property in jet engines and high-speed air-frames. Because of their reactive nature, these alloys are usually melted in closed systems. During processing of ingots to wrought shapes, there is scale formation, and various grinding and machining operations that produce comminuted material. Most of these are not recycled, but the materials are quite inert and do not become airborne. Both acid and base solutions may be used for pickling of plates, sheets, and forgings. Sludge and spent pickling solutions are usually mixed to neutralize each other. Neutralization usually results in a precipitate that is rich in halide salts of vanadium.

## Chemical

The principal uses of vanadium in the chemical industry are as catalysts in the synthesis of sulfuric acid and the oxidation of various organic compounds to commercial products. The oxidation of sulfur dioxide to sulfur trioxide in the production of sulfuric acid consumes by far the largest amount of vanadium by the chemical industry (estimated at 164 tons in 1991 (16)). Vanadium oxide catalysts are used in two closely related processes involving the oxidation of aromatic hydrocarbons to phthalic anhydride and the oxidation of benzene to maleic anhydride. Vanadium oxide catalysts are also used in the catalyzed process (Stretford Process) used to remove hydrogen sulfide from gas streams. Total consumption of vanadium in these chemical processes is small when compared to consumption in metallurgical applications. Catalytic uses result in little or no loss or consumption of vanadium and are not expected to contribute significantly to emissions to the environment.

The chemical industry is probably the only end use sector where significant dissipative losses may occur. Most vanadium uses do not result in dissipative losses. However, normal operating conditions, screening, and reuse-recycling procedures may result in dissipative losses of about 1% or 1 to 3 tons of vanadium in 1991. (See table 1.)

Table 1.—U.S. consumption of vanadium in 1991, by end use

(Tons of contained vanadium)

| End use | 1991 |
|---|---|
| Steel: | |
| Carbon | 919 |
| Stainless and heat-resisting | 37 |
| Full alloy | 739 |
| High-strength low-alloy | 919 |
| Tool | 242 |
| Total steel | 2,857 |
| Cast irons | 15 |
| Superalloys | 14 |
| Alloys (excluding steel and superalloys): | |
| Cutting and wear-resistant materials | W |
| Welding and alloy hard-facing rods and materials | 6 |
| Nonferrous alloys | W |
| Other alloys | 350 |
| Chemical and ceramic uses: | |
| Catalysts | 9 |
| Other | W |
| Miscellaneous and unspecified | 33 |
| Grand total | 3,285 |

W  Withheld to avoid disclosing company proprietary data, included with "Miscellaneous and Unspecified."
NOTE:— Totals may not equal sum of components because of independent rounding.

Source: U.S. Bureau of Mines 1991 Vanadium Annual Report.

# NON-METALLURGICAL SOURCES OF VANADIUM IN THE ATMOSPHERE

Up to this point, the discussion of vanadium emissions has been limited to mining and metallurgical operations. However, the largest vanadium emissions to the environment are those that are due to the combustion of coal and petroleum products.

## COAL

During the combustion of coal, vanadium and other metallic elements are partitioned between the slag or bottom ash and fly ash. Bottom ash is deposited in the ash pit below the flame zone and does not contribute to emissions. Fly ash is deposited between the radiant furnace outlet and the stack tip. On average, about 65% of the total ash produced from coal combustion is fly ash. (See table 2.)

The disposition of coal consumed in the United States in 1991 is shown in table 3. From these data, estimates were prepared of the amount of vanadium emitted into the air as a result of the combustion of coal. The estimates were made with the following assumptions:

1. Fly ash constitutes 65% of the total coal ash with the remaining 35% remaining in the furnace as slag or bottom-ash.

2. The average vanadium content of the coal was 26.9 ppm.

3. Ninety-nine percent application of control and 93% efficiency of control.

4. The coking of coal results in zero vanadium emissions into the air, assuming that essentially all of the vanadium remains in the coke and eventually appears in the blast furnace slag.

