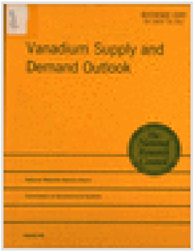

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VANADIUM SUPPLY AND DEMAND OUTLOOK

Report of

The Panel on Trends in Use of Vanadium

of the
Committee on the Technical Aspects of
Critical and Strategic Materials

NATIONAL MATERIALS ADVISORY BOARD
Commission on Sociotechnical Systems
National Research Council

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1978

NOTICE

The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the Councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the panel responsibile for the report were chosen for their special competence and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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PREFACE

Changing technology and requirements in the marketplace necessitate a periodic review of the various materials contained in the national stockpile. The U. S. Bureau of Mines of the Department of the Interior compiles statistics monthly and annually on the availability and usage of various minerals and materials required by U. S. industry. Some of the more critical materials, especially those that are totally or heavily imported, undergo an in-depth periodic review by experts. Vanadium is one such critical material. The last in-depth examination of vanadium was the study NMAB-267, "Trends in the Use of Vanadium," issued in 1970.

To get a wide viewpoint on current and projected trends in the use of vanadium, the Federal Preparedness Agency of the General Services Administration, the Bureau of Domestic Commerce of the U. S. Department of Commerce, and the U. S. Bureau of Mines of the U. S. Department of the Interior requested the National Materials Advisory Board to conduct a panel study in this regard. Data provided by this study were intended to provide guidance on the updated forms and the relative quantities of vanadium, its alloys and compounds to be considered for inclusion in the national stockpile. The panel also considered the bearing import dependency for this material has upon the nation's industrial posture and capability, especially at a time of national emergency.

The statement of charge to the panel was as follows:

<u>Purpose</u>: To assess the implications of technological change and usage trends, from the viewpoint of essential civilian needs and military requirements, on the supply/demand balance of vanadium in applications utilizing, or likely to utilize, vanadium.

<u>Approaches</u>:

1. Study the applications utilizing vanadium.

2. Identify areas of growth.

3. Indicate where technological change may affect the usage of vanadium.

4. Recommend areas of research.

The study is based on information collected through November 1977.

ACKNOWLEDGMENTS

This study was conducted by a select panel of technical experts under the chairmanship of Dr. William Rostoker, Professor of Metallurgy at the University of Illinois in Chicago, Illinois. The panel embodies the viewpoints of the raw materials supplier, the processor, the user and the technical economist. All these individuals gave of their time from important industrial and academic positions to prepare this survey. Grateful acknowledgment is made for the support from the sponsoring agencies: General Services Administration, Department of Commerce and the U. S. Bureau of Mines.

Equally important are the statistical contributions made by the liaison representatives. Usually this group lends guidance to the panel, but in this study they also made important data contributions to the report.

We are most thankful for the dedicated effort by the entire group. Also acknowledged is the work of now-retired NMAB Staff Officer Mr. Ben A. Kornhauser, who prepared the scope of the study topic and assembled the panel.

PANEL ON TRENDS IN USE OF VANADIUM

of the Committee on
Technical Aspects of Critical and Strategic Materials

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ABSTRACT

A review has been made of the reserves and resources for vanadium minerals in the United States and foreign countries. While both domestic and foreign sources are presently utilized, domestic production could provide, for some time, for national needs. Foreign sources are now used to provide a substantial part of national demand because of price advantages. There are so many functioning foreign sources for vanadium that it is difficult to conceive of circumstances that would shut all of them off. Recovery of vanadium as a byproduct of processing Venezuelan petroleum looms as a major new large supply in the near future.

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Chapter One

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

A. SUMMARY

There are a number of well-established uses of vanadium as an addition to steels and irons; uses that will persist in the foreseeable future and will represent a stable demand that will grow with the demand for these conventional steels and irons. The use of vanadium in titanium alloys also is in a stable pattern and growth demand will follow the demand for titanium alloys. There is a wide variety of applications for vanadium oxides and compounds in the chemical and polymer industries which represents 7 to 11 percent of the total usage of vanadium in this country.

By far the greatest growth potential for vanadium demand lies in the changing patterns of use of high-strength, low-alloy (HSLA) steels. There is an increasing demand for these steels for weight saving with no reduction in strength.

Projected demands for vanadium up to 1990 do not appear to challenge available resources. This country is in the happy position of having substantial resources of its own and a diversity of sources worldwide that would make embargo or consortium problems unlikely. New potential sources of vanadium from petroleum processing are nearly developed and might supplant mining sources. However, substantial future demands for vanadium for domestic consumption will probably be met in part by imported mineral materials from outside North America, primarily due to economic factors.

There are no applications of vanadium in metals for which substitution by other alloying elements is unacceptable. However, the present usages of vanadium are based on sound technical preference and competitive pricing. In most chemical industry uses, there are no currently acceptable alternatives to vanadium oxides and chemicals.

Projected demands for vanadium in the United States (all uses) for the years 1980, 1985 and 1990 are detailed and summarized in Table 1. For the definitions of what each use category implies and the technical justification, the reader is referred to individual sections in the text under these

TABLE 1 Projected United States Demand for Vanadium (1,000 pounds contained vanadium)

Use	1980	1985	1990	Chapter References
Tool Steels	1,130	1,130	1,130	8 — Assumes no growth
Engineering Alloy Steels	3,500	4,050	4,820	9 — Assumes Bureau of Mines data
Carbon Steels	1,400	1,500	1,600	10
High-Strength, Low-Alloy Steels	6,200	7,500	8,300	11
Cast Steel	530	689	895	12
Cast Iron	378	493	673	13
Stainless and Heat Resisting Steels	51	61	72	14
Superalloys	45	50	55	15
Titanium Alloys	1,030	1,090	1,140	16
Chemical Applications	1,074	1,452	1,930	18
TOTAL	15,338	18,015	20,615	

titles. In most cases, these numbers project reasonably from the 1976 demand figures published by the U.S. Bureau of Mines (Table 2). There is one serious discrepancy. For engineering alloy steels (full alloy steels), the AISI Form 7A and Bureau of Mines figures differ by as much as a factor of four, and there is no sufficient explanation. One factor is the voluntary industrial reporting system, which does not contain complete or accurate data. Table 1 is a projection based on the Bureau of Mines data. The difference in the total projected demand would be as much as 15 percent.

Some additional errors in estimating vanadium demand are inescapable at this time. Unknown quantities of vanadium are imported into the United States in the form of finished products. These are not identified; they fluctuate in identity and volume transacted, and the presence of vanadium is not always in the chemical specification. In domestic production as well, there is a large volume of steel produced to which vanadium is added in small amounts to meet performance requirements -- contents which are not required by specification nor reported.

Recycling of vanadium is confined to "home scrap" of manufacturers of products containing relatively high concentrations in alloys and represents in-plant circuits. Otherwise, most vanadium in obsolete steel scrap is lost in the general steel recycle.

The national stockpile goals for 1976 indicate a reserve of about 16 million pounds of contained vanadium in an unspecified variety of grades of ferrovanadium and vanadium pentoxide. This amount represents substantially more than one year's needs for this country at the present time. These stockpiled items should be applicable to most of the <u>major</u> vanadium-bearing materials actually used by U.S. industry, but not all are covered. For example, there is no fraction for vanadium-aluminum, which is essential in the titanium industry. In an emergency requiring the use of the stockpile, this would have to be processed from the V_2O_5 reserves in the stockpile.

These estimates of demand are made with the assumption that import/domestic production ratios will not change. However, it is already obvious that this is a changing or at least fluctuating pattern in the tool steel industry. These estimates of demand could be substantially changed by heavier imports with a consequent impact on the vanadium-producing industries.

TABLE 2 Consumption of Vanadium in the United States by End Use, 1976*
(1,000 pounds contained vanadium)

End Use	Vanadium Consumption
Steel	
Carbon	1,032
Stainless and Heat Resisting	42
Full Alloy	2,622
High-Strength, Low-Alloy	3,272
Electric	not available
Tool	1,130
Cast Irons	122
Superalloys	38
Welding and Hard Facing Rods and Materials	18
Nonferrous Alloys (Including Magnetic)	626
Chemical and Ceramic (Including Pigments)	424
Miscellaneous and Unspecified	114
TOTAL	9,440

NOTE: Data from U.S. Bureau of Mines, 1976.

* The consumption of vanadium (as well as other materials) in 1976 was substantially lower than in previous years.

B. CONCLUSIONS

Examination of current and projected consumption of vanadium in the United States has brought out some conclusions of specific interest:

1. The vanadium reserves of the North American continent could satisfy the United States demand for many years. It is likely, however, that it will be more attractive economically to import vanadium products such as slags and residues for processing in existing facilities rather than constructing new facilities to work new domestic deposits.

2. Vanadium imports are from many diverse foreign sources and are based on advantageous prices. It is unlikely that all of these sources would ever be closed off at any one time.

3. Recovery of vanadium from Venezuelan petroleum crude oils is likely to become a major new source of supply. The process would remove vanadium in the refinery so that the petroleum products would be substantially vanadium-free.

4. Vanadium is a critical component of the national stockpile.

5. Vanadium carbide, vanadium-silicon alloy can be used interchangeably with ferrovanadium and could be represented in the national stockpile.

6. The national stockpile lacks a vanadium-aluminum master alloy necessary for the production of high-strength titanium alloys, especially critical in times of national emergency.

7. Continuous billet casting of steel may become a diminishing user of vanadium because of improved technology.

8. The largest future growth in vanadium consumption

is likely to be in expanded use of high-strength low-alloy steels.

9. Titanium alloy technology relies heavily on vanadium as one of the most important alloying elements.
10. Vanadium oxides and chemical compounds are essential in numerous chemical catalytic processes.
11. Vanadium and molybdenum could be used in place of imported tungsten for tool steels in a national emergency.
12. The use of vanadium alloys in nuclear fission reactors is not a first choice.
13. No wrought vanadium (unalloyed or alloyed) production capability exists in the United States, but it could be reactivated if a market develops for such products.

C. RECOMMENDATIONS

From the foregoing discussions, the following advances in technology appear to be feasible and desirable in the national interest:

1. Investigation of the economics and feasibility of recovery of vanadium from Idaho phosphate ores.
2. Development of improved sintered carbide formulations for cutting tool applications which utilize vanadium in place of tungsten.
3. Development of engineering steels with pearlite structures that utilize vanadium to strengthen by carbo-nitride precipitation.
4. Study of the mechanisms of vanadium in grain refinement of cast steels.
5. Development of micro-alloying as a basis for strengthening of cast steels.

6. Development of an economical technology for the recovery of vanadium from crude oil and from refinery residues.

7. Development of vanadium as a substitute for nickel in wear-resistant white cast irons.

8. Improvement in design of "net shape" forgings of titanium alloys to reduce the consumption of vanadium (among other reasons).

9. Investigation of the advisability of including the 65%V-35%Al master alloy as an appropriate component of the National Stockpile.

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Chapter Two

INTRODUCTION

Vanadium has a relatively long history of use as an alloying addition to steel. Its widespread use in steelmaking occurred after World War II. This development was enhanced by the ready availability of domestic vanadium supplies as a byproduct of uranium extraction operations in the United States. The maturing titanium industry also created a new outlet for vanadium production. Nuclear applications for unalloyed metallic vanadium received some attention, but this never materialized as a substantial market. The use of vanadium in steels, the major user, has now been well established and has become one of the essential elements in the industry.

There are a number of well recognized functions that these additions provide to the performance of a large number of different classes of steels. In almost no instance is the role of vanadium unique. Other elements can serve the various alloying functions but the choice of vanadium is consistent and is based on current considerations of availability, efficient utilization, and price. Vanadium in the form of oxides or chlorides serves a variety of functions in the chemical and plastics industries. While the tonnage demand in the chemical industry is less than in steel, alternatives to the use of vanadium in chemicals are fewer. In the titanium industry, vanadium is a major alloying addition.

For metallurgical purposes vanadium is provided in several forms: ferrovanadium (low and high carbon), vanadium-aluminum, vanadium carbide, vanadium nitro-carbide, molybdenum-vanadium-aluminum, and vanadium-iron-chromium-silicon-manganese. The vanadium-aluminum (alumino-thermic) master alloy serves the titanium industry; the others serve the steel industry. For simple addition of vanadium to steel, the ferrovanadiums and vanadium carbide may be used interchangeably.

Mining and extraction for vanadium occurs in many parts of the world. There are no sources or resources that can dominate world supply. Processing to metallic material may occur in stages in several different places. For example, an iron ore mined in one location will be converted to steel in another location along with a vanadium-rich slag, made soluble by roasting and recovered as vanadium pentoxide in still another location and finally smelted to a metallurgical product in a fourth location. The United States gathers vanadium oxides and vanadium-rich slags from various parts of the world for domestic use and some exports.

Vanadium can be produced as a pure metal which is ductile enough to allow production in all finished forms: sheet, wire, tube, etc. There is no facility in the United States which currently manufactures vanadium-base alloys in fabricable form. However, the technology was developed in this country and still exists (see bibliography).

This document reviews the technical issues involved in the recovery and use of vanadium with the intent of projecting the demand, supply and their interrelationships for the next two decades. A similar task was performed some years ago and report NMAB-267, Trends in the Use of Vanadium, was issued in March 1970. The present report has reexamined the subject completely.

There exists a worldwide association of vanadium producers and users called VANITEC. It is an international technical organization dedicated to the promotion of technical and scientific research to increase the knowledge of vanadium and of its effects on the properties of steel and other materials. It consists of 18 members from countries in Europe, North America, South America, and Japan. Since its inception, it has sponsored research projects at several research organizations including Contro Sperimentalo Metallurgico in Rome, National Physical Laboratory and Welding Institute in the United Kingdom, the Swedish Institute for Metals Research, and the Massachusetts Institute of Technology. It has also sponsored projects at steel companies. VANITEC also sponsors technical seminars and publishes data sheets and monographs on the technical use of vanadium. (VANITEC's mail address is: VANITEC, Vanadium International Technical Committee, Westgate House, 9 Holborn, London, EC1N 2NE, England.)

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Chapter Three

VANADIUM RESERVES AND RESOURCES

Current world reserves and resources were reported to be 10.7 million and 62 million short tons of vanadium, respectively (Broderick, 1977). If additional amounts for which only limited data are available are included (Fischer, 1975), world resources of vanadium may be at least 78 million short tons. Thus, in comparison to a recent annual world production rate of about 42,000 short tons, the identified world reserves and resources of vanadium are sufficient to meet demand for hundreds of years even at greatly expanded production rates.

Because reserves are considered not only on the basis of identified quantities of suitable source materials, but also on the basis of existing and planned production capabilities for making the materials available for use, it is important that the latter be considered.

Mill capacities for production of vanadium in the United States and in the other market economy countries have been estimated to be 19 million pounds and more than 42 million pounds, respectively, for 1973 (Shortsleeve, 1975). Milling capacities were expected to be increased to 21.1 million pounds for the U.S. by 1976 and to 62.4 million pounds for the other market economy countries. Thus, both the reserve base and the milling capabilities are considered to be adequate to meet near-term demand, providing the mining capacity is maintained at an appropriate level.

A. DEFINITIONS

The term "reserves" is used to denote identified mineral materials that can be mined at a profit or to economic advantage under existing and anticipated near future conditions. The broader term, "resources," refers to both reserves and identified potential ores--those materials that may be mined to economic advantage when conditions become more favorable for their utilization. The mineral resource total is subject to continuing appraisal, and the classification of materials as reserves is subject to revision as economic and technologic conditions change.

Because vanadium is produced mainly as a coproduct or byproduct of other mineral materials, amounts of reserves for the U.S. are discussed in terms of contained vanadium (V) in source materials that are expected to be extracted by the year 2000 and from which vanadium is expected to be recovered. Recovery rates are less than 100 percent. In some cases, a vanadium source material, such as phosphate rock, for example, may be mined and processed for its major mineral component and much of the vanadium may not be recovered because of lack of facilities or of market incentives. An alternative would be to set aside these tailings as a future source of ore when needed.

B. GEOLOGICAL CHARACTER OF VANADIUM RESOURCES

The geochemical nature of the element vanadium is such that deposits of vanadium generally contain less than two percent of the metal. Therefore, most vanadium is produced as a coproduct or byproduct of other materials. In some deposits, vanadium is present in discrete vanadium mineral species, but much of the vanadium currently produced is recovered from ores in which no specific vanadium ore mineral is recognized (Fischer, 1973).

The following vanadium-bearing ore minerals are of importance and are included as background information:

	Approximate Percent V
In Sandstone-Type Deposits	
Montroseite (V,Fe)O(OH)	45
Fervanite $Fe_4(VO_4)_4 \cdot 5H_2O$	24
Hewettite $CaV_6O_{16} \cdot 9H_2O$	39
Roscoelite $K(V,Al,Mg)_3(Al,Si_3)O_{10}OH$	12
Carnotite $K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$	11
Tyuyamunite $Ca(UO_2)_2(VO_4)_2 \cdot 5\text{-}8H_2O$	11

	Approximate Percent V
In Base Metal Deposits	
Vanadinite $Pb_5(VO_4)_3Cl$	11
Descloizite-Mottramite Series $PbZn(VO_4)(OH)/PbCu(VO_4)(OH)$	12
In Asphalt Deposits	
Patronite VS_4	up to 28
In Magnetic Iron Deposits	
Coulsonite $(Fe,V)_3O_4$	up to 46
Magnetite (titaniferous) $(Fe,Ti,V)_3O_4$	generally less than 2

The principal types of deposits which contain vanadium in economic concentrations, or from which vanadium is potentially recoverable, include the following (see Table 2 for worldwide distribution), some of which contain ore minerals listed above:

Magnetite Deposits -- principally titaniferous magnetite in hard rock ore bodies, but also in placer sand deposits

Minette-Type Iron Ore Deposits

Uranium-Vanadium Deposits in Sandstone

Vanadiferous Shales and Clays

Vanadiferous Phosphate Rock

Tar Sands and Asphaltite Deposits

Petroleum Deposits

Vanadiferous Base Metal Deposits

Vanadiferous Vein Type Deposits of Gold, Tellurium, or Vanadium

Bauxite Deposits Derived from Mafic and Ultramafic Rocks

Not all of these are currently exploited for the U.S. industrial market. Vanadium reserves and conditional reserves in types of deposits from which the element is currently being recovered in the U.S. are estimated to be:

	1,000 pounds Contained Vanadium
Vanadiferous Phosphate Deposits (Idaho)	254,000
Vanadiferous Uranium Deposits (Western States)	90,000
Vanadiferous Shale (Arkansas)	60,000
TOTAL	404,000

Although vanadiferous/titaniferous magnetite concentrates are available in the U.S., and vanadium is extracted from similar material in other countries, this material is currently not considered to be in the category of reserves in the U.S., but is part of the resources.