Electric Utilities:

$$772,268,000 \times 2.69 \times 10^{-5} \times 0.65[1 - (0.99 \times .93)]$$

$$= 1,070.8 \text{ short tons V.}$$

Other Industrial:

$$75,405,000 \times 2.69 \times 10^{-5} \times 0.65[1 - (0.99 \times 0.93)]$$

$$= 104.6 \text{ short tons V.}$$

Residential and commercial:

$$6,094,000 \times 2.69 \times 10^{-5} \times 0.65[1 - (0.99 \times 0.93)]$$

$$= 8.5 \text{ short tons V.}$$

The estimates indicate that about 1,184 tons of vanadium were emitted to the atmosphere resulting from coal combustion in 1991.

Table 2.—Vanadium content of coal from important coal producing regions and States

| Coal-producing State | Average vanadium content, ppm[1] | Distribution by origin State[2] (Thousand short tons) | Percent of total vanadium |
|---|---|---|---|
| **Eastern** | | | |
| Alabama | 34 | 27,679 | 2.8 |
| Eastern Kentucky | 40 | 117,462 | 11.8 |
| Maryland | 23 | 3,773 | .4 |
| Ohio | 24 | 30,023 | 3.0 |
| Pennsylvania | 33 | 65,459 | 6.7 |
| Tennessee | 35 | 4,274 | .4 |
| Virginia | 42 | 43,495 | 4.4 |
| West Virginia | 35 | 165,576 | 16.7 |
| Average | 33 | Total .. 457,736 | Total .. 46.2 |
| **Central** | | | |
| Arkansas | 35 | 1 | <.1 |
| Illinois | 30 | 58,553 | 5.9 |
| Indiana | 33 | 31,412 | 3.2 |
| Iowa | 30 | 350 | <.1 |
| Kansas | 15 | 424 | <.1 |
| Louisiana | NA | 3,151 | .3 |
| Missouri | 38 | 2,203 | .2 |
| Western Kentucky | 34 | 40,828 | 4.1 |
| Average | 31 | Total .. 136,922 | Total .. 14.0 |
| **Western** | | | |
| Alaska | NA | 1,483 | .1 |
| Arizona | 10 | 12,933 | 1.3 |
| California | NA | 23 | <.1 |
| Colorado | 13 | 17,757 | 1.2 |
| Montana | 10 | 38,119 | 3.8 |
| New Mexico | 21 | 22,378 | 2.3 |
| North Dakota | 9 | 29,741 | 3.0 |
| Oklahoma | NA | 1,867 | .2 |
| Texas | NA | 54,243 | 5.5 |
| Utah | 12 | 21,444 | 2.2 |
| Washington | 43 | 5,096 | .5 |
| Wyoming | 17 | 194,407 | 19.6 |
| Average | 17 | Total .. 399,491 | Total .. 40.3 |
| | | Grand total .. 994,146 | |

NA Not available.

[1]Abernethy, R. F., M. J. Peterson, and F. H. Gibson. Spectrochemical Analyses of Coal Ash for Trace Elements. USBM RI 7281, July 1969, 30 pp.

[2]Quarterly Coal Report, Oct.-Dec. 1992. U.S. Dep. Energy, Energy Inf. Administration, DOE/EIA - 0121(92/4Q), May 1993, 162 pp.

NOTE.—Totals may not equal sum of components because of independent rounding.

Table 3.—Estimated emissions of vanadium resulting from burning of coal in the United States, 1991

(Thousand short tons)

| End use | Consumption[1] | Vanadium in coal | Vanadium emitted |
|---|---|---|---|
| Electric utilities | 772,268 | 21.0 | 1.070 |
| Coke plant | 33,854 | 1.0 | 0.000 |
| Other industrial | 75,405 | 2.0 | 0.100 |
| Residential and commercial | 6,094 | .2 | 0.008 |
| Total | 887,621 | 24.0 | 1.200 |

[1]Quarterly Coal Report. Oct.-Dec. 1992. U.S. Dep. Energy, Energy Inf. Administration, DOE/EIA - 0121(92/4Q), May 1993, 162 pp.

## OIL

Virtually all crude oil contains some vanadium, concentration ranging from nearly zero for some middle-eastern crudes to more than 1,400 ppm for some Venezuelan heavy crudes. When oil is refined, vanadium and other trace metals tend to concentrate in the heavy fractions such as residual fuel oil. U.S. 1991 demand for residual fuel oil was 497 million barrels. Imports were 160 million barrels, and the remainder were from domestic production.

The 497 million barrels of residual fuel oil contained about 3,855 tons of vanadium pentoxide (see table 4). When this fuel was burned in powerplants, two grades of waste vanadium ash were produced. One was produced within the furnace proper and deposited in the ash pit beneath the flame zone. This ash, with vanadium pentoxide concentrations between 30% and 40%, was classified as high-grade. The other grade of ash was deposited between the radiant furnace outlet and the stack tip. This low-grade ash, containing 5% to 20% vanadium pentoxide, fouls the furnace gas passes and must be removed 2 to 3 times annually by water washing (17). A typical powerplant recovered 33% of the injected vanadium pentoxide as high-grade ash; 57% was deposited as a component of the low-grade ash, and 10% lost via the stack and presumably to the atmosphere (18). The U.S. Energy Information Administration reported that 497 million barrels of fuel oil were consumed in the United States in 1991. Electric and other utilities consumed about 37% of the total or about 185 million barrels. Treatment of the low- and high-grade ash has been discussed previously in this

Table 4.—Vanadium in residual fuel oil consumed
in the United States in 1991

| Source[1] | Quantity[2] (million barrels) | $V_2O_5$ (ppm) | $V_2O_5$ (tons) |
|---|---|---|---|
| United States ................. | 337.990 | 46 | 2,450 |
| Arab OPEC[3] ................. | 12.667 | 62 | 124 |
| Other OPEC ................. | 43.850 | 107 | 742 |
| Non-OPEC ................. | 103.015 | 33 | 962 |
| Total ................. | 497.455 | | 3,855 |

[1]International Petroleum Encyclopedia, 1983 and 1984, v. 16-17.
[2]Petroleum Supply Monthly. U.S. Dep. Energy, Energy Inf. Administration, Dec. 1991.
[3]OPEC is the Organization of Petroleum Exporting Countries.

study. Based on 10% loss via the stack, vanadium pentoxide emissions to the atmosphere in 1991 due to the combustion of fuel oil by utilities totaled 143 tons. Pollution control by consumers of the remaining 312 million barrels of fuel oil was insignificant, resulting in the emission of 2,421 tons of vanadium pentoxide for a total emission by fuel oil of 2,564 tons vanadium pentoxide (1,436 as V) in 1991.

# NATURAL SOURCES OF VANADIUM EMISSIONS

## THE ANNUAL GLOBAL VANADIUM CYCLE

The flow of vanadium through the global environment was characterized by Bengtsson and Tyler (19). Bengtsson and Tyler attributed only minimal releases of vanadium to human activity, but cautioned that knowledge of vanadium in the atmosphere is still scanty. The total amounts present in the earth's crust may be estimated with a fair degree of accuracy, but little is known of how much of this is actually biologically available. According to Bengtsson and Tyler, the amounts of vanadium present in the other segments of the global environment can only be stated with an accuracy of about one order of magnitude, which is insufficient as a reliable data base that can be used in an environmental model.

Vanadium is quite abundant in the earth's crust, at 110 ppm, ranking 10th in abundance of the minor elements. In seawater, vanadium ranks 15th of all non-gaseous elements. Natural vanadium occurs in igneous rocks and shales, in titaniferous magnetites, in some phosphate deposits, in uranium ore, and in asphaltic deposits on all continents.

Fresh water contains varying amounts of vanadium, depending on the source. The uranium ores of the Colorado Plateau supply its rivers with vanadium up to 70 ppb. Wyoming waters may contain up to 220 ppb (20). On the other hand, some rivers are totally devoid of vanadium (21). When the soluble vanadium in rivers empties into the sea, much of it is precipitated, enriching marine mud. The concentration of vanadium in seawater is about 2ppb (22).

Vanadium probably does not occur in clean air, unless it is carried in dust from vanadiferous soils, volcanoes, or seasalt sprays. The National Air Sampling Network has analyzed air from a number of areas (23). The highest concentrations of vanadium were found in cities along the Eastern Seaboard. (See table 5.)