C. VANADIUM RESERVES AND RESOURCES

Reserves of vanadium in the various types of ores from which vanadium is currently being recovered in the United States are equivalent to more than 20 years of supply at recent annual domestic production rates. Estimates reported by the U. S. Bureau of Mines (Taylor and Broderick, 1976) list domestic reserves of 115,000 short tons and resources of almost 10 million short tons of vanadium. An additional amount of 87,000 tons of contained vanadium has been identified as conditional reserves in similar types of deposits that will be available for extraction if environmental and other technical factors are resolved. Overall domestic vanadium resources are about 28 million short tons if some large low-grade resources in Alaska are included. Alaska accounts for some 94 percent of the total U.S. resources, a source not currently exploited for domestic consumption; see breakdown in Table 3.

Presently identified domestic reserves of vanadium would be totally depleted by the year 2000 if average production rates increase by 3 percent annually from the 1975 rate, assuming 85 percent recovery of vanadium from ores. The overall domestic resource base, however, is adequate for substantial expansion of the vanadium industry. Data obtained from the U.S. Geological Survey (Hollingsworth, 1967), the U. S. Bureau of Mines (Broderick, 1977), and the Department of Energy have been used in this assessment of the status of vanadium resources.

World resources of vanadium are shown in Table 3. Free world sources are mainly in Australia, Southern Africa, Canada and Alaska.

TABLE 3 World Resources of Vanadium

Country and Location	Ore Type	Vanadium Content (%)	Resources (million pounds contained V)		Status
			Known	Inferred	
United States					
Arkansas	Vanadiferous Clays	0.4-0.7	60 (0.14%)*	Unknown	Being worked for V only.
Colorado, New Mexico, Utah, Arizona, South Dakota, and Wyoming	Vanadiferous Uranium Ores	0.06-0.5	90 (0.21%)	Unknown	Being worked or planned for production of U and V.
Idaho	Vanadiferous Phosphate Rock	0.08-0.46	254 (0.59%)	16,000 plus	Being worked for P and V.
Idaho and Wyoming	Vanadiferous Shale	0.4-0.7	600 (1.40%)	Very large	Inactive
New York	Titaniferous Magnetite	0.15-0.3	500 (1.17%)	Unknown	Processed for Ti. V not recovered.
Rhode Island	Titaniferous Magnetite	0.17	42 (0.10%)	None	Inactive
Minnesota	Titaniferous Magnetite	0.05-0.11	180 (0.42%)	Unknown	Inactive
Wyoming	Titaniferous Magnetite	0.02-0.36	500 (1.17%)	Unknown	Inactive
California	Titaniferous Magnetite	0.3	60 (0.14%)	Unknown	Inactive
Alaska					
Snettisham	Titaniferous Magnetite	0.05	450 (1.05%)	Unknown	Inactive
Klukwan	Titaniferous Magnetite	0.17-0.2	26,000 (60.84%)	Unknown	Inactive
Iliamna Lake	Titaniferous Magnetite	0.02	14,000 (32.76%)	Unknown	Inactive
Total United States			43,000 (100.0%)**		
Argentina					
Province of Mendoza	Vanadiferous Asphaltite and Petroleum Residues	0.3-0.8	Unknown	Unknown	—

* Percent of total United States known resources.

** Figures may not add due to individual rounding.

TABLE 3 World Resources of Vanadium (continued)

Country and Location	Ore Type	Vanadium Content (%)	Resources (million pounds contained V) Known	Inferred	Status
Chile					
Province of Coquimbo (El Romeral)	Vanadiferous Magnetite	0.4	896	Unknown	Worked for Fe and V.
Peru					
Province of Pasco, Department of Junin	Vanadiferous Asphaltite	0.25-0.85	Unknown	Unknown	Formerly a major source of V.
Venezuela	Crude Oil	230 ppm in crude oil	200	2,800	Being processed for V.
Canada					
Quebec					
Allard Lake	Titaniferous Magnetite	0.15-0.2	1,000	Unknown	Worked for Ti and Fe.
Magpie Mountain	Titaniferous Magnetite	0.1-0.2	5,000	Unknown	Inactive
St. Urbain	Titaniferous Magnetite	0.1-0.2	80	Unknown	Inactive
Other Deposits in Quebec, Ontario, Manitoba, and British Columbia	Titaniferous Magnetite	0.05-0.4	Unknown	Unknown	Inactive
Alberta	Tar Sands	150 ppm	7,000	Unknown	V not recovered.
	Crude Oil	230 ppm in crude oil	Unknown	Unknown	Being processed for V.
U.S.S.R.					
Urals					
(Mt. Kachkanar, Kusinskoe, Pervouralsk)	Titaniferous Magnetite	1.9	14,000	Unknown	Worked for Fe and V.
Karolo-Kola (Pudozhgarskoe)	Titaniferous Magnetite	0.3-0.6	2,600	Unknown	Not available.

TABLE 3 World Resources of Vanadium (continued)

Country and Location	Ore Type	Vanadium Content (%)	Resources (million pounds contained V) Known	Inferred	Status
Finland					
Otanmaki	Titaniferous Magnetite	0.6	250	Unknown	Being worked for Fe, Ti and V.
Sweden					
Routivare, Kramsta, Ulvo, Taberg	Titaniferous Magnetite	0.1-0.6	836	Unknown	Not available.
Norway					
Hattevarre, Selvag, Rodsand, Storgangen	Titaniferous Magnetite	0.3-0.5	240	Unknown	Not available.
Australia					
Barrambie	Titaniferous Magnetite	0.3-0.4	1,200	Unknown	—
Windowe	Titaniferous Magnetite	1.1	280	Unknown	—
Jameson Range, Balla Balla, Andover, Gabarinthe-Yarrabuda	Titaniferous Magnetite	0.3-1.4	66	Unknown	—
New Zealand					
Kawhia-Aotea	Titaniferous Magnetite Sands	0.2	57	Unknown	—
South Africa					
Bushveld Complex	Titaniferous Magnetite	0.8-1.0	34,000	Unknown	Worked for Fe and V.
South West Africa					
Otavi District	Vanadiferous Base Metal Deposits	0.5	—	—	Base metals and V recovered.
Mozambique					
Tete	Titaniferous Magnetite	0.3	1,600	Unknown	—

TABLE 3 World Resources of Vanadium (continued)

Country and Location	Ore Type	Vanadium Content (%)	Resources (million pounds contained V)		Status
			Known	Inferred	
Tanzania					
Eastern Upanga (Liganga)	Titaniferous Magnetite	0.4	320	Unknown	—
Upper Volta					
Dori	Titaniferous Magnetite	0.3	300	Unknown	—
China, Peoples Republic of					
Ssuchuan (Panchihua)	Titaniferous Magnetite	0.3	Large	Unknown	Probably being worked for Fe and V.
Japan					
Provinces of Hokaido, Tohuku, Kanto, Chugoku and Kyushu	Titaniferous Magnetite (Beach Sands)	--	Large	Unknown	—
India					
Bibar, Orissa, Karnakata	Titaniferous Magnetite	0.4-2.7	400	Unknown	Being worked for Fe and V or production planned.
Mahdya Pradesh, Uttar Pradesh, Karnakata	Bauxite	0.005-0.1	Moderate	Unknown	Worked for Al. Red Sludge containing 4 to 5% V recovered.

NOTE: Data from Fischer, 1975a, 1975b, 1975c; Kett, 1948; Pitman, 1977; Rose, 1973; Taylor, 1976; and Thacker, 1976.

D. UTILIZATION OF DOMESTIC VANADIUM RESERVES

The established pattern of utilization of domestic reserves of vanadium has evolved in a competitive market economy. The fact remains that potentially recoverable vanadium is discarded in waste material from some phosphate ores, and also is not recovered from domestically mined titaniferous magnetite ores. Some waste of domestic vanadium resources is inevitable in a competitive economic system, but it is in the national interest that it be minimized, especially in the present situation in which a substantial part of the vanadium consumed in the United States is obtained from imported materials.

Vanadium is presently being recovered from some phosphate ores from federally leased lands in Idaho, as a coproduct of phosphorus. Much more could be recovered if there were economic incentives to do so. The U.S. Bureau of Mines (Stowasser, 1976) has projected that phosphate reserves in Florida and Tennessee will be depleted by about the end of this century, and that increasing amounts of phosphate will be obtained from Western States. Increased vanadium production from Idaho phosphate ores may be possible as a result of the expected increase in phosphate mining and processing, and this should be investigated.

In the case of vanadium recovery from titaniferous magnetite, the possibility of processing the magnetite that accumulated as a result of mining of magnetite-ilmenite ores may be worthy of reexamination.

Discovery of vanadiferous uranium ores in the United States appears to have kept pace with depletion of previously known ores of this type. However, the domestic resource base for such ores is considerably smaller than the resource bases for vanadiferous phosphate ores and vanadiferous titaniferous magnetite ores. The rate of depletion of the vanadiferous uranium ores seems likely to exceed the rate of new discoveries. Mining of shales for vanadium as the sole or principal product is expected to continue as known deposits are phased into production.

Processing of petroleum to remove impurities for environmental and other purposes, or to produce byproduct vanadium, may also augment the vanadium supply to a greater extent. Large quantities of Venezuelan petroleum, which contains vanadium, are imported by the United States.* (See page 28 for further discussion.)

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* In 1975, the U.S. imported an average of 697,600 barrels per day from Venezuela of a total import of 12,442,000 barrels per day -- about six percent of the total U.S. imports (Fischer, 1975). In 1976, the average imports increased to 699,200 barrels per day of the total imports of 13,416,000 barrels per day -- about five percent of the total U.S. imports (Department of Energy, 1975, 1976).

The Venezuelan refining process employed today is such that vanadium, concentrated in the heavy fraction of the fuel oil, is a marketable product. Wherever the fuel oil is burned without significant dilution, the potential for vanadium recovery exists. In many instances, because the operation is small, vanadium recovery is neglected. Where recovery is practiced, two general products may be collected. They are boiler slag and fly ash. Many locations recover boiler slag as a result of periodic boiler cleanout. A few large utilities collect fly ash in off gas systems in addition to boiler slag. A very few locations, such as Long Island Lighting Company, actually recycle a part of the fly ash collected to increase efficiency and to upgrade the vanadium content of the fly ash collected. In brief, the recovery of vanadium from Venezuelan crude oil today is very low and it is spread around the world. In the future, when flexicoking is employed, vanadium recovery will be at the refinery; it will be several-fold more efficient than at present and it will be in a different product.

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Chapter Four

CURRENT AND FUTURE VANADIUM PRODUCTION

Table 4 summarizes the estimated world vanadium requirements by geographic areas. Our knowledge of Communist nations' requirements is not at the same confidence level as our knowledge of Western World requirements but the data may be regarded as reasonably accurate.

A. CURRENT VANADIUM OXIDE SOURCES

Five years ago, the U.S.S.R. exported vanadium-bearing slag (a byproduct of steelmaking based on vanadium-bearing magnetite ore) and imported vanadium master alloys. Today, only a small quantity of slag is offered to Western producers on a conversion basis, wherein fused V_2O_5 is exchanged for the slag, and purchases of vanadium master alloys from the West have declined. Evidently, after many years, the U.S.S.R. slag conversion facility is operating and the country is nearly self-sufficient regarding vanadium. Other Eastern European countries, however, still purchase vanadium pentoxide and vanadium additives from Western producers -- perhaps as much as half of the requirements listed in Table 4.

Table 5 lists sources of vanadium within the Western World that are currently supplying Western World requirements. These data are plotted in Figure 1 to show more clearly the supply-demand relationships, actual (up to 1976) and projected (1977-1990). The data do not include a number of potential sources which are known but are not now being employed, and the apparent shortfall shown in Figure 1 starting about 1979 is due to the speculative aspects of these new sources of supply. In truth, the supply will probably keep pace with the demand.

In each instance the values shown may be regarded as an estimate of the maximum that can be expected from each source. Each source has its own characteristics, and the manner in which these characteristics affect the materials flow through the normal recovery processes is described below. In these descriptions, reference is made to Figure 2, a diagram showing the flow of material through the world vanadium system.

For a number of years prior to 1968, the Colorado Plateau uranium-vanadium ores served as the major source of vanadium for United States requirements. In 1968, vanadium production from Arkansas ore was initiated as the output from the Colorado Plateau

TABLE 4 Estimated World Demand for Vanadium (million pounds V_2O_5 — 56% contained vanadium)

	1975	1976	1977	1978	1979	1980	1981	1985	1990
United States	22.1	22.4	24.6	25.7	27.0	28.7	29.8	32.6	35.4
Other Western Hemisphere	4.2	4.9	4.8	5.4	6.2	7.3	8.2	12.0	17.9
Total Western Hemisphere	26.3	27.3	29.4	31.1	33.2	36.0	38.0	44.6	53.3
Western Europe	23.8	28.0	29.6	32.7	33.8	36.0	37.5	43.7	52.6
Asia (except North Korea and Peoples Republic of China)	8.8	10.0	12.1	13.3	14.6	16.4	17.4	21.8	29.0
Africa and Mid East	0.8	1.0	1.2	1.3	1.5	1.7	2.0	3.5	6.3
Total Western World	59.7	66.3	72.3	78.4	83.1	90.1	94.9	113.6	141.2
Eastern Europe	6.7	7.3	7.8	8.6	9.1	9.5	9.7	10.8	12.8
U.S.S.R.	27.9	24.7	31.2	32.4	33.6	34.5	34.7	40.7	47.8
China (Peoples Republic of) and North Korea	2.6	2.7	3.2	3.6	4.0	4.4	4.9	6.5	9.1
Total Communist Nations	37.2	34.7	42.2	44.6	46.7	48.4	49.3	58.0	69.7
GRAND TOTAL	96.9	101.0	114.5	123.0	129.8	138.5	144.2	171.6	210.9

NOTE: Independent projection by the Panel on Trends in Use of Vanadium, based on various source data.

TABLE 5 Current Western World Vanadium Oxide Sources (million pounds V_2O_5 -- 56% contained vanadium)

Country and Source of Vanadium Oxide	1975	1976	1977	1978	1979	1980	1981
United States							
Colorado Plateau Uranium-Vanadium Ore	8.9	10.9	13.5	15.5	15.5	15.5	14.8
Vanadium Bearing Ferrophosphorous	5.0	5.0	4.4	5.0	6.0	6.0	6.0
Arkansas Vanadiferous Clay*	5.0	5.0	4.5	7.0	7.0	7.0	7.0
Residues and Spent Catalyst	4.0	5.0	5.0	5.0	5.0	5.0	5.0
Subtotal	22.9	25.9	27.4	32.5	33.5	33.5	32.8
Africa							
Vanadium Bearing Slag	24.6	24.6	27.9	38.2	38.2	38.2	38.2
Oxide from Titaniferous Magnetite	14.5	16.5	24.5	26.0	26.0	26.0	26.0
Subtotal	39.1	41.1	52.4	64.2	64.2	64.2	64.2
Chile							
Vanadium Bearing Slag	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Norway							
Titaniferous Magnetite	1.5	3.0	4.0	4.0	4.0	4.0	4.0
Finland							
Titaniferous Magnetite	4.4	9.0	11.5	11.5	11.5	11.5	11.5
Japan							
Spent Catalyst and Residues	1.7	2.1	5.4	8.7	8.7	8.7	8.7
France							
Aluminum Sludge	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TOTAL	72.6	84.1	103.7	123.9	124.9	124.9	124.2

NOTE: Independent projection based on various source data.

* Only one plant having a total capacity of about 15 million pounds per year processes this ore. The quantities shown represent an estimate of the fraction of total production that will be derived from ore.