Table 5.—Vanadium in air, yearly average for selected cities

| City | 1965 $\mu g/m^3$ | 1967 $\mu g/m^3$ |
|---|---|---|
| New York, NY ............... | 0.388 | 0.905 |
| Paterson, NJ ............... | — | 0.565 |
| New Haven, CT ............... | 0.328 | 0.490 |
| Jersey City, NJ ............... | 0.263 | 0.487 |
| Bayonne, NJ ............... | — | 0.445 |
| Perth Amboy, NJ ............... | 0.153 | 0.390 |
| Newark, NJ ............... | 0.258 | 0.345 |
| Providence, RI ............... | 0.341 | 0.271 |
| Philadelphia, PA ............... | 0.133 | 0.264 |
| Baltimore, MD ............... | 0.255 | 0.200 |
| Wilmington, DE ............... | 0.116 | 0.190 |

Source: Reference 23.

Much of the vanadium in the atmosphere along the eastern seaboard and other parts of the world can be attributed to the burning of fuel oil that contains vanadium. But this source does not account for all of the vanadium nor does it account for the presence of measurable concentrations of vanadium in areas where little or no fuel oil is burned. Nriagu et al. have stated that natural sources, such as volcanoes, seasalt spray, and the weathering of soil and rocks, contribute to the threshold (24). Nriagu, on the other hand, disagreed with the quantitative estimates of natural emissions, stating that in many instances the estimates are based on educated guesses and are not confirmed by measurements. Also, in those cases where some

measured data are available for a certain natural source, e.g., volcanic eruptions, vast disagreements between measurements by different investigators make this information virtually useless. Using the most recent data available, Nriagu estimated the worldwide emissions of vanadium from natural sources at $1.6 - 54 \times 10^9$ g/yr with a median value of $28 \times 10^9$ g/yr *(25)*. Nriagu estimated anthropogenic emissions of vanadium to the atmosphere in 1983 at $86 \times 10^9$ g/yr. A comparison of Nriagu's median values of the worldwide emissions of vanadium from natural and anthropogenic sources suggests that industrial emissions of vanadium exceeds natural emissions by a factor of 3.

A brief mention of vanadium in titanium concentrates is warranted. In 1991, the United States consumed 738,089 tons of ilmenite concentrate, 341,379 tons of titanium slag, and 368,643 tons of rutile concentrate *(26)*. The ilmenite and rutile concentrates contained about

0.14 wt % $V_2O_5$; the titanium slag contained about 0.6 wt % $V_2O_5$. Given this information, the amount of vanadium in these materials was calculated:

$$(738,085 \times 0.0014) + (341,379 \times 0.006) + (368,643$$

$$\times .0014) = 3,598 \text{ tons } V_2O_5$$

About 90% of the titanium concentrates processed in the United States were consumed by the paint industry, using the chloride process *(27)*. Vanadium ends up in the chlorinator waste and, at present, does not enter into the vanadium use/reuse cycle. The Bureau of Mines Albany Research Center, Albany, OR, has developed a process that recovers about 65% of the vanadium in chlorinator waste. At this rate of recovery, titanium chlorinator wastes could supply 30% to 35% percent of U.S. vanadium demand.

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# APPENDIX.—HISTORY OF VANADIUM

Vanadium was first isolated from lead ores from Zimapan, Mexico by Mexican mineralogist Andres Manuel del Rio in 1801. Del Rio gave his new substance the name erythronium, from the Greek erythrose (red), because of the red color produced when the metal salts were heated in acids. However, the new material was not thoroughly characterized, and del Rio's claim to have discovered a new element was challenged a few years later by H. V. Collet-Discotils. Collet-Discotils declared that del Rio's discovery was nothing more than impure chromium. Del Rio accepted this criticism and agreed that in all probability the material was lead chromate. In 1830, Swedish chemist N. G. Sefström examined an iron ore sample obtained from an orebody in Taborg, Sweden and isolated what he thought was a new element. Sefström named his new element vanadium, from Vanadis, the Scandinavian goddess of love, beauty, and fecundity. Sefström named the new element after Vanadis because of the beautiful colors it produced in solution. In the same year that Sefström made his discovery, German chemist F. Wöhler re-examined the lead ore from Zimapan and determined that the substance found and abandoned by del Rio was indeed a new element and identical to the material Sefström called vanadium.

Berzelius worked out much of the basic chemistry of vanadium, but erroneously concluded that the oxide was the metal itself. The English chemist, Henry Roscoe, made extensive studies of the chemistry of vanadium and its compounds in the 1860's and showed that all of the compounds studied by Berzelius had contained oxygen. Roscoe also prepared the relatively pure metal for the first time in 1868 and placed it properly in group V of the periodic table.

Because of its great affinity for carbon, nitrogen, and oxygen, vanadium was extremely difficult and expensive to produce in pure form. This high cost and scarcity of vanadium in the early 1870's restricted its commercial development. Commercial use of vanadium was limited to the use of salts, to some extent, in the manufacture of aniline black (probably as an oxidant), the manufacture of vanadium writing ink (usually of poor quality), and the production of blue, brown, green, and purple colors in glass. The metallurgical investigations of Choubley (1896), Hèlouise (1897), Arnold (1900), and Guillet (1904) focused attention on the usefulness of vanadium as an alloying agent for steel. Other scientists such as Mossan, who in 1894 produced vanadium metal in an electric furnace, and Gin, who made ferrovanadium aluminothermically, added to the general knowledge of the properties of vanadium and its compounds.

Despite the knowledge gained of the chemistry and metallurgy of vanadium, at the turn of the century it remained little more than a chemical curiosity with no commercial value because it was rare and its high cost prohibited extensive use. The supply and cost restrictions were significantly altered in 1905, when Antenor Rizo-Patron discovered the first large deposit of rich vanadium ore in the Peruvian Andes mountains. The mineral, an impure sulfide, was named patronite in honor of Rizo-Patron. The deposit, known as the Mina Ragra deposit, provided the bulk of the world's vanadium requirements for many years. Continued field work in 1909 and 1910 revealed new sources of vanadium in South Africa and Turkestan. In the United States, vanadium-bearing minerals were found in Arizona, Colorado, Nevada, New Mexico, Oklahoma, Oregon, Utah, and Arkansas. With the possible exception of the Arkansas deposits, none of the mineral deposits outside the Colorado plateau area have since become important sources of vanadium. The first recorded commercial production of vanadium ores in the United States was in 1910. By 1941, the United States had become the world's largest producer of vanadium.

**Historical Consumption.**—Trends in U.S. consumption of vanadium from 1920 to 1990 are shown in figure A-1. The beneficial effects of adding vanadium to tool and structural steel were discovered in the early 1900's. At about the same time, vanadium pentoxide was found to be an effective catalyst in the production of sulfuric acid by the contact process. Because of these applications, historical consumption of vanadium has closely paralleled general economic conditions and industrial activity. Vanadium consumption is especially influenced by conditions in the steel industry.