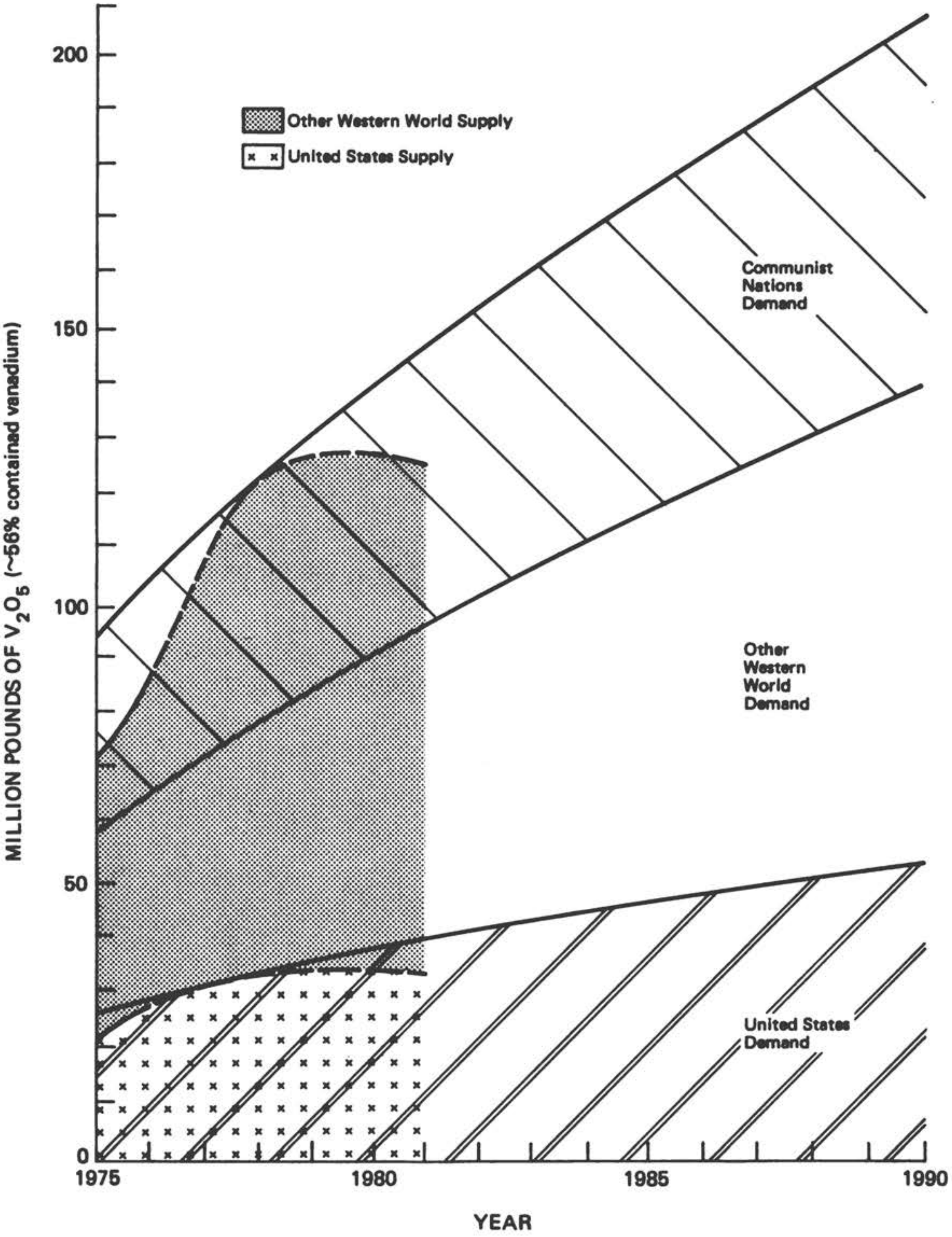
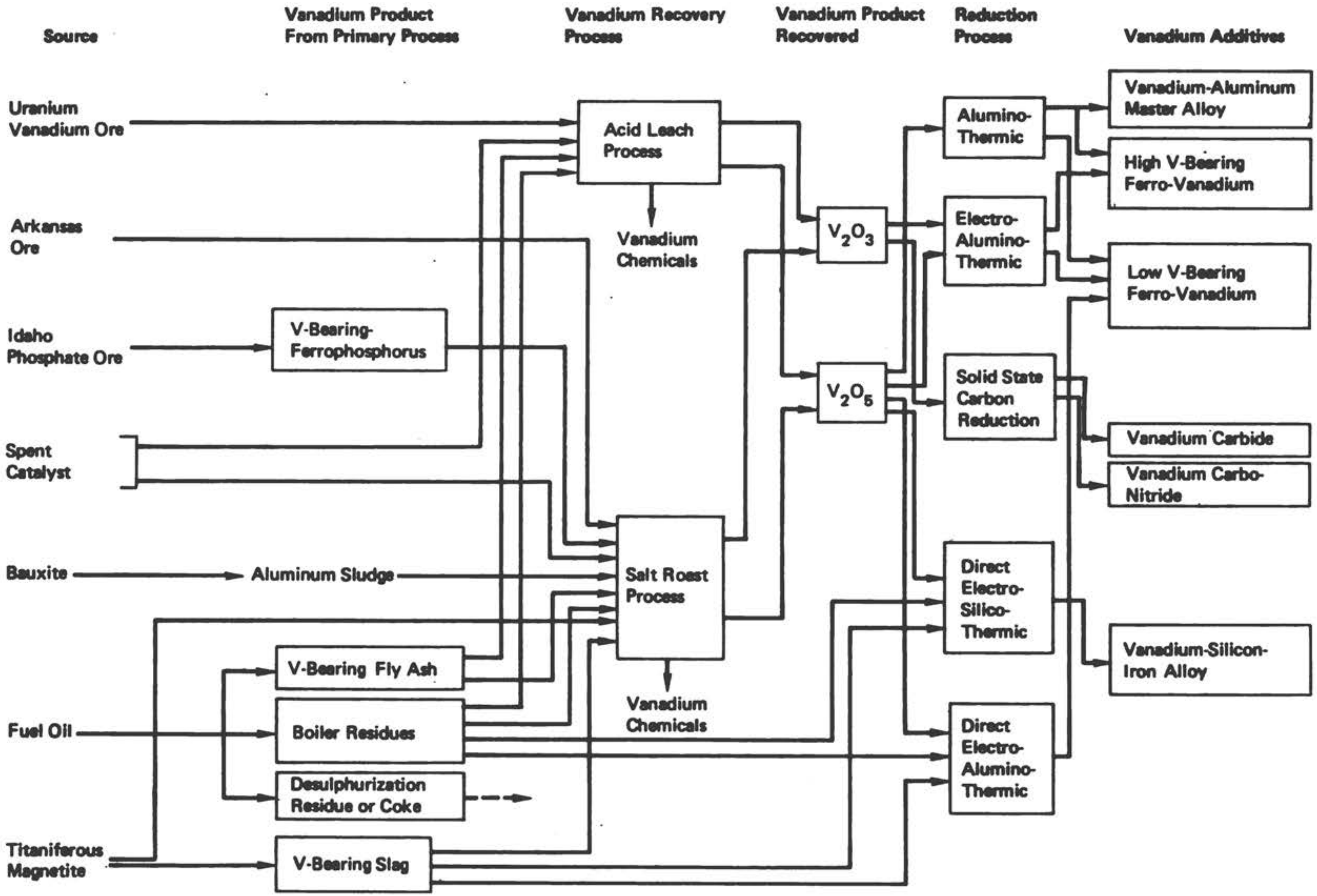


FIGURE 1 Actual and Projected Supply-Demand Picture for Vanadium Oxide

FIGURE 2 Generalized Flowsheet of Minerals Processing to Vanadium Products



declined. The recent surge in the demand for uranium, coupled with a significant increase in U_3O_8 price, has stimulated production from the Colorado Plateau. It is anticipated that production will increase, as shown, as two new facilities are brought on-stream. It is estimated that production will begin to decline after 1980 as ore grade decreases, and this trend will continue until production is terminated by uranium economics -- probably near 1990. Throughout all of this period, production will be dictated by uranium requirements, which are expected to be such that capacity production levels will be maintained. The mills processing these ores all produce fused V_2O_5 as their vanadium product. One mill also produces V_2O_3 and vanadium chemicals.

The phosphate ores of Idaho and Wyoming are the only known vanadium-bearing phosphates. At the present time, three companies process Idaho phosphates for the recovery of elemental phosphorus. Vanadium-bearing ferrophosphorus is a byproduct of these operations. Vanadium is recovered from the byproduct by salt roasting (see Figure 2). The Idaho district ore reserves are very large and the phosphorus plants of this area are among the more efficient in the industry. Therefore, this source is expected to be steady and will grow with increases in the demand for phosphorus. However, electric furnacing based on hydroelectric power is involved, and production is affected in the western area during times of drought.

The vanadiferous clays of Arkansas are found in the Magnet Cove area near Hot Springs and are processed by a mill in that district. The mill has a capacity of about 15 million pounds of V_2O_5 per year. It is anticipated that about 7.0 million pounds per year will be derived from Arkansas ore with the required balance from other materials. On this basis, the ore reserves will support the operation for at least 14 years.

The combustion of vanadium-bearing fuel oil in power plants and other boilers results in the collection of a variety of residues of varying grades and general composition. Premium materials contain as much as 40 to 50 percent V_2O_5. Other materials range from 5 to 30 percent V_2O_5 with widely varying compositions. Most have a high carbon content. The lower grade fractions constitute the bulk of this category, and these (because of grades and other undesirable characteristics) are utilized only in times of high vanadium demand. (This is covered more extensively on page 30.)

Spent vanadium-bearing catalyst (primarily sulphuric acid catalyst) is a small but steady source. The material is amenable to most processing cycles and is, therefore, utilized under most circumstances.

With the exception of a small quantity from Southwest Africa, all of the vanadium from Africa originates in South Africa. All of the vanadium from South Africa comes from the Bushveld deposits where reserves are very high grade and very large. A little more than half of the vanadium produced in South Africa is in the form of a high grade V_2O_5 slag recovered from Bushveld ore as a co-product with steel. This product is exported to the United States and to Western Europe, where vanadium is extracted by various means and processed to vanadium alloys. The balance of the South African production is in the form of high grade V_2O_5 and V_2O_3 extracted from Bushveld ore by salt roasting. Approximately 20 percent of the oxides produced are converted locally to ferrovanadium, vanadium carbide, and vanadium carbonitride, all of which are exported.

Vanadium-bearing open-hearth slag, relatively low in vanadium is imported into the United States from Chile. It is, in limited quantities, a feed material suitable for salt roast recovery plants.

In Norway, vanadium-bearing slag is reduced by a silicothermic process to produce a low vanadium ferrovanadium.

The titaniferous magnetites of Finland are unique in that titanium may be separated from the ore by physical means. The remaining magnetite is roasted to recover vanadium and the iron ore, free of titanium and vanadium, becomes blast furnace feed. Vanadium is recovered as fused V_2O_5. Increasing quantities of this material are being made available to Western Europe as Finland expands production, while the U.S.S.R., which formerly took a large fraction of Finland's production, becomes more self-sufficient.

Japan recovers a small quantity of V_2O_5 from oil residue and this capacity will grow as desulphurization of crude oil provides increasing quantities of feed.

France and India have from time to time recovered vanadium from a sludge which is a byproduct of aluminum reduction.

Figure 2 is an attempt to design a generalized flow diagram that incorporates the materials and operations that make up the world vanadium system. It serves to illustrate the character of the vanadium production complex and helps to visualize the directions in which it might evolve in the future. Vanadium is derived for the most part as a byproduct of other operations. Under these circumstances, vanadium output is relatively insensitive to vanadium demand because its production is part of the primary product processing cycle. In periods of low vanadium demand, ferrophosphorus and vanadium-bearing slags can be inventoried. Ferrophosphorus finds a market in general metallurgical applications. Fly ash, however, is normally deposited in collection ponds where it may not be recovered again. This latter situation could be changed by storing the fly ash in a reclaimable concentration and location.

The diagram also shows that the bridges between raw materials and high purity oxides are the acid leach and salt roast extraction processes. Their versatility is apparent and it is likely that these processes will continue to be employed as new byproduct vanadium forms are introduced in the future. There are some indications regarding such new products. Desulphurization of Venezuelan crude oil will probably be accomplished via the flexicoking technique, with the necessary new refinery installations coming on-stream in the early part of the next decade (see page 28). Initial installation is likely to be capable of producing about 7.5 to 10 million pounds of V_2O_5 per year in the form of a coke byproduct. A similar development is taking place in Canada. It now appears likely that the extraction of oil from tar sand will result in a vanadium byproduct containing as much as 8 to 12 million pounds of V_2O_5 per year in the latter part of the next decade. These developments are quite significant relative to the future vanadium extraction industry in the United States. The availability of such quantities of vanadium feed will, on the basis of economics, lead toward utilizing existing roast/leach capacity to recover vanadium from these byproducts, rather than developing domestic vanadium ore deposits requiring an on-site capital investment of significant magnitude.

B. VANADIUM IN PETROLEUM CRUDES

In addition to organically combined nitrogen and sulfur, a number of other inorganic elements are present in small amounts in petroleum, shale oil and crudes recovered from tar sands. Some of the more common elements, such as aluminum, calcium, iron, magnesium, sodium, and silicon, can be present as salts (organic or inorganic) or as suspended colloidal particles, as well as metal-organic compounds. Of the heavy metals, vanadium and nickel occur to varying degrees in essentially all crudes, with iron, copper and chromium also frequently found in smaller amounts. A recent text is devoted entirely to this topic (Yen, 1975).

The heavy metals, particularly vanadium and nickel, are present largely as stable porphyrin-metal compounds, or as metal-organic complexes with porphyrin-like structures. Because vanadium and nickel are ubiquitous in petroleum and have important effects on its recovery, refining and utilization, their pertinent chemistry and technology have been extensively studied. It is interesting to note that several workers have proposed to identify or characterize an unknown crude oil by measuring the concentrations of vanadium and nickel in it (and their ratio).

Porphyrins are organic compounds containing four condensed pyrrole rings and are chemically related to chlorophyll and haemoglobin (haem). The almost universal presence of vanadium porphyrins in petroleum or related crudes is construed as one additional bit of evidence supporting the marine sedimentary origin of petroleum and similar deposits.

Vanadium concentrations in petroleum crudes range from about 1 ppm to about 1200 ppm in one particular Venezuelan crude. In general, high vanadium concentrations seem to be associated with highly asphaltic crudes and/or high sulfur concentrations. Outside Venezuela, the vanadium contents of crudes rarely exceed 100 ppm and in most cases are below 50 ppm, with a significant number below 10 ppm. Most crudes recovered from oil shales or tar sands apparently have vanadium concentrations in a range around 100 ppm.

Typical concentration of vanadium in Venezuelan crudes averages about 200 ppm, which equates to 60 million pounds of contained vanadium per year at an annual petroleum production rate of 150 million tons. In 1976, the United States imported 279.9 million metric tons of crude oil, of which some 15.7 million metric tons were from Venezuela. It is clear that, if this vanadium can be recovered economically, Venezuelan oil could represent a major new source of vanadium. It should also be noted that vanadium will be concentrated in the heavier, asphaltic fractions when other, lower vanadium crudes are refined. Specifically, some mid-Eastern crudes, shale oils, or the like could conceivably supply substantial vanadium even at an average initial concentration of approximately 100 ppm.

Unfortunately, the presence of vanadium in petroleum and related crudes is currently more of a problem than a resource. When hydrocarbons containing vanadium are burned, the vanadium acts as a catalyst to promote formation of sulfur trioxide and sulfuric acid from any sulfor compounds present. This, in turn, promotes corrosive attack of downstream equipment exposed to combustion gases; i.e., boilers, turbines or auxiliary equipment. There is extensive literature on this subject, and considerable research on it is continuing.

Another problem posed by the presence of vanadium is deactivation of hydrocracking or hydrodesulfurization catalysts. It is also an increasing problem in the catalytic cracking industry. Current industry practice is to treat many high-sulfur crudes or fractions with hydrogen in the presence of cobalt-molybdenum (or nickel-molybdenum) catalysts supported on porous silica or silicates, thus removing sulfur as hydrogen sulfide. Vanadium and nickel in the feedstock will accumulate on the catalyst and gradually reduce its activity. When total metal content of the catalyst reaches approximately 10 to 20 percent, the catalyst must be discarded because the cost cannot justify recycling the material. A third problem, which probably is due more to the presence of porphyrins than to vanadium (and nickel) per se, is the tendency of these compounds to promote stable petroleum-water emulsions. This phenomenon is troublesome in refining operations, but also appears to have benefit as an aid in displacing crude oil from underground reservoir surfaces.

To summarize, vanadium in petroleum currently causes severe problems in refining and oil utilization, but also represents a potentially valuable raw material source. All that is lacking is an economically reliable technology for removing and recovering it. Venezuela recognizes the problem (and the opportunity) and sponsored an international meeting on the topic in 1973. The published proceedings (Kapo, 1975) are an important source of information.

A number of possible methods for recovering vanadium have been suggested, but almost all are still in the early stages of development. Achieving the objective at tolerable cost is a major obstacle. These removal techniques may be categorized as follows:

1. Removal by solid adsorbents or "guard" catalyst beds.
   (Papers I-E, III-C and III-G in Kapo, 1975)

2. Solvent or ligand extraction.
   (Papers I-E, III-C, III-E and III-F in Kapo, 1975)

3. Concentration into a low sulfur coke by fluidized bed coking or gasification.
   (Papers I-E, III-C, III-H, III-I, IV-C, IV-D, IV-F, IV-H, and V-H in Kapo, 1975)

4. Use of vanadium sulfides or other compounds as insoluble hydro-treating catalysts, with accretion of feedstock vanadium to form excess catalyst which is separated by filtration or the like.
   (Paper III-G in Kapo, 1975, and U. S. Patents 3,694,352 [Glein, 1972]; 3,558,474 [Glein, 1971]; 3,553,106 [Hamilton et al., 1971]; and others.)

5. Removal of asphaltenes by electrodeposition, solvent extraction or other means, preferably preceded by noncatalytic hydrogenation to concentrate metals in the asphaltenes.
   (Papers I-E, II-H, III-D, III-H, and IV-E in Kapo, 1975)

It should be noted that all of these techniques are essentially methods for concentrating low levels of vanadium into a relatively small volume byproduct or side-stream which must be processed further to recover vanadium in a commercially usable form. Techniques and costs for this final recovery step are not well defined in the literature, but there are undoubtedly many problems. One recent reference (Millensifer, 1977) gives a general description of methods for recovering various metal values from spent catalysts. A process involving combustion of pulverized coke (plus other fuels) followed by vanadium recovery from the fly ash is described by Whigham (1965). Other techniques for regenerating metal-fouled catalysts or removing metals are described in U. S. Patents 3,160,998 (Payne, 1964) and 3,226,335 (Humes and Steward, 1965), and by Benther and Flinn (1963).

Minicozzi (1973), Kapo (1975, Papers V-C, V-D, V-E) and Exley et al. (1966) describe recovery of vanadium from oil combustion ash. It has also been reported that vanadium recovery from oil combustion ash is (or was) practiced in Japan, but a specific literature reference on this has not been found.

Boiler slag is recovered by many utilities and small boiler operators where Venezuelan fuel oil is burned relatively undiluted. A few large utilities such as Canadian Petrofina (Whigham, 1965), Long Island Lighting (Exley and O'Neal, 1966) and Niagara Mohawk (Electrical World, 1977) also recover fly ash. A number of other utilities also collect fly ash with varying degrees of proficiency. Vanadium is recovered from boiler slag and fly ash by the basic U. S. producers; i.e., Reading Alloys, Shieldalloy, Foote Mineral and Union Carbide. Petrofina did operate a small recovery circuit at one time but it was discontinued when Venezuelan oil was eliminated as a feed. With the introduction of flexicoking in Venezuelan refineries, the fly ash and boiler slag collected in U. S. boilers will no longer contain significant quantities of vanadium.

REFERENCES

Note: An extensive or critical literature review has not been attempted because of the very large number of papers concerned with vanadium in petroleum, plus a very large additional number of papers or books dealing with petroleum technology which contain incidental information on vanadium. Several hundred references from Chemical Abstracts for the period 1963-1973 are given in Paper I-E of Kapo (1975). Selected references used in preparing this summary, or which may be of value, are listed below.

A primary source is Kapo (1975) which is listed first, followed by selected individual papers contained in it. Because pages of Kapo (1975) are not numbered, individual papers are identified by Roman numbers followed by a letter suffix. Each Roman number signifies a particular volume of the set.

Kapo, G. (ed). "International Symposium on Vanadium and Other Metals in Petroleum, August 19-22, 1973." (6 vols.). Maracaibo, Venezuela: Institute de Investigiones Petroleras, Universidad del Zulia, 1975.

Paper I-E: P. Hoppes, L. Katan and G. Sepulveda. "Review of the Literature on Vanadium in Petroleum," 67 p.

Paper II-H: J. G. Salas. "Chemistry and Composition of Asphaltenes." (French), 41 p. (including discussion).

Paper III-C: E. Edler. "Techniques for Removal of Metals from Petroleum," 26 p.

Paper III-D: P. M. Lichaa, L. Herrera, O. Bracho and G. Kapo. "Electro-Deasphalting of Petroleums," (Spanish), 22 p. (including discussion).

<u>Paper III-E:</u> E. L. Bertha. "Extraction of Vanadium from Petroleum with Ligands," (Spanish), 7 p. (summary and discussion only).

<u>Paper III-F:</u> C. W. Clump and J. E. Dumelow. "Vanadium Removal from Venezuelan Crude Oil by Liquid-Liquid Extraction," 12 p.

<u>Paper III-G:</u> T. Martinez, W. Arvelo, A. Mata, G. Sepulveda, L. Katan, P. Roa, N. Rosa-Brussin and G. Kapo. "Simultaneous Demetalization and Hydrodesulfurization with Minerals of High Vanadium Crudes," 23 p.

<u>Paper III-H</u>: A. Reyes, J. Huebler, C. W. Matthews and J. G. Patel. "Metal By-Products from Venezuelan Heavy Crudes," 15 p. (including discussion).

<u>Paper III-I:</u> I. Rondon, A. Ramirez and G. Kapo. "Desulfurization of Coke in a Stratified Fluidized Bed Coker," (Spanish), 11 p. (including discussion).

<u>Paper IV-C:</u> M. Ramos. "The Economics of Simultaneous Desulfurization and Demetalization of Venezuelan Petroleum," (Spanish), 33 p. (including discussion).

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<u>Paper IV-E:</u> Y. Jacquin, A. Deschamps, J. F. LePage and A. Billon. "Problems of Pollution by Sulfur from Crude Oil in European Countries," 22 p.

<u>Paper IV-F:</u> A. M. Squires. "Vanadium Recovery and the Production of Methane and Light Aromatics by Hydrogenation of Venezuelan Residuum in High Velocity Fluidized Beds," 11 p. (including discussion).

<u>Paper V-B</u>: M. Minicozzi. "The Economics of Vanadium Recovery in a Thermoelectric Plant Equipped with a Stack Desulfurization Unit," (Spanish), 22 p. (including discussion).

Paper V-C: J. O'Neal. "Vanadium Recovery from the Combustion of Venezuelan Fuel Oil," 18 p. (including discussion).

Paper V-D: G. Kapo, L. Gomez, F. Pena, E. Torres, J. Bilbao, and K. Mazeika. "The Vanox Process for Stack Desulfurization and Vanadium Flyash Recovery," 11 p. (including discussion).

Paper V-H: A. M. Squires. "Vanadium Recovery in the Production of Low Btu Gas by Partial Oxidation of Venezuelan Residuum," 15 p.

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Chapter Five

INDUSTRIAL AND FEDERAL STOCKPILE SPECIFICATIONS

An alloy specification is an agreement between a producer and a user of the alloy as to mutually acceptable limits on chemical and physical properties. Emphasis is on the word "acceptable." It correctly implies that a negotiation between the user and producer has taken place.

The negotiation essentially resolves a basic conflict of interest between the principals, who both want maximum flexibility in their own operations. The user achieves flexibility by purchasing products with as much purity as possible. With that, he can meet the wide range of restrictions likely to be placed upon him by his customers. The producer achieves flexibility by marketing products with as much relaxation on purity as possible. With that he can satisfy the users with products producible from a wider range of raw materials available to him and offer a lower market price where the product is acceptable.

In addition to flexibility, both the user and the producer want lowest possible prices. As a rule, the tighter the specification, the higher the price. This gives the user accordingly an incentive to develop proprietary skills so as to utilize cheaper and less pure materials while meeting customers' restrictions. Similarly, it gives the producer an incentive to develop proprietary skills to utilize a wider range of raw materials while meeting users' needs for higher purity. Thus, the negotiation between user and producer is to reach a compromise on specifications that will retain highest possible overall flexibility and lowest possible overall costs.

In fact, every individual sale involves specifications considerations between the specific user and specific producer involved. The specification of a lot appropriate in one transaction may not be so for another. Yet underlying many similar transactions are threshold chemical and physical characteristics that are commonly acceptable to all. These become minimum selling specifications for all lots of a given alloy type. Satisfactory for most transactions, these minimums are, for any given transaction at hand, subject to "specific negotiation" attending any departures from commonality. Agreed departures carry with them agreed price premiums to cover added costs of alloying and special handling.

Sales specifications, normally satisfactory for the bulk of materials being bought and sold, are freely available from producers, such as Foote Mineral Company and Union Carbide Metals Company, for vanadium addition agents. Such specifications generally evolve as a result of doing business over a long period of time. Otherwise, they may be derived from ASTM specifications developed in Committee negotiations by user and product representatives. Table 6 represents a summation of presently marketed additive agents.

Stockpile specifications include more items than do common commercial specifications, primarily because the stockpile is a surrogate user in the transaction between producer and stockpile. When stockpile lots pass on to real users later on, the user may take a lot or leave it, based on the specifications he sees. Thus, the broader specifications communicate commodity value to both common and special users, which is certainly a fundamental requirement for the stockpile in the supplier role.

Stockpile commodities, however, are limited as much as possible to the fewest and most basic commodities in the range of commodity variants; that is, those basic varieties of product having the widest application in user industries. For vanadium, there are two basic products: oxide and vanadium addition agents. The oxide is the more basic of the two, being the starting material from which all other vanadium alloys and chemicals derive downstream. Because in the past ferrovanadium has been the highest volume vanadium commodity derived from oxide, it has for convenience also been stockpiled. The current stockpile specifications for these two products are found in Specifications A and B.

It should be noted that fused oxide is difficult to dissolve; hence, most chemical applications utilize either ammonium vanadate or granular oxide derived from calcining the ammonium salt.

Today in the United States, vanadium carbide and vanadium-silicon alloy are both used in greater volume than ferrovanadium, and they should be evaluated for stockpiling. Also, vanadium-aluminum, which is an important and widely

TABLE 6 Vanadium Addition Agents to Steel

Element	Grade A	Grade B	Grade C	Grade D	Grade E*	Grade F	Grade G
Vanadium	50.0-60.0 or 70.0-80.0	50.0-60.0 or 70.0-80.0	50.0-60.0 or 70.0-80.0	35.0-45.0 or 50.0-60.0	68.0-71.0	82.0-86.0	78.0-82.0
Carbon	0.20 max.	1.5 max.	3.0 max	3.0 max.	15.0 max.	14.5 max.	12.0 max.
Phosphorus	0.05 max.	0.60 max.	0.05 max.	0.10 max.	0.05 max.	0.05 max.	0.05 max.
Sulfur	0.05 max.	0.05 max.	0.10 max.	0.10 max.	0.05 max.	0.10 max.	0.10 max.
Silicon	1.0 max.	2.5 max.	8.0 max.	8.0 max. or 7.0-11.0	1.0 max.	0.10 max.	0.10 max.
Aluminum	0.75 max.	1.5 max.	1.5 max.	1.5 max.	0.75 max.	0.10 max.	0.10 max.
Manganese	0.50 max.	0.50 max.	--	--	0.50 max.	0.05 max.	0.05 max.
Nitrogen	--	--	--	--	--	0.20 max.	6.0 min.
Oxygen	1.00 max.	1.00 max.	1.00 max.	1.00 max.	1.00 max.	1.00 max.	1.00 max.
(Balance Iron)							

NOTE: Grades A, B, C, and D are based on data from ASTM A102-73 (1975); Grade D is Foundry Grade of ASTM. Grades F and G are commercial grades.

* A nitrogen grade is also produced, ranging from 3.0 to 7.0 percent; commercial grade.

accepted ingredient for titanium alloy making, is also under study. The current purchasing specification for this master alloy is given in Specification C.

Of course, demand is only part of such considerations. Substitutability, recyclability, and production capacity are factors to consider as alternatives to stockpiling, or as supplements to stockpile goals (Buttner, 1974). If and when these and/or other vanadium commodities are deemed worthy of stockpiling, stockpile specifications for these will appear.

SPECIFICATION A -- VANADIUM PENTOXIDE

EXECUTIVE OFFICE OF THE PRESIDENT
Office of Emergency Preparedness

Prepared and Issued by the Industrial Resources Division
Bureau of Domestic Commerce
Department of Commerce

NATIONAL STOCKPILE PURCHASE SPECIFICATIONS	P-58-R1 Effective Date December 10, 1971 (Supersedes issue of Dec. 11, 1957)

VANADIUM PENTOXIDE

I. DESCRIPTION

These specifications cover one grade of fused black vanadium pentoxide, suitable for use in the production of ferrovanadium, alloy steel, and nonferrous alloys.

II. CHEMICAL AND PHYSICAL REQUIREMENTS

Each lot of vanadium pentoxide purchased under these specifications shall conform to the following chemical and physical requirements:

A. Chemical Requirements:

			Percent by Weight (Dry Basis)
Vanadium Pentoxide	(V_2O_5)	Minimum	99.2
Silica	(SiO_2)	Maximum	0.2
Iron	(Fe)	Maximum	0.1
Phosphorus	(P)	Maximum	0.03
Total Alkali		Maximum	0.5

B. Physical Requirements:

All vanadium pentoxide shall be supplied in broken flake form. All Material shall pass a screen with 2-inch square openings and not more than 5 percent by weight shall pass a U.S. Standard Sieve No. 4 (ASTM Designation E 11).

III. PACKAGING, MARKING, IDENTIFICATION, AND SHIPPING

A. Packaging:

Vanadium pentoxide shall be packed in new 55-gallon, 18-gauge steel drums, hot-dipped galvanized after fabrication, conforming to the requirements of National Stockpile Container Specification C-1. Drums: Steel, Hot-Dip, Galvanized, latest revision. All drums in a lot shall be of the same size and shape.

B. Marking:

All marking shall be in English. Each drum shall have attached adhesively, three aluminum tags 3 by 5 inches by 0.10-inch thick. Tags are to be glued to each flat side of the cover (lid) and one to the side of the drum midway between the locking ring and the upper rolling hoop on the outside. Prepare the tags by embossing with the following:

Name of Product
Name of Producer
Country of Origin
Form
Gross and Net Weights
Government Contract Number
Lot Number and Drum Serial Number
(e.g., 1/20, 2/20, etc.)

The following procedures shall be used to affix tags:

1. Preform the tag to be attached to the side of the drum to the same curvature as the container so that the tag will adhere properly.

2. Use dry cleaning solvent, Federal Specification, P-D-680, latest revision, to clean surface dirt and grease from those sections of the lid and drum to which tags are to be affixed.

3. Apply Class I stabilized chloroprene polymer adhesive (Neoprene WRT) (Federal Specification, MMM-A-121, latest revision) to the sections described in III.B. above and wait for sufficient time to elapse so that the bonding material becomes "tacky" enough to ensure proper adhesion before affixing the identification tags.

The drum shall not include a security classification or anything indicating National Stockpile Ownership other than the contract number.

C. Identification:

Appropriate identifying documents shall accompany each shipment.

D. Shipping:

Vanadium pentoxide shall be loaded, braced and blocked in the carrier's conveyance in compliance with applicable rules and regulations set forth in the carrier's classifications and other tariffs. For rail shipments, the applicable rules and regulations published by the Association of American Railroads (AAR) in Pamphlet Numbers 4 and 14, and Circular 42-D, latest revision, shall be followed.

IV. SAMPLING, INSPECTION AND TESTING

Each lot of vanadium pentoxide shall be subject to sampling, inspection, and testing by the purchaser or his designee.

SPECIFICATION B - FERROVANADIUM

P-100

December 8, 1958

NATIONAL STOCKPILE
PURCHASE SPECIFICATION

FERROVANADIUM

1. DESCRIPTION

This specification covers three Grades of ferrovanadium suitable for adding vanadium to iron and steel.

Grade I, 70 to 80 percent
Grade II, 70 to 80 percent
Grade III, 50 to 55 percent

2. CHEMICAL AND PHYSICAL REQUIREMENTS

Each lot of ferrovanadium purchased under this specification shall conform to the following applicable chemical and physical requirements:

a. Chemical Requirements:

		Percent by Weight (Dry Basis)		
		Grade I	Grade II	Grade III
Vanadium (V)		70.00-80.00	70.00-80.00	70.00-80.00
Silicon (Si)	Maximum	1.25	2.25	2.25
Aluminum (Al)	Maximum	1.25	1.25	1.25
Carbon (C)	Maximum	0.20	0.50	0.50
Molybdenum (Mo)	Maximum	0.50	0.50	0.50
Manganese (Mn)	Maximum	0.25	0.25	0.25
Copper (Cu)	Maximum	0.10	0.10	0.10
Titanium (Ti)	Maximum	0.10	0.10	0.10
Sulfur (S)	Maximum	0.10	0.10	0.10
Phosphorus (P)	Maximum	0.10	0.10	0.10
Other Metallic Elements Other than Iron1/ (Each)	Maximum	0.05	0.05	0.05

1/ Analyses for "Other Metallic Elements" may be made spectrochemically.

b. Physical Requirements:

All ferrovanadium shall pass a screen with 2-inch square openings and not more than 5 percent by weight shall pass a U.S. Standard Sieve No. 4 (ASTM Designation E 11).

Specification C-1-R, Drums: Steel, Hot-Dip, Galvanized.

Grade III ferrovanadium shall be packed in 55-gallon, 16-gauge drums conforming to the above requirements.

b. Marking:

Each drum shall have attached to the clamp ring bolt by a 12-gauge aluminum wire, a 28-gauge three-inch by five-inch aluminum tag on which shall be embossed the following:

Name of Product
Name of Producer
Grade (Range of V Content)
Gross and Net Weights
Government Contract Number
Lot Number and Drum Serial Number
    (e.g., 1/20, 2/20, etc.)
The Notice "DUPLICATE TAG INSIDE DRUM"

A duplicate aluminum tag shall be placed inside of each drum except the reference to duplicate tag may be omitted from the tags placed inside the drums. The duplicate tag shall be attached to a nonferrous wire which shall have a diameter not exceeding that of 18-gauge wire. The end of the wire shall be hooked over the edge of the drum so that it will be held in place by the cover and clamp ring when the drum is closed.

The drums shall not carry a security classification or any marking, other than the contract number, indicating National Stockpile ownership.

Appropriate identifying documents shall accompany each shipment.

c. Shipping:

Shipments in railroad cars shall be secured in accordance with "Rules Regulating the Safe Loading of Carload Shipments of Barrels, Drums, or Kegs in Closed Cars and Protection of Equipment," Pamphlet No. 4, Association of American Railroads. (Latest Revision)

4. SAMPLING, INSPECTION, AND TESTING

Each lot of ferrovanadium shall be subject to sampling, inspection, and testing by the purchaser or his designee.

SPECIFICATION C -- ALUMINUM-VANADIUM MASTER ALLOYS

Type	RAW MATERIALS PURCHASING SPECIFICATION	Specification No.	M-101
		Date Issued	7-21-69
Title	60% VANADIUM-35%ALUMINUM, 60% ALUMINUM - 40% VANADIUM- AND 50% ALUMINUM-50% VANADIUM MASTER ALLOYS FOR TITANIUM ALLOYING	Date Effective	7-21-69
		Date Revised	5-27-77

PURPOSE: This specification details the requirements to be met for the purchase of aluminum-vanadium type master alloys.

1.0 GENERAL:

1.1 Chemistry:

ALUMINUM - VANADIUM MASTER ALLOYS

Elements	*Type 1 65V-35Al
Aluminum	34-39%
Vanadium	60-65%
Iron	0.80% Max
Silicon	0.40% Max
Carbon	0.18% Max
Oxygen	0.10% Max
Nitrogen	0.04% Max
Boron	0.003% Max
Hydrogen	0.015% Max
Sulfur	0.024% Max
Phosphorus	0.035% Max
Molybdenum	0.15% Max
Magnesium	0.25% Max
Others Each	0.10% Max
Others Total	0.40% Max

*1.2 Size: - 1/4" + 65 mesh (0.0082"), 2% maximum undersize to 100 mesh (0.0059") minimum, 3% maximum oversize to 5/16" maximum.

*Denotes change or addition

1.3 Sample:

Furnish a one-pound true sample from each lot.

2.0 CERTIFICATION:

2.1 Furnish chemical analysis of each lot plus sieve analysis. All elements listed shall be reported.

*2.2 Vendor will certify that each lot of Master Alloy has been produced by the approved process. The vendor shall notify the company in writing before making any significant changes in the production of the Master Alloy.

2.3 The alloy is to be 100% inspected fluoroscopically and certified to be free of all discrete impurity particles. Failure to pass fluoroscopic examination will cause the material to be rejected.

2.4 The alloy shall be 100% inspected under black light to assure removal of all slag.

2.5 The alloy is to be produced in equipment not common to the production of high density materials.

2.6 Each lot shall be homogeneous and fully alloyed.

2.7 The vendor shall maintain detailed records of heat formulation, melting and processing procedure and be available for review. These records shall be maintained for at least 10 years.

3.0 SHIPPING INSTRUCTIONS:

Ship in sealed containers, properly identified as to metal, lot number and purchase order number.

REFERENCES

American Society for Testing and Materials, A102-73, "Standard Specification for Ferrovanadium." In 1975 Annual ASTM Standards, Vol. 2 (April), p. 87. Philadelphia, Pa.: ASTM, 1975, Table 1.

Buttner, F. H., "Stockpiling for the Future." In Huddle, F. P. (ed.), Requirements for Fulfilling a National Materials Policy (proceedings of Engineering Foundation Conference, New England College, Henniker, N. H., August 1974). Washington, D. C.: Office of Technology Assessment, 1974.

Chapter Six

STOCKPILE GOALS

In a broad sense, stockpile goals result when, under national emergency conditions, requirements for a material exceed the expected supply. Over the years, there have been several methods employed in estimating stockpile goals (previously called objectives). The method now in use is considerably more intricate than methods previously used. It recognizes that different sectors of the economy have different priorities for claims on stockpile materials, and it also takes cognizance of the fact that failing to satisfy the priorities incurs penalties ranging from severe to uncomfortable.

The new method for estimating stockpile goals is called the "variable confidence level" approach because:

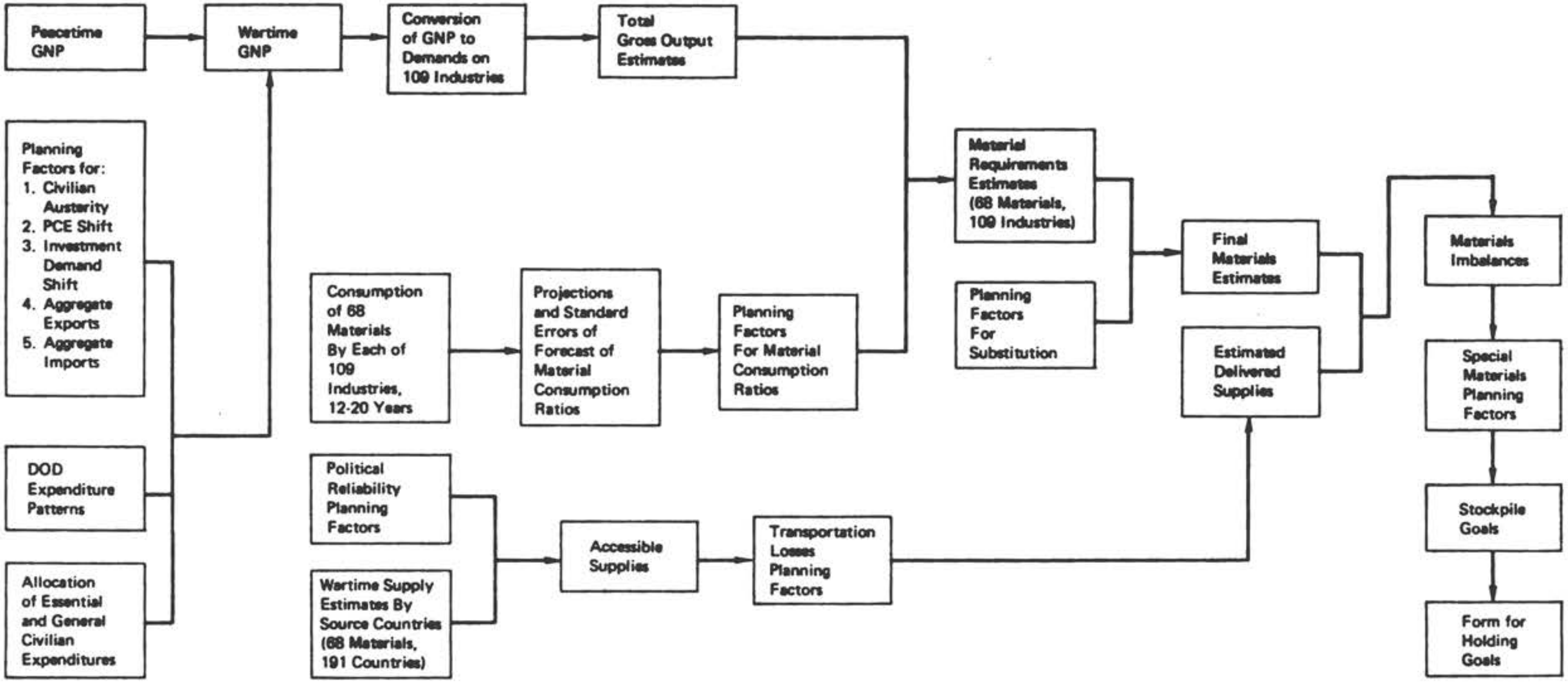
- Three economic sectors or "tiers" (defense, essential civilian and general civilian) are defined as users of stockpile materials, and the assigned priorities of use are in the order just cited; and

- Planning factors that reflect the willingness to accept risk of not meeting the wartime needs of these tiers are explicitly assigned to the tiers.

Thus, the needs for the defense tier are considered to be of higher priority than the needs for general civilian applications. Planning factors (described later) are assigned to the defense tier in a way that minimizes the possibility of not meeting defense needs in an emergency. More risk is permitted with respect to essential civilian needs, but less than for general civilian needs. These "variable confidence level" planning factors differ not only among tiers, but also among years.

Figure 3 presents a simplified overview of the new process of estimating stockpile goals. The figure illustrates how the method is applied to any one of the three tiers (defense, essential civilian, or general

FIGURE 3 Stockpile Goal Estimation Methodology (once for each year, once for each tier, as appropriate)



civilian) in any one of the first three years of an emergency.

A. ESTIMATING REQUIREMENTS FOR STOCKPILE MATERIALS

This section provides a description of how the materials requirements estimates are built up by interrelating economic and war planning assumptions with data and stockpile planning factors.

1. Developing Estimates of Gross Industrial Output

Beginning from projections of peacetime gross national product (GNP) in the wartime period, adjustments are made to the econometric model used to characterize the economy in peace and wartime. In addition to the usual estimates of things such as interest rates, corporate retained earnings, and the like, some of the planning factors are used to further modify the picture of a wartime economy:

- Civilian austerity; i.e., the level of prewar personal consumption expenditures per capita (PCE) in constant dollars is lowered in steps to 90 percent of the prewar level over the three-year period.
- PCE shift is used to reallocate total consumer expenditures from durable goods more toward nondurable goods and services, to lessen the demand for stockpile materials.
- Investment demand is shifted from private residential housing and structures into machinery and equipment investment needed for the emergency.
- The level and composition of aggregate exports and imports are structured to conform to an emergency condition.

In addition to the planning factors, defense expenditure patterns incorporating both the newest weapons systems technology and the backup expenses, such as operations and maintenance costs, are introduced to the calculations, as are divisions of civilian expenditures into "essential" and "general" categories.

(The planning factors, defense expenditure patterns and civilian expenditure classifications, it should be noted, were developed by interagency working groups and reviewed by an Interagency Steering Committee before being employed in the methodology.)

After the calculations just mentioned are made, the estimates of wartime GNP are developed separately for the defense, essential civilian and general civilian sectors of the economy. The GNP sectors then are spread into a total of about 250 categories and distributed through a Demand Impact Transformation Table that converts the GNP data into estimated final demands for output from each of 109 industries. These demands, in turn, are processed in a specially-adapted input-output table; the results of the processing provide estimates of the total gross output of each industry necessary to meet the demands for defense, essential and general civilian requirements. These estimates include the indirect (suppliers of producers) as well as the direct production requirements for each of the three GNP sectors.

2. Estimating Rates of Consumption of Specific Materials

Industry analysts in the Department of Commerce provide estimates of the consumption of each of the 68 basic stockpile materials in each of the 109 industries. Files on these data go back from 12 to 20 years. The physical consumption of each material by each industry in a given year is divided by that industry's gross output. The resulting figure is called a material consumption ratio (MCR). Using the MCRs for a specific material in a specific industry for the 12 to 20 year period, a projection is made to cover the time period encompassed by the emergency. In all, over a thousand separate projections are made.

At this point, planning factors are used to reflect the willingness to accept risk of shortfalls for the three tiers of stockpile planning. Since all projections are subject to error, a forecast error band (known as the "standard error of forecast") is estimated based on how well the projection "fits" the data and also on how far the projection extends into the future. The upper edge of this error band is used to estimate wartime MCRs for defense planning, in keeping with the principle that risks of shortfalls in defense requirements are to be minimized, and therefore the higher possible consumption rates should be assumed for defense uses. The lower edge of the error band is used to estimate general civilian MCRs, reflecting the willingness to accept more risk in this tier. The original projections of the MCRs are used to estimate essential civilian requirements.

3. Determining the Final Material Requirements Estimates for Specific Materials

Total gross output estimates are stated in terms of constant dollars. MCRs are stated in terms of physical consumption of a material per dollar of gross output. When an MCR is multiplied against a gross output, the result is an estimate of the physical consumption of a material by that industry. Calculations of this type are performed for:

- Each material's consumption by each industry
- Each tier (defense, essential and general civilian)
- Each year of the war.

Final adjustments must be made for substitution possibilities. For each material, the Federal Preparedness Agency (FPA) has data on the possibilities of substituting other materials in particular industrial uses. In the aggregate, substitution possibilities can amount to 10 to 12 percent, but they range from 0 in some materials (chromium in stainless steel) to up to 100 percent in others (quinine in soft drinks). Even given a warning period, however, industry cannot be expected to convert to substitutes instantaneously, so planning factors geared to variable risk are used to modify the rates at which industry may be expected to approach the maximum feasible possibilities of substitution. These "modifiers" are applied to the substitution rates and the materials requirements are then reduced by the net result. The adjusted material consumption estimates in the separate industries are totaled for each material and become the estimates of the total requirements for that material in a particular tier in a given year.

B. ESTIMATING SUPPLIES OF STOCKPILE MATERIALS

Estimated supplies of stockpile materials from foreign countries may differ considerably in terms of amounts and quantities available in wartime as opposed to peacetime. This section will discuss the major reasons for these variations.

1. Data

Data on the supplies of stockpile materials are provided by experts in the Department of the Interior (Bureau of Mines) and the Department of Commerce (Bureau of Domestic Commerce). These experts track actual import quantities of materials and also provide projections of materials supplies by source countries throughout the period covered by the emergency. The projections are provided in two ways:

- Normal supply patterns
- Expanded production possibilities, where mines and other production facilities are assumed to operate at capacity. (No estimates of wartime expansion of new plant and equipment are requested or used.) It is assumed that the U. S. gets a proportionate share of the increased supplies.

2. Political Reliability Factoring

Once the supply estimates are developed, a factoring process is applied to reflect assumptions about the accessibility of those sources in time of emergency. First, countries in the zone of action are removed, since it is very unlikely that their productive facilities will be available under those conditions. Next, a political reliability factoring procedure is applied to the remaining supplier countries in a manner that reflects the tiered-risk approach. Each of the 113 supplier countries is rated on the following major factors:

- Political orientation toward the United States
- Ability to sustain stockpile material exports in wartime.
- Dependability of the labor force in wartime.
- Vulnerability to sabotage.

Each of these major factors is developed through rating a number of subfactors (usually four to six). The ratings are done by State Department Desk Officers with higher level review. The major factors are assigned weights, and the scores are combined into a separate index for each country. The indexes then are evaluated by State Department experts for reasonableness in terms of the absolute scores and the country rankings implied by the scores. FPA has a mathematical rating technique which is used to cross-check the State Department results.

For purposes of tiered-risk considerations, the country ratings are arrayed in rank order. Countries ranked below the 35th probability percentile of a "normal" (bell-shaped) distribution are not considered as reliable supply sources. Countries above the 35th percentile are acceptable for purposes of supplying the general civilian tier, and countries above the 70th percentile are acceptable as supply sources for the essential civilian tier. Countries above the 90th percentile are acceptable on a politico-economic basis as supply sources for the defense tier, except that only Canada and Mexico are considered as suitable "assured" suppliers because of their adjoining borders.

3. Transportation Losses

Stockpile materials sent by ship or air run the risk of loss through enemy engagement or other means. Estimates of transportation losses are modest and also include provisions for tiered risk. Transportation loss estimates are applied to the supplies after the political reliability discounts.

C. MATERIALS IMBALANCES

Once net material requirements and supplies are established for the three tiers, estimates of imbalances (i.e., shortfalls of requirements versus supplies) can be made.

1. Year-Tier Estimates

For each of the three tiers in each of the three years, requirements are matched against supplies. If a requirement exceeds its supply, the difference (imbalance) is recorded for the tier and year.

In addition, the amount of the supply or requirement, whichever is smaller, is charged off against the supply available to the next tier. This is necessary because of the way in which supplies to the tiers are calculated -- using different planning factors for each tier and year which leads to the use in the defense and essential civilian tiers of any part of the total supply available.

2. Unadjusted Stockpile Goals

An unadjusted stockpile goal for a given material is calculated by summing up the imbalances from among the nine possibilities in the three-year, three-tier combination.

3. Final Stockpile Goals

Once the unadjusted goals are developed, they must be evaluated in the light of some six "special materials" criteria. This process takes cognizance of special circumstances that may surround a material's stockpile status. For example, if a material has 60 percent or more of its end uses in DoD applications (titanium, tantalum and others), it will be given a special review with respect to supply, requirements and planning factors. If the U. S. is 100 percent import-dependent on one or two supply sources of a stockpile material outside of North America, a special review will be given the material.

Whatever the basis for any special adjustments to the stockpile goals, it is important to note that an audit trail is provided to track all changes to goals, just as trails are provided at every other stage of the estimation process.

4. Forms for Holding Goals

Ideally, stockpile materials should be held in basic forms, such as ores. In most cases the basic form is cheaper to purchase and store. In addition, risks of physical deterioration and technological obsolescence are reduced significantly. When upstream production is insufficient to handle the stockpile goal quantities, however, consideration must be given to holding all or part of the material in an "upgraded" form. Consider, for example, the bauxite-alumina-aluminum processing chain. The desired form for the stockpile goal is bauxite, but because alumina production capacity is insufficient to process the bauxite under emergency conditions, most of the goal will be held as alumina. If the capacity constraints had occurred in the aluminum production process, some aluminum would need to be held also. (As it turns out, some aluminum is being held in the stockpile, but not for its own sake -- it is held as a credit against the alumina goal.)

D. STOCKPILE GOALS (PRESENT AND PAST)

Present and past stockpile goals for vanadium are shown in Table 7, and the 1976 overall stockpile goals in Table 8. Table 7 shows that historically changes in plans and in the emergency time duration have brought about rather wide variations in the Stockpile Objectives. Only recently has the inventory been reduced markedly. As shown in Table 8, the October 1, 1976 Stockpile Goal (formerly Objective) for vanadium has been increased from the "zero" value set in April 12, 1973. The Stockpile Goals listing is included here to show the values of other critical and strategic materials relative to vanadium and to each other.

REFERENCE

Federal Preparedness Agency, GSA News Release No. 6681. Washington, D.C.: General Services Administration, October 1976.

TABLE 7 A History of Stockpile Fluctuations for Vanadium

Total Inventory		Stockpile Objectives		
Date	Short Tons	Date Established	Short Tons	Reason for Change in Objective
—	--	11/20/44	2,450	Initial objective.
12/31/50	3,025	11/9/50	4,100	Increase in requirements without comparable increase in supply.
12/31/51	4,179	10/25/51	6,500	Increase in requirements without comparable increase in supply.
12/31/52	4,753	10/2/52	6,500	Reaffirmed objective.
6/30/54	6,683	9/28/54	7,084	Establishment of provisional long-term objective.
12/31/55	7,918	12/13/55	1,850	Reduction in requirements.
12/31/56	7,913	11/8/56	1,850	Reaffirmed objective.
6/30/58	7,911	6/30/58	0 Basic 73 Max.	Planning period reduced from 5 to 3 years; interim objectives.
6/30/58	7,911	6/30/58	0 Basic 1,000 Max.	Interim maximum objective increased to cover the 1,000 short tons of vanadium to be in form of ferrovanadium.
6/30/60	7,900	7/7/60	0 Basic 1,000 Max.	Reaffirmed objectives; total quantity to be in ferrovanadium.
12/31/63	7,865	4/2/64	1,400	Increased requirements.
12/31/66	6,462	1/5/67	1,500	Increased requirements; 1,200 short tons to be in ferrovanadium to cover Year I deficit.
12/31/66	6,462	1/5/67	60	(Nuclear Objective) Nuclear less than existing conventional objective.
12/31/68	5,609	3/27/69	2,100	Increased requirements.
12/31/69	5,306	3/4/70	540	Revised policy on discounting for concentration and inclusion of Indonesia and Southern Rhodesia as potential sources of supply.
3/31/73	1,740	4/12/73	0	Planning period reduced to 1 year of emergency.

NOTE: Data from IMACS (Interdepartmental Materials Advisory Committee Studies). These nonpublished studies are jointly produced by various U.S. government agencies.

TABLE 8 Stockpile Goals, October 1, 1976

Materials	Quantities	Units
Aluminum Oxide, Fused Crude	147,615	short tons
Aluminum Oxide, Abrasive Grain	75,000	short tons
Antimony	20,130	short tons
Asbestos, Amosite	26,291	short tons
Asbestos, Chrysotile	0	short tons
Bauxite, Metal Jamaica	523	1,000 long dry tons
Bauxite, Metal Surinam	0	1,000 long dry tons
Alumina	11,532	1,000 short tons
Aluminum	0	1,000 short tons
Bauxite, Refractory	2,083	1,000 long dry tons
Beryl Ore, 11% BeO Concentrates	0	short tons
Beryllium Copper Master Alloy	16,710	short tons
Beryllium Metal	895	short tons
Bismuth	771	1,000 pounds
Cadmium	24,701	1,000 pounds
Castor Oil, Sebacic Acid	0	1,000 pounds
Chromite, Chemical	734	1,000 short tons
Chromite, Metallurgical, Ore	2,550	1,000 short tons gross weight
Chromium, Ferro, High Carbon	236	1,000 short tons
Chromium, Ferro, Low Carbon	124	1,000 short tons
Chromium, Ferro, Silicon	69	1,000 short tons
Chromium, Metal	10	1,000 short tons
Chromite, Refractory	642	1,000 short tons gross weight
Cobalt	85,415	1,000 pounds contained
Columbium Concentrates, contained Cb	3,131	1,000 pounds
Columbium Carbide Powder, contained Cb	0	1,000 pounds
Columbium, Ferro, contained Cb	0	1,000 pounds
Columbium, Metal, contained Cb	0	1,000 pounds
Copper	1,299	1,000 short tons
Cordage Fibers, Abaca	24	million pounds
Cordage Fibers, Sisal	114	million pounds
Diamond Dies, Small	0	number
Diamond, Industrial Bort	14,974	1,000 karats
Diamond, Industrial Stone	5,559	1,000 karats
Feathers and Down	6,494	1,000 pounds

TABLE 8 Stockpile Goals, October 1, 1976 (continued)

Materials	Quantities	Units
Fluorspar, Acid Grade	1,594	1,000 short tons
Fluorspar, Metallurgical	1,914	1,000 short tons
Graphite, Natural, Ceylon	6,271	short tons
Graphite, Natural, Malagasy	20,472	short tons
Graphite, Other	34,748	short tons
Iodine	3,333	1,000 pounds
Jewel Bearings	224,623	1,000 units
Lead	865	1,000 short tons
Manganese, Battery, Natural	12,736	short tons
Manganese, Battery, Synthetic Dioxide	19,105	short tons
Manganese Ore, Chemical	247,136	short tons
Manganese Ore, Metallurgical	2,052	1,000 short tons
Manganese, Ferro, High Carbon	439	1,000 short tons
Manganese, Ferro, Low Carbon	0	1,000 short tons
Manganese, Ferro, Medium Carbon	99	1,000 short tons
Manganese, Ferro Silicon	81	1,000 short tons
Manganese Metal, Electrolytic	15	1,000 short tons
Mercury	54,004	76 pounds/flask
Mica, Muscovite Block	6,188	1,000 pounds
Mica, Muscovite Film, 1 and 2 Quality	90	1,000 pounds
Mica, Muscovite Splittings	12,631	1,000 pounds
Mica, Phlogopite Block	206,064	pounds
Mica, Phlogopite Splittings	932	1,000 pounds
Molybdenum Disulphide, contained Mo	0	1,000 pounds
Molybdenum, Ferro, contained Mo	0	1,000 pounds
Nickel	204,335	short tons contained
Opium, Gum	0	pounds
Opium, Salt	75,000	pounds
Platinum Group, Iridium	97,761	troy ounces
Platinum Group, Palladium	2,450	1,000 troy ounces
Platinum Group, Platinum	1,314	1,000 troy ounces
Pyrethrum	377,851	pounds
Quartz Crystals	0	1,000 pounds
Quinidine	6,841	1,000 avoirdupois ounces
Quinine	3,045	1,000 avoirdupois ounces

TABLE 8 Stockpile Goals, October 1, 1976 (continued)

Materials	Quantities	Units
Rubber	513,134	long tons
Rutile	173,928	short tons
Sapphire and Ruby	0	1,000 karats
Shellac	8,529	1,000 pounds
Silicon Carbide, Crude	306,628	short tons
Silver	0	1,000 troy ounces
Talc, Steatite Block and Lump	104	short tons
Tantalum Minerals, contained Ta	5,452	1,000 pounds
Tantalum Carbide Powder, contained Ta	889	1,000 pounds
Tantalum Metal, contained Ta	1,650	1,000 pounds
Thorium Nitrate	418	tons ThO_2
Tin	32,499	long tons
Titanium Sponge	131,503	short tons
Tungsten Ores and Concentrates	8,823	1,000 pounds contained
Tungsten Carbide Powder	12,845	1,000 pounds contained
Tungsten, Ferro	17,769	1,000 pounds contained
Tungsten, Metal Powder	3,290	1,000 pounds contained
Vanadium, Ferro	10,095	short tons
Vanadium Pentoxide	2,576	short tons
Vegetable Tannin, Chestnut	6,942	long tons
Vegetable Tannin, Quebracho	37,998	long tons
Vegetable Tannin, Wattle	20,208	long tons
Zinc	1,313	1,000 short tons

NOTE: Data from Federal Preparedness Agency, October, 1976.

Chapter Seven

VANADIUM IN TOOL STEELS

Tool steels are described by the American Iron and Steel Institute (AISI) as:

> "...either carbon or alloy steels, capable of being hardened and tempered. They are usually melted in electric furnaces and produced under tool steel practice to meet special requirements. They may be used in certain hand tools or in mechanical fixtures for cutting, shaping, forming and blanking of materials at either ordinary or elevated temperatures. Tool steels are also used in a wide variety of other applications where resistance to wear, strength, toughness, and other properties are selected for optimum performance.
>
> "The foregoing description of tool steels is not intended to include those types of 'mass produced steels' that are used in the manufacture of hollow drill steel, or of such products as mechanic's hand tools, hammers, picks, files, mining bits, mining cutters, large mill rolls and low alloy die blocks. Those exceptions are stated as a matter of guidance only and are not all-inclusive." (American Iron and Steel Institute, Steel Products Manual, © 1976)

Also excluded are steels primarily intended for structural applications, maraging steels and "superalloys." The above-cited reference groups tool steels in seven main categories:

- High Speed Tool Steels
- Hot Work Tool Steels
- Cold Work Tool Steels
- Shock Resisting Tool Steels
- Mold Steels
- Special Purpose Tool Steels
- Water Hardening Tool Steels

According to the AISI manual, "Tool steels are produced in the form of hot and cold finished bars, special shapes, forgings, hollow bar, wire, drill rod, plate, sheets, strip, tool bits, and castings."

The commonly-used tool steels which contain vanadium and their approximate vanadium content as listed in the AISI Steel Products Manual (1976) are shown in Table 9.

The amount of vanadium used in tool steels has varied widely from year to year and some fluctuation can be expected in the future as the economy fluctuates. Probably the most elusive factor in predicting the domestic consumption of vanadium in tool steels is the impact of imports.

Table 10 shows the variation in amount of vanadium used in tool steels for several years as well as other information on tool steel tonnages.

Reviewing the five-year period starting with 1972 and continuing through 1976, the apparent U. S. demand for tool steels has averaged 108,300 tons on an annual basis of which 91,900 tons on an average have been supplied by domestic producers. This latter amount has required 706 tons of contained vanadium annually, again using an average for the same five years. It should be noted that not only has an increasing percentage of the apparent U. S. demand been provided by imports but the actual tons of tool steels imported into this country have increased in each of the five years. This has persisted even in 1975 and 1976, when the apparent U. S. demand was appreciably less than the previous two years. Unless this trend is arrested, the amount of tool steel produced domestically will continue to decline and the amount of vanadium required for tool steels will probably also decline. One need only compare the figures for 1976 with the five-year averages to note the effects of this trend. A continuation of the trend in the importation of tool steels, particularly high-speed steels, could materially reduce the domestic requirements for vanadium in tool steels. This, of course, could have serious implications for the domestic vanadium industry and the domestic tool steel industry, and, of greatest importance, could make our country dependent on foreign sources of tool steels with all its drastic implications in times of national emergency.

TABLE 9 Vanadium Contents of Tool Steels

AISI Type	Approximate Vanadium Content (%)	AISI Type	Approximate Vanadium Content (%)
High Speed Tool Steels		Cold Work Tool Steels	
M1	1.00	A3	1.00
M2	2.00	A7	4.75
M3 Class 1	2.40	A9	1.00
M3 Class 2	3.00		
M4	4.00	D2	1.00
		D7	4.00
M6	1.50		
M7	2.00	Hot Work Tool Steels	
M10	2.00		
M30	1.25		
M33	1.15	H10	0.40
		H11	0.40
M34	2.00	H12	0.40
M36	2.00	H13	1.00
M41	2.00		
M42	1.15	H19	2.00
		H26	1.00
M43	1.60	H42	2.00
M44	2.00		
M46	3.20	Special Purpose Tool Steels	
M47	1.25		
T1	1.00	L2	0.20
T2	2.00		
T4	1.00	Water Hardening Tool Steels	
T5	2.00		
T6	1.50	W2	0.25
T8	2.00		
T15	5.00		

NOTE: Based on data from American Iron and Steel Institute, 1976.

TABLE 10 Vanadium Use in Tool Steels (short tons)

Year	Vanadium Consumption (contained V)	Tool Steels Apparent United States Demand*	Domestic Shipments	Imports	Exports
1972	620	102,113	90,230	15,041	3,158
1973	997	125,770	110,744	21,709	6,683
1974	936	129,355	113,335	24,540	8,520
1975	413	85,705	69,021	24,603	7,919
1976	565	98,340	76,321	27,609	5,590

NOTE: Consumption data from U.S. Bureau of Mines, 1972-1975; import and export data from private communication with American Iron and Steel Institute, 1977.

* Apparent United States Demand = Domestic Shipments + Imports - Exports.

A. NEW TECHNOLOGY (NEW PRODUCTS)

The advent of powder processes for making tool steels enables the production of new grades which heretofore could not be produced by the conventional melting and wrought production techniques. Such new tool steel grades might contain greater percentages of vanadium in order to achieve greater wear resistance. Although it is possible that such new grades might eventually make major inroads into the tool steel markets, it does not seem probable for some years to come.

It is beyond the scope of this report to study the implications of possible future increase in the use of carbides for cutting tools, but it would seem that the greater relative abundance in this country of molybdenum and vanadium (both used extensively in high-speed tool steels) compared to tungsten (the principal ingredient of carbides) would be a distinct advantage in times of national emergency. This circumstance would seem to justify research and development in this direction.

B. SUBSTITUTABILITY

Since the inception of tool steels, vanadium has been added primarily for grain size control, and also for imparted extra hardness and wear resistance. Vanadium can be added during normal melting in electric arc furnaces with good recovery, as it is not a strong oxide former. Titanium, zirconium, columbium, and tantalum (the last two are frequently in combination) have very similar metallurgical properties, and might have possibilities as substitutes for vanadium in tool steels. However, the solubility of their carbides in austenite is even more limited than vanadium-carbide, and thus the temper resistance would be reduced. A further drawback to the use of titanium and zirconium is their reactivity with oxygen. Accordingly, vacuum melting is required for their effective recovery.

C. RECYCLABILITY

A large portion of the vanadium contained in tool steels is recycled. Practically all tool steels are melted in electric arc furnaces and a significant percentage of the furnace charge, particularly for high-speed steel melting, is worn-out tools and revert scrap of the same or similar grade as that to be melted.

REFERENCES

American Iron and Steel Institute. "Tool Steels." In Steel Products Manual. Washington, D. C.: American Iron and Steel Institute, 1976.

U. S. Bureau of Mines. "Vanadium." In Minerals Yearbook Washington, D. C.: U. S. Bureau of Mines, 1972-74, 1975 (preprint).

Chapter Eight

VANADIUM IN ENGINEERING ALLOY STEELS

This category of steels includes the vanadium-containing standard AISI alloy steels plus various ASTM specified plate and forging grades. Vanadium is present in these steels in amounts from 0.03 to 0.25 percent. Vanadium is added to these engineering or constructional alloy steels as either ferrovanadium, Carvan, Ferovan, Nitrovan, or any other form. The deciding criterion for the form of the vanadium addition is purely economics. The addition of vanadium is made to obtain grain size control, elevated temperature properties, precipitation strengthening, and hardenability. The primary markets for the vanadium alloy steels are automotive parts (bolts, springs and valves) and heavy forgings for power-generating equipment.

Vanadium-containing alloy steels include the AISI 6100 (CrV) grades, ASTM 4-99 and 500 forging grades, and the ASTM plate grades A-514 and 517. The nominal vanadium content of all these grades appears to be approximately 0.10 percent (2 lbs/ton). This figure also was used for the determinations made for vanadium consumption in the 1970 report, <u>Trends in the Use of Vanadium</u> (National Materials Advisory Board). Using this figure for average vanadium content in vanadium-containing alloy steels, and reported production figures for these steels (AISI Form 7-A), the consumption of vanadium in alloy steels for the past five years was determined (Table 11). Data are also listed from the U.S. Bureau of Mines <u>Mineral Industry Surveys</u> for vanadium consumption in the United States for the "full alloy" category. It will be noted that the Bureau of Mines consumption quantities are larger by about a factor of four. In part, the discrepancy between the two sets of data may be attributable to forging grades; however, it is doubtful that these steels would account for the total large difference in the data.

The forecast of vanadium consumption in these steels through the year 1990 is shown in Table 12. In this forecast, projected total alloy steel production (Townsend and Greenspan projections) was used as a basis. In making this

TABLE 11 Vanadium Contained in Engineering Alloy Steels, 1972-1976

Year	Vanadium Steel Production Based on AISI 7-A Data (1,000 ingot tons) CrV Steels	NiCrMoV Steels	CrMoV Steels	Vanadium Consumed (1,000 pounds) Based on AISI 7-A Data	Bureau of Mines Data
1972	68.6	105.7	134.3	617	3,297
1973	66.0	122.8	174.1	726	3,088
1974	53.4	144.1	228.4	852	3,481
1975	35.0	154.2	152.5	682	2,614
1976	54.5	191.8	125.2	743	2,622

NOTE: Based on data from American Iron and Steel Institute, Form 7-A, and U.S. Bureau of Mines, 1977.

TABLE 12 Forecast of Vanadium Consumption in Engineering Alloying Steels, 1977-1990

Year	Vanadium Steel Production (1,000 tons)	Vanadium Consumed (1,000 pounds) Based on AISI 7-A Data Trend	Bureau of Mines Data Trend
1977	374	748	2,800
1980	471	942	3,500
1985	545	1,090	4,050
1990	649	1,298	4,820

NOTE: 1977 data based on American Iron and Steel Institute, Form 7-A, and U.S. Bureau of Mines, 1977; 1980-1990 estimates based on private communications from industrial specialists.

forecast, the historic trend of the production of vanadium-containing alloy steels, as compared to total alloy steel production, was then considered in developing the forecasted vanadium consumption. The last column of Table 12 is a forecast based on Bureau of Mines "full alloy steel" data (see comments made above about the difference in consumption figures based on two sources of consumption data).

When vanadium is added to steel for increasing its hardenability (e.g., in the chromium-vanadium carburizing steels) this addition could be substituted with modifications of the chromium, molybdenum, manganese, and/or silicon contents. Modification of the silicon content in spring steels probably would take care of the role that vanadium has. On the other hand, it would be difficult to substitute for the vanadium addition in the CrMoV and NiCrMoV steels which are used for elevated temperature service (e.g., large rotors). These elevated temperature steels are well balanced compositions, and each alloying element has an important contribution; thus, eliminating one of the alloying elements upsets the delicate balance. For the small amount of vanadium used in these steels, it is doubtful whether substitution for the vanadium would be economically justified.

Additional research and development of engineering steels containing vanadium appears fruitful in steels having a pearlitic microstructure that depend upon additional strengthening through vanadium carbo-nitride precipitation. These types of steels could find applications as heavy-duty rails and for abrasion resistance in the mining industry (e.g., grinding rods).

REFERENCES

American Iron and Steel Institute. Form 7-A, 1977.

National Materials Advisory Board. Trends in the Use of Vanadium. Report No. NMAB-267. Washington, D.C.: National Academy of Sciences, 1970.

U.S. Bureau of Mines. Mineral Industry Surveys. Washington, D.C.: U.S. Bureau of Mines, 1977 (monthly).

Chapter Nine

VANADIUM IN CARBON STEELS

Vanadium (or columbium may be substituted) is sometimes used as a deoxidant and grain refining addition for continuous cast carbon and alloy steels. The use of vanadium is largely restricted to billet casting as opposed to slab casting. Moreover, within the context of billet casting it is primarily used for small billet sections (e.g., four to seven inches square). Table 13 summarizes the figures given for the use of vanadium in carbon steels from Bureau of Mines data. The amount of vanadium is seen to be relatively constant as a function of total steel production, and, in absolute terms, constitutes a relatively small amount of total usage.

As time goes on, more and more billet steel will be produced by the continuous casting process. However, technological developments are such that it is likely that vanadium will not be used at an increasing rate for fine grain control. This is because of the specific design of continuous casting machines being built most recently, and significant progress being made with the use of aluminum for fine grain control. The traditional problems with the use of aluminum for fine grain control for small billets have been associated with nozzle clogging and breakouts. However, these casting problems have been obviated in many cases by recent technical developments. Moreover, there are certain applications where not only cost but end-use requirements favor aluminum. Given this, the figures in Table 13 for projected usage of vanadium for fine grain control in 1980, 1985 and 1990 are given as a relatively constant figure versus their usage at this point in time. There is no projection of a rate of increase which would see a large consumption of vanadium for this particular application.

TABLE 13 Vanadium Use in Carbon Steels (Historical Data and Future Projections)

Year	Vanadium (short tons)
1972	630
1973	687
1974	900
1975	931
1976	498
1980	700
1985	750
1990	800

NOTE: 1972-1976 data are from U. S. Bureau of Mines, 1972-1976; projections are professional judgment by the panel based upon knowledge of changing technology and plans underway in the industry.

REFERENCE

U. S. Bureau of Mines. _Minerals Yearbook_. Washington, D. C.: U. S. Bureau of Mines, 1972-1976.

Chapter Ten

VANADIUM IN HIGH-STRENGTH LOW-ALLOY STEELS

High-strength low-alloy steels (HSLA) are most often carbon-manganese steels to which a small amount of alloying elements (less than 0.2 percent) has been added. These steels are also commonly referred to as microalloyed steels. The alloying elements most commonly used are the carbide-nitride formers vanadium, columbium, titanium, and molybdenum, although the ASTM A588 grade contains silicon, nickel, chromium and copper. In recent years, high-strength low-alloy (HSLA) steels have constituted ~ three percent of the total steel market. The data in Table 20 describe the end-use markets for high-strength low-alloy steels for the years 1974 and 1976. It is seen that five end-use areas constitute the large majority of applications for high-strength low-alloy steels. These areas are: (1) construction and contractor products, (2) railroad cars and locomotives, (3) machinery and industrial equipment, (4) automotive, and (5) line pipe. Future projections on the market for high-strength low-alloy steels will deal largely with these five market areas.

All microalloyed steels obtain the desired increase in strength through the metallurgical mechanisms of grain refinement, transformation, and precipitation strengthening. Depending upon the specific steel product, columbium, vanadium and titanium may be used interchangeably; in other cases, a certain element will have a specific advantage in terms of the desired metallurgical reactions and cost. Particularly potent strengthening is obtainable with the addition of vanadium in combination with nitrogen. Analysis of figures for the amount of vanadium used in the production of HSLA steel vs. the total production of HSLA steels in the last five years shows a reduction in the amount of HSLA steels which are V-modified; i.e., a relative decrease of 15 to 20 percent for 1976 vs. 1972. As discussion proceeds for developing trends in the various market areas, consideration will be given to the particular alloy system preferred.

Of the five major market areas indicated in Table 14, developments in the automotive area are by far the most

TABLE 14 HSLA Steel Usage in the United States: Historical Data

	HSLA Steel (short tons) *		% of Total HSLA	
	1974	1976	1974	1976
1. Construction and Contractor Products	1,065,000	757,000	30	28
2. Railroad Cars and Locomotives	506,000	438,000	14	17
3. Machinery and Industrial Equipment	441,000	332,000	13	13
4. Automotive	420,000	426,000	12	16
5. Line Pipe	386,000	196,000	11	7
6. Trailers	141,000	77,000	4	3
7. Agriculture	72,000	38,000	2	1
8. Marine	69,000	99,000	2	4
All Other Areas	433,000	292,000	12	11
Total Short Tons of HSLA Steel	3,533,000	2,655,000	100	100

	Contained Vanadium (pounds)**	
	1974	1976
Total Pounds of Contained Vanadium	4,800,000	3,260,000

NOTE: Based on data from American Iron and Steel Institute, 1974, 1976; and U.S. Bureau of Mines, 1974, 1976.

* The short tons given for HSLA steels in 1974 and 1976 are 3.1% and 2.5% of total steel shipments for these years, respectively.

** Total calculated contained vanadium in HSLA steels is from data supplied by Mineral Industry Surveys, U.S. Bureau of Mines, 1974 and 1976.

important. To meet mandated safety and fuel economy requirements, dramatic changes are taking place in automotive design and manufacture. Many parts traditionally made from mild steel are now, or shortly will be, made from HSLA steel, aluminum or plastic. By 1980, it is reasonable to project that the tonnage of HSLA steel used for automotive applications will be twice the 1976 level. Between 1981 and 1985, dramatic downsizing will continue. This large overall decrease in the weight of materials will counterbalance the expected increased usage of HSLA steel, but a three-fold increase over the 1976 tonnage is projected.

Up until recently, vanadium, columbium and titanium-modified steels have been largely used interchangeably for automotive applications. In the last two years, the potential of the latest type of HSLA steel has been demonstrated -- the dual-phase steels.* These steels provide the best available combination of strength and formability. Formability is a prime consideration for automotive applications, and a significant quantity of dual-phase steels is included in the figures projected for the 1980's. Although this is a rapidly developing and changing area, it appears that vanadium-modified steels will play a major role in the usageof dual-phase steels.

In the other four major areas (construction, rail transportation, machinery, and line pipe) rapid growth is not anticipated. The actual tonnages will largely reflect the health and expansion of the economy. A slight increase in the relative percent of HSLA vs. total steel used in these areas might be seen, but steel developments and product requirements are not of the dynamic nature existing in the automotive arena. However, the energy shortage, as it would pertain to the availability of heat-treated steel products, or the opportunity for customer heat treatment, could significantly alter the low growth rate projected above. HSLA steels can in some cases be substituted for heat-treated steels with significant energy savings. If

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* Dual-phase steels are steels consisting of a mixture of ferrite and martensite or lower bainite. The dispersion of the strong phase in the highly ductile ferritic matrix is obtained by carefully controlled chemistry and heat treatment.

deterioration of the energy situation continues, users may be forced to use HSLA steels although the traditional considerations of cost and engineering requirements dictate otherwise.

Of the current areas of relatively small usage, the agricultural is a possibility for significant growth. A 50 percent increase by 1980 is quite reasonable but the total tonnage is still relatively small. Moreover, wider acceptance could result in the other low usage areas as a result of favorable publicity from the increased application in the automotive area.

Table 15 summarizes the tons of high-strength low-alloy steel projected to be produced in 1980, 1985 and 1990, along with the pounds of vanadium projected to be used in these high-strength low-alloy steels based upon the foregoing discussion.

REFERENCES

American Iron and Steel Institute. Annual Statistical Report. Washington, D. C.: American Iron and Steel Institute, 1974-1976.

U. S. Bureau of Mines. Minerals Yearbook. Washington, D. C.: U. S. Bureau of Mines, 1974-1976.

TABLE 15 HSLA Steel Usage in the United States: Future Projections to 1990

		HSLA Steel Usage (short tons)			Percent of Total HSLA		
		1980	1985	1990	1980	1985	1990
1.	Construction and Contractor Products	1,200,000	1,300,000	1,400,000	26	23	23
2.	Railroad Cars and Locomotives	600,000	700,000	800,000	13	13	13
3.	Machinery and Industrial Equipment	550,000	650,000	750,000	12	12	12
4.	Automotive	1,000,000	1,400,000	1,400,000	22	25	23
5.	Line Pipe	550,000	650,000	750,000	12	12	12
6.	Trailers	150,000	200,000	250,000	3	3	8
7.	Agriculture	100,000	125,000	150,000	2	2	2.5
8.	Marine	100,000	125,000	150,000	2	2	2.5
	All Other Areas	400,000	450,000	500,000	8	8	8
	Total Short Tons of HSLA Steel	4,650,000	5,600,000	6,150,000	100	100	100

	Contained Vanadium (pounds)		
	1980	1985	1990
Predicted Pounds of Contained Vanadium in HSLA Steels	7,500,000	7,800,000	8,700,000

NOTE: Data are professional judgment of the Panel on Trends in Use of Vanadium, based upon knowledge of changing technology and plans underway in the industry.

Chapter Eleven

VANADIUM IN CAST STEELS

The tremendous growth in the size and power of heavy machinery (such as used in the fabricating industry and mining) to sustain both static and dynamic loads under severe conditions such as low temperature, impact, and wear, has led to the development of high-quality, high-strength steel castings with good impact toughness and wear resistance. Vanadium is one of the alloying elements which imparts such properties to cast steel. The use of vanadium markedly influences the structure and properties of the cast steel in the "as-cast" condition before heat treatment. The addition of vanadium in amounts of about 0.1 percent (1) reduces grain size markedly, (2) reduces dendritic segregation and (3) refines the Widmanstatten pattern within grains. These improvements in the "as-cast" structure are important (1) in avoiding cracking of intricate castings during heating and cooling cycles and (2) in affecting the properties of the heat-treated casting.

While the usual treatment of vanadium steel castings consists of normalizing and tempering, castings of suitable shape and dimensions may be given a more drastic quenching. This is followed by tempering to produce better mechanical properties approaching those of quenched and tempered, forged or rolled steel of similar composition.

Some quenched and tempered vanadium cast steels contain as much as 0.1 percent vanadium. Among the major applications in the normalized state are wheel centers, cross heads, driving boxes, cylinder heads, truck frames, bolsters, eccentric cranks, end sills, center plates, rail clamps and draft gear housings in railway equipment; ladle trunnions, forging hammer rams, pinions, gears, coupling boxes, bearing caps, crankshafts and rolls in steel plant machinery; cylinders, side plates and valve bodies in hydraulic presses and pumps.

In the quenched and tempered form or in the differentially-hardened or surface-hardened condition, it is used for miscellaneous gears, pinions and jaws, and hammers and dies, in crushing and pulverizing machinery. Other fields to which these castings have contributed their excellent properties are industrial cars, power shovels, drag-line equipment, miscellaneous road machinery, automobile trucks and buses, dredging machinery, stokers and oil refinery and oil field equipment.

A. CONSUMPTION

Table 16 summarizes the steel casting shipments in the U. S. from 1971 to 1976, and projected to 1990, assuming a six percent annual growth rate. From these figures the consumption of vanadium in the steel casting industry is calculated, using the assumptions outlined in the table.

B. FORM OF CONSUMPTION

Most of the vanadium additives available in the market can be used by the cast steel industry.

C. SUBSTITUTABILITY

If one substitutes vanadium for molybdenum to enhance the hardenability of a steel, only about 0.12 percent of vanadium can be utilized, since this is the maximum amount that can be dissolved in austenite at the heat-treating temperatures; the 0.12 percent vanadium is thus equivalent to about 0.25 percent molybdenum with respect to hardenability (Grossman, 1952). Best results were obtained with lower carbon, higher manganese and higher austenitizing temperatures. Vanadium is far superior to molybdenum and chromium in achieving higher tempered martensite hardness levels, especially in higher tempering temperature ranges. This property makes the use of vanadium essential for high-temperature creep-resistant steel applications.

D. RESEARCH OPPORTUNITIES

1. Effect of Vanadium as a Grain Refiner

Work is needed to study the effect of vanadium as a grain refiner in steel castings, specifically in steels containing high nitrogen levels.

TABLE 16 Vanadium Consumption by the Steel Casting Industry in the United States, 1971-1990

	1971	1972	1973	1974	1975	1976	1980	1985	1990
				Cast Steel Consumption (short tons)					
Steel Castings Shipped									
Carbon Steel	1,072,421	1,085,255	1,277,000	1,393,750	1,301,750	1,188,360 (66.0%)	--	--	--
Low Alloy Steel	464,717	470,278	555,300	627,336	572,558	550,237 (30.5%)	--	--	--
Stainless and High Alloy	51,635	52,253	61,700	69,704	63,618	61,138 (3.5%)	--	--	--
Total Steel Castings Shipped	1,588,773	1,607,786	1,894,000	2,091,960	1,934,635	1,803,375 (100%)	2,350,000	3,045,000	4,000,000
Total Alloy Steel Melted (60% yield)	860,587	870,885	1,028,333	1,161,733	1,060,293	1,018,958	--	--	--
Alloy Steel Containing Vanadium (12% of total)	103,270	104,506	123,399	139,407	127,235	122,274	--	--	--
				Vanadium Consumption (pounds)					
Total Vanadium Consumption (0.15% V average assuming 90% V recovery)	344,233	348,354	411,333	464,693	424,117	407,583	530,000*	689,000*	895,000*

NOTE: 1980-1990 data from Foundry Management and Technology, January 1977.

* Vanadium consumption is projected at a 6% annual growth rate.

2. Effect of Vanadium in Microalloyed Steels

The microalloying effects of vanadium in wrought steel have been studied extensively; however, very little work is done on the microalloying effect of vanadium in cast steel. A recent publication by Wellner et al. (1977) shows the superiority of microalloyed cast steel over conventional grades, when special toughness and weldability is demanded together with high yield strengths. More work is needed along these lines to optimize the composition and heat treatment of microalloyed steel castings.

3. Effect of Vanadium in High-Strength Austenitic Manganese Steel Castings

Another development which has tremendous potential in wear-resistant applications is the effect of vanadium on the strength of Hadfield manganese steels which have a proven record of wear resistance. U. S. Patent No. 3,075,838 (Avery and Chapin, 1960) describes the effect of vanadium in raising the yield strength levels of austenitic manganese steels to 90 ksi minimum. More work is needed to optimize the composition and heat treatment of such steels.

REFERENCES

Avery, H. F. and Chapin, H. J. "Effect of Vanadium in High Strength Austenitic Manganese Steel Castings." U.S. Patent No. 3,075,838 issued to Abex Corporation February 24, 1960.

Foundry Management and Technology. "Casting Shipments Will Rise 9.9 Percent." Foundry Management and Technology (January 1977): 26-34.

Grossman, M. A. Elements of Hardenability, pp. 133-5. Metals Park, Ohio: American Society for Metals, 1952.

Wellner, P., Mikkerjee, A. and Mayer, H. "Microalloyed Steel for Castings." Foundry Trade Journal (February 1977): 321.

Chapter Twelve

VANADIUM IN CAST IRONS

The technological benefits of vanadium in irons have been known for a number of years; however, its use, compared to chromium, molybdenum, nickel, etc., has been limited because of economic factors. In the Soviet Union, where large quantities of vanadium-bearing slags are available, the production of vanadium-bearing irons is high, and irons containing as high as three percent vanadium are used for their excellent wear resistance.

A. PROPERTIES IMPARTED BY VANADIUM TO CAST IRONS

Vanadium influences the micro- and macro-structure of cast irons as follows:

1. Stabilization of Cementite. Vanadium prevents graphitization of white irons up to about 2000°F. In the range of 0.25 to 0.50 percent vanadium, one part of vanadium counteracts the graphitization effect of four parts nickel.

2. Small, Uniform Graphite Flakes. In pearlitic cast irons, vanadium not only reduces the flake size, but also promotes uniformity in graphite flake size from center to surface of a given section.

3. Persistence of Fine Pearlite Structures. Vanadium promotes fine carbides and fine lamellar pearlite. Vanadium irons exhibit fine pearlite structure with their increased strength and resistance to wear.

4. Modified Dendritic Structure. Vanadium produces smaller and less pronounced dendritic structure.

5. Stabilizing Carbides at Elevated Temperatures. Vanadium produces stable carbides which resist decomposition at elevated temperatures.

The effect of small vanadium additions on the casting properties is negligible. Vanadium additions do not affect the shrinkage and fluidity of gray iron. Because of its carbide-stabilizing effect, vanadium increases the depth of chill in cast irons. The magnitude of the increase depends upon the amount of vanadium and the composition of the iron as well as upon the condition of casting and the section.

B. EFFECT OF VANADIUM ON PROPERTIES OF CAST IRONS

The beneficial effects of vanadium upon the mechanical properties are similar in all irons, but vary in degree according to the remainder of the composition, the melting practice, the casting conditions, the section, etc. The addition of vanadium to cast iron in amounts of 0.1 to 0.2 percent increases its hardness, tensile strength, transverse strength, and compressive strength, together with improvements in ductility and impact resistance.

Vanadium has very little effect on machinability. Vanadium additions have a marked effect on wear resistance. The influence of heat treatment on vanadium-bearing irons is strong and can be used for developing higher strengths.

C. CONSUMPTION

Table 17 summarizes gray iron shipments in the United States from 1971 to 1976, and projected to 1990 assuming a five percent annual growth rate. From these figures, the consumption of vanadium in alloy gray iron is calculated, using the assumptions outlined in the table. The discrepancy between these figures and those reported by the U.S. Bureau of Mines is also shown in this table.

D. FORM OF CONSUMPTION

Most of the vanadium additives available in the market can be used by the cast iron industry.

E. SUBSTITUTABILITY

Vanadium is interchangeable with molybdenum and chromium for wear-resistant applications. Additions of vanadium improve mechanical properties of gray iron and improve its heat resistance.

TABLE 17 Vanadium Consumption by the Cast Iron Industry in the United States, 1971-1990

	1971	1972	1973	1974	1975	1976	1980	1985	1990
				Cast Iron Consumption (short tons)					
Total Gray Iron Shipped	13,839,313	14,200,000	14,801,000	13,459,248	10,621,555	11,935,362	14,300,000	18,900,000	23,400,000
Alloy Gray Iron Shipped	2,500,000	2,750,000	3,000,000	3,000,000	2,800,000	3,150,000 (40%)	--	--	--
Alloy Gray Iron Melted (assuming 80% yield)	3,125,000	3,437,500	3,750,000	3,750,000	3,500,000	3,937,500	--	--	--
Vanadium-Bearing Gray Iron Melted (assuming 3% of alloy iron)	93,750	103,125	112,500	112,500	105,000	118,125	--	--	--
				Vanadium Consumption (pounds)					
Vanadium Consumption (0.12% V average at 90% recovery)	250,000	274,993	299,992	299,992	279,993	314,999	378,000	493,000	673,000
Bureau of Mines Data*	112,000	--	112,000	104,000	118,000	--	--	--	--

NOTE: 1980-1990 data from Foundry Management and Technology, January 1977.

* Based on incomplete reporting by industry.

F. RESEARCH OPPORTUNITIES

1. Substitution of Ni-Hard Type Cast Irons

There is quite a bit of work going on in the Soviet Union on the use of vanadium-bearing irons for wear-resistant applications. More work is needed to study the effect of vanadium (0.5 to 3 percent) on properties of cast irons (white irons).

REFERENCES

Carpenter Technology Corporation. Compendium of High Temperature Alloys and Selected Other Alloys. Reading, Pa.: Carpenter Technology Corporation, January 1970.

Foundry Management and Technology. "Casting Shipments Will Rise 9.9 Percent." Foundry Management and Technology (January 1977): 26-34.

Chapter Thirteen

VANADIUM IN STAINLESS STEELS

Stainless steels are used for their corrosion resistance, high temperature strength, and appearance. Chromium is the essential element in these alloys, but nickel and molybdenum are frequently added to improve mechanical and corrosion properties. Vanadium does not find major application in stainless steels; its principal uses in these materials are to improve the temper resistance of martensitic stainless steels, and stabilize a special austenitic alloy. It has been reported that vanadium additions to some stainless steels, particularly those containing boron and nitrogen, improve the creep resistance of these alloys. Ferrovanadium and vanadium carbide are the forms in which vanadium is usually added in the manufacture of stainless steels.

The overall trend of the use of vanadium in stainless steels, based on U.S. Bureau of Mines data through 1976, is downward; projections of its use based on this trend are shown in Table 18.

Only two commercially significant stainless steels contain vanadium. Both alloys, Type 422 and Nitronic 50, contain 0.15 to 0.3 percent vanadium. Type 422 is a 12Cr-Mo-V-W martensitic steel used for turbine components. Nitronic 50, a proprietary grade from Armco Steel, is austenitic and contains 22Cr, 13Ni, 5Mn, 2Mo, 0.15Nd, and 0.15V. It has excellent strength and corrosion resistance and is used where this combination of properties is required. Vanadium is also added occasionally to high-carbon martensitic stainless steels, such as Type 440 C, used for cutlery.

Although separate statistics are not reported for these grades, it is unlikely that their combined production can account for the consumption of the 20 tons of vanadium attributed to stainless steels in 1976. The 1970 National Materials Advisory Board report, Trends in the Use of Vanadium, contained the same observation, so that it may be that the decreasing trend for vanadium in stainless steel is the result of better reporting rather than technological change.

TABLE 18 Consumption of Vanadium in Stainless and Heat-Resisting Steels

Year	Production of Stainless and Heat-Resisting Steels (short tons)	Vanadium Used in Stainless and Heat-Resisting Steels (pounds contained vanadium)
1967	1,560,000	73,700
1970	1,280,000	80,000
1971	1,260,000	51,700
1972	1,560,000	57,500
1973	1,890,000	51,200
1974	2,150,000	73,100
1975	1,110,000	40,000
1976	1,670,000	42,000
1980*	2,040,000	51,000
1985*	2,430,000	60,700
1990*	2,890,000	72,200
1995*	3,490,000	87,200

NOTE: Based on data from American Iron and Steel Institute, Form 104, 1967-1976; and U.S. Bureau of Mines, 1967-1976.

* 1980-1995 predictions are based on a 2% per year increase from 1976 base value.

The report pointed out that some confusion can arise from classifying the iron-base superalloy A-286 (consuming about 10,000 pounds per year of vanadium) as a stainless steel. This is not a general industry practice, but could cause some inflation in the statistics. The similarity between martensitic 12Cr-Mo-V stainless steels and the AISI D series of tool steels may also be a cause of some errors in counting.

Niobium and titanium would certainly seem to be logical substitutes for vanadium as a stabilizing element. Niobium, and perhaps molybdenum and tungsten, could be used in place of vanadium for increasing temper resistance.

There is not a great deal of current research directed to the use of vanadium in stainless steels. However, there are indications that it might be useful in stabilizing ferritic stainless steels and improving their toughness.

REFERENCES

National Materials Advisory Board. Trends in the Use of Vanadium. Report No. NMAB-267. Washington, D.C.: National Academy of Sciences, 1970.

U.S. Bureau of Mines. Mineral Industry Surveys. Washington, D.C.: U.S. Bureau of Mines, 1967-77 (monthly).

U.S. Bureau of Mines. Minerals Yearbook. Washington, D.C.: U.S. Bureau of Mines, 1967-76, 1976 (preprint).

Chapter Fourteen

VANADIUM IN SUPERALLOYS

The superalloy category of materials is usually defined as those alloys containing more than 50 percent of nickel and/or cobalt. In accounting for the uses of vanadium in superalloys, not only are the nickel and/or cobalt-base alloys included, but even some iron-base alloys (e.g., A-286) since their application is primarily in elevated temperature service. One of the minor uses of vanadium-containing iron-cobalt-base alloys is for permanent magnet alloys. Vicalloy I and Vicalloy II, which contain 10 to 15 percent vanadium, are used for magnets in computers where high field strengths are required. "Soft" magnetic materials, those whose magnetism is induced by electric current (e.g., Permendur, Supermendur and Remendur) again are iron-cobalt-base and contain two percent vanadium. The total amount of vanadium consumed by magnetic and superconductivity alloys is very small (about 20,000 pounds per year of vanadium, as ferrovanadium or pure vanadium metal), and no significant increase in consumption is predicted through 1990.

Vanadium-containing superalloys and their applications are listed in Table 19.

TABLE 19 Superalloys Containing Vanadium

Alloy Name	Weight Percent Vanadium	Typical Applications
A-286	0.30	Fastners, Discs, Sheet Metal Components
AFC-77	0.50	Fasteners
Hastelloy B	0.2-0.6	Chemical Processing
Hastelloy C	0.4	Chemical Processing
Hastelloy C-276	0.35 max.	Chemical Processing
Hastelloy W	0.60	Shroud Rings
IN-100	1.0	Blades and Discs
V-57	0.30	Discs and Nozzles

NOTE: Data from Carpenter Technology Corporation, 1970.

Even though some of the alloys in Table 19 are iron-base, they all contain large amounts of chromium for oxidation resistance, and nickel and/or cobalt. The more modern superalloys have been avoiding the vanadium addition because of its tendency to form the embrittling sigma phase. On exposure to oxidizing atmosphere at elevated temperatures (above 690°C/ 1275°F), formation of V_2O_5 tends to result in deterioration of the protective films, leading to catastrophic oxidation. The addition of vanadium to superalloys is predicated on its contributing to solid solution strengthening and carbide formation; however, there are usually other alloying elements that contribute these roles more effectively, without the deleterious effects. The IN-100 alloy is an exception; the positive role of the vanadium addition to strengthening has been confirmed, and the addition is well justified.

In the chemical industry, for the high-temperature corrosive manufacture of certain acids and salts, use of vanadium is making some gains. With chromium, it may impart additional passivation in the presence of liquid media. Here, Hastelloy B and Hastelloy C-276 (0.35 percent vanadium maximum) are typical examples.

During the melting of superalloys, vanadium is added before pouring as ferrovanadium (FeV), vacuum quality (VQ) ferrovanadium, FerroVan, or Carvan (13.5 percent carbon) when a small amount of iron and high carbon can be tolerated. Only rarely, if there is concern about certain trace elements, would additions of vanadium metal (scrap) and vanadium-aluminum alloy be used. Vanadium pentoxide is generally not added to superalloys.

The consumption of vanadium in the United States in magnetic superconductivity and superalloys is not well documented, and is confusing since iron-base alloys are included in the category. Accepting the U.S. Bureau of Mines statistics through 1976, and then projecting the vanadium consumption in this category of materials through 1990, results in the data summarized in Table 20.

With respect to substitutability and interchangeability of vanadium-containing superalloys, vanadium-free alloys exist that perform on a competitive basis with the vanadium-containing type. The effect of vanadium in elevated-temperature and in corrosion-resistant alloys is such that other alloy additions (e.g., chromium, molybdenum, and/or niobium) could well be utilized to cause the beneficial properties. It is doubtful if any research is required on vanadium-containing superalloys or magnetic materials.

TABLE 20 Vanadium Consumption in the U.S. for Superalloys and Magnetic Materials

Year	Vanadium Consumption (pounds)
1972	28,111
1973	75,300
1974	106,906
1975	48,000
1976	38,000
1977	40,000
1980	45,000
1985	50,000
1990	55,000

NOTE: Data for 1972-1977 are from U.S. Bureau of Mines, Mineral Industry Surveys; 1980-1990 predictions are based on approximately 2 percent per year increase over the 1976 base.

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Chapter Fifteen

VANADIUM IN TITANIUM ALLOYS

As the amount of vanadium used in nonferrous alloys other than titanium is very minor, this section will deal only with vanadium in titanium-base alloys.

Next to aluminum, vanadium is the most important alloy addition to titanium-base alloys which are primarily used in commercial and military aircraft, and in gas turbine applications. Vanadium promotes the formation of the body-centered cubic beta phase and forms no undesirable intermediate phases with titanium. As a beta stabilizer, it improves the hot and cold workability of titanium alloys. When added in amounts up to one percent, it improves the strength of alpha alloys and promotes their thermal stability in the presence of moderate to large amounts of aluminum. When added in amounts of four percent and greater, it provides the very important ability of alpha-beta and beta alloys to be significantly strengthened by heat treatment.

The following figures, showing the major commercial titanium alloys containing vanadium additions and their relative percent of total mill product shipments in 1973, illustrate their importance:

Alloy	Percent of Total Shipments*
Ti-6Al-4V	57
Ti-6Al-6V-2Sn	9
Ti-8Al-1Mo-1V	2
Ti-13V-11Cr-3Al	<1
Ti-3Al-2.5V	<1
Other Alloys	~30

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* Except for Ti-3Al-2.5V, data are from "Current Status of the U. S. Titanium Industry," MCIC CR-74-01, March 1, 1974, "A Special Study for the Office of the Director of Defense Research and Advanced Technology," conducted at the Battelle Columbus Laboratories.

In addition to the commercial alloys, the following alloys, which are in various stages of advanced development, support the continued importance of vanadium as an alloy addition to titanium:

Ti-10V-2Fe-3Al
Ti-8Mo-8V-2Fe-3Al
Ti-3Al-8V-6Cr-4Mo-4Zr
Ti-8V-4Cr-3Al-2Mo-2Fe
Ti-15V-3Cr-3Al-3Sn
Ti-2Al-11V-2Sn-11Zr

Vanadium is added to titanium-consumable-electrode, vacuum-arc melted alloys as one of two master alloys 65%V-35%Al or 50%V-50%Al. These alloys are produced by the aluminothermic process in electric furnaces using V_2O_5 of a grade equivalent to National Stockpile Purchase Specification P-58-R. Although a master alloy specification exists (National Stockpile Specification C, No. M-101; page 49 of this report), there is no listing in the Stockpile Goals (Table 8, page 63) of this alloy (Type 1: 65V-35Al). The panel feels that the advisability of including this master alloy in the National Stockpile should be investigated, as it is a material critical to the needs of the military airframe industry.

The following are the nonferrous alloy contained vanadium consumption figures for the past five years as reported by the U.S. Bureau of Mines (1977):

Year	Pounds of Vanadium
1972	706,000
1973	1,054,000
1974	1,444,000
1975	850,000
1976	633,930

These values roughly parallel the titanium and titanium alloy mill product shipment figures for these years and reflect the fluctuations in demand for titanium alloys by the aerospace industry.

Revert in the form of recovered primary mill producers', secondary fabricators', and airframe and engine manufacturers scrap is a major source for vanadium additions as reflected by the following data for 1974:

	Weight (pounds)
A. Total titanium ingot production (U.S. Department of Commerce, April 1975)	72,300,000
B. Estimated total vanadium used (assuming that 68 percent of titanium production was for vanadium-containing alloys at an average of 4.2% V content)	2,065,000
C. Vanadium used for nonferrous alloys (U.S. Bureau of Mines, 1975)	1,444,000
D. Vanadium from revert (B-C)	621,000

These figures would indicate that roughly one-third of the vanadium used in producing titanium alloy ingots originated from the only source other than vanadium-aluminum master alloys (i.e., revert). With revert being such a major factor in the production of vanadium-containing alloys, variations in its availability to the ingot producers can markedly affect the usage of the vanadium-aluminum master alloys.

The steel and aluminum industries consume large volumes ot titanium scrap for grain refining and alloy additions. For example, during the 1960 to 1970 decade, about 35 percent of the total titanium scrap supply was consumed by the steel industry. The users are companies producing steel, stainless steel, and other high-strength iron-, chromium-, nickel-, and cobalt-base alloys. Also, according to the Department of Commerce, large quantities of titanium scrap are exported. The availability of titanium scrap to the titanium industry is a function of its price relative to the price of titanium sponge. When the price is excessive because of high demand for scrap from other industries, titanium producers are forced to use larger proportions of the basic raw materials, including the vanadium-aluminum master alloys. Fluctuations in the demand for titanium scrap, therefore, become a very important unknown in forecasting the titanium industry's usage of primary vanadium.

The following vanadium forecast for nonferrous alloys is based on these assumptions: (1) the B-1 bomber program is not reactivated to a major extent; (2) the supersonic transport program in the United States is not revived to the production stage; (3) no major swings in the economy occur through 1990; and (4) increase in demand by the aerospace industry for titanium products is approximately 1.5 percent annually.

Year	Vanadium (pounds)
1980	1,030,000
1985	1,090,000
1990	1,140,000

These figures reflect the fact that usage of titanium alloys by the aerospace industry will continue to grow at a moderate rate, but that the major growth in the titanium market will be in the chemical-industrial area. For example, whereas chemical industry titanium usage in 1976 was about 30 percent of the total of 29 million pounds of mill products shipped, a conservative forecast would indicate that in 1990 more than 50 percent of the 56 million pounds of titanium mill products produced will go into chemical-industrial applications. These applications primarily involve the use of unalloyed commercially pure titanium mill products; however, it is important to note that the preceding forecast of vanadium usage through 1990 could be 25 percent higher should the Ti-6Al-4V alloy or alternative vanadium-containing alloys be selected for several industrial applications currently in the early stages of development.

The major factor which could markedly affect the previously given vanadium forecast would be a national emergency requiring the production of large numbers of military aircraft. Each F-14 fighter aircraft requires about 1800 pounds of vanadium, and each F-15 requires about 2500 pounds of vanadium in the form of titanium alloys. These examples illustrate the major effect the construction of large numbers of military aircraft could have on the vanadium requirements for titanium alloys. For this reason, it is suggested that vanadium in the form of 65%V-35%Al master alloy be stockpiled by the General Services Administration, in addition to stockpiling V_2O_5. In case of national emergency, it could take six or more months for the master alloy producers to construct the electric furnace facilities required to produce the special purity vanadium-aluminum master alloys. With sufficient master alloy in the stockpile, titanium mill production could be increased to required levels without delay. A preceding section of this report presents an example of a titanium industry specification for vanadium-aluminum alloys which could be used as a model for a National Stockpile Purchase Specification.

In case of a vanadium shortage, the most efficient substitute as an alloy addition to titanium alloys would be molybdenum, which is a stronger beta stabilizer than vanadium. Molybdenum would be required at about two-thirds the weight percent level of vanadium to achieve roughly the same effect on properties. However, the melting, fabrication, mechanical property characteristics of such alloys are not as desirable as those which can be achieved with vanadium. It is also quite likely that molybdenum would be in as short supply as vanadium, or even more scarce. Although other beta stabilizers such as iron, chromium, manganese, etc., could be used in case neither vanadium nor molybdenum is available, such alloys would have markedly inferior high-temperature creep stability and fracture toughness characteristics compared to the more popular alloys such as Ti-6Al-4V.

Current manufacturing technology programs being sponsored by the Department of Defense are aimed at reducing the input weight of titanium mill products for airframe and engine components. Such "Net Shape" programs as isothermal forging, superplastic forming combined with diffusion bonding and casting, combined with hot isostatic pressing (HIP), should be encouraged as they will serve to conserve vanadium and titanium in addition to the cost savings they offer.

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Chapter Sixteen

VANADIUM IN SOME FUTURE NUCLEAR POWER GENERATING REACTORS

A. FUSION POWER REACTOR

The fusion reaction involves a reaction of deuterium with tritium under conditions of enormous magnetic and electric fields to produce helium, heat and neutrons. The heat and neutrons are absorbed by a molten lithium blanket. The molten lithium becomes the basis for heat absorption and transmission to conventional steam generation. The thin wall containment of lithium has two major material candidates -- stainless steel, and a vanadium alloy. In principle, the optimal design favors the vanadium alloy choice (see Table 21).

It should be realized that a self-sustaining fusion reaction has not yet been achieved. A full-scale power reactor is perhaps 20 years away. Its design can only be conceptualized. It would use somewhere between 100 and 1000 tons of vanadium alloy (approximately 65 percent vanadium). It should also be noted that wrought vanadium and vanadium alloy in sheet or tube form are not produced by any commercial organization in the United States. It must presently be procured