A comparison of vanadium consumption by end-use in 1981 and 1991 is shown in figure A-2. The data indicates that the end-use pattern did not change significantly over the 10 year period covered. The pattern has changed only slightly since vanadium was established as the alloying element of choice for producing tough, wear resistant steel.
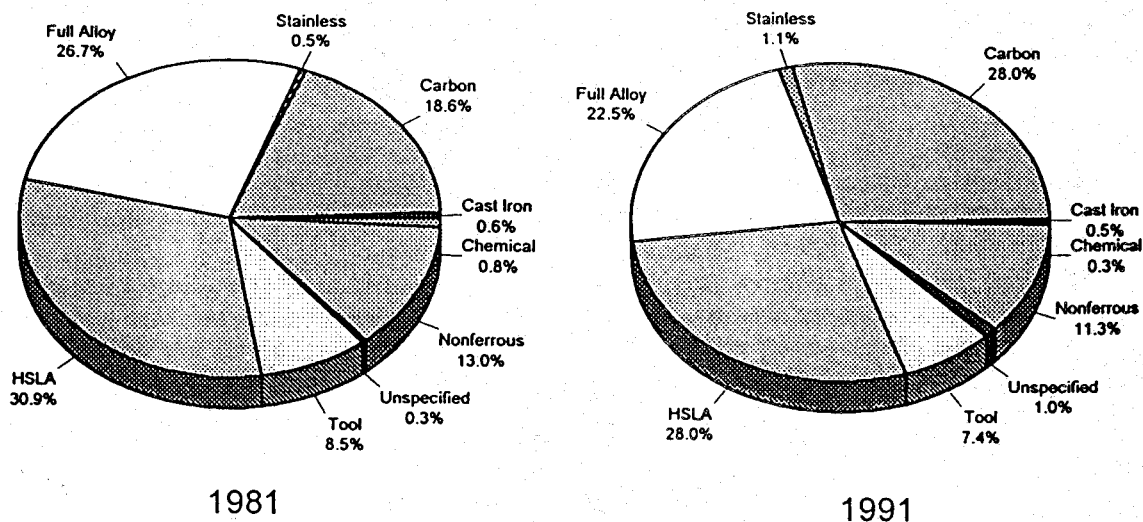
*Figure A-1*
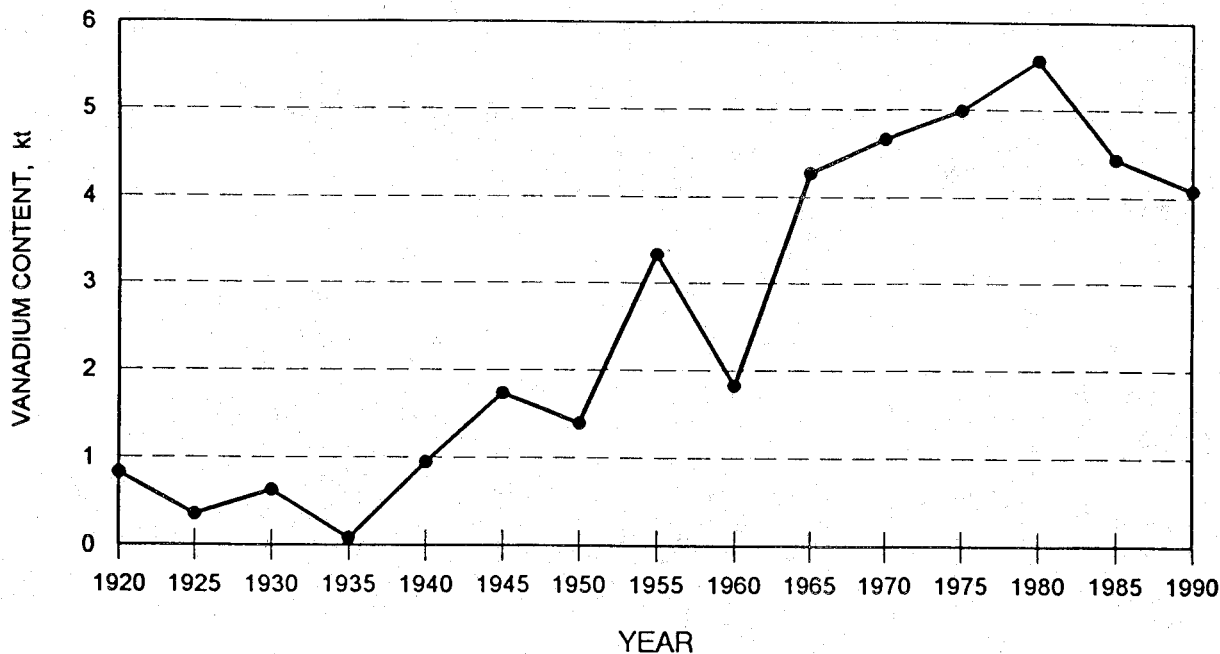


Source: U.S. Bureau of Mines. Minerals Yearbooks 1920-1990.

*Vanadium consumption, 1920-1990.*

*Figure A-2*



Source: U.S. Bureau of Mines. Minerals Yearbooks 1981, 1991.

*Trends in vanadium use.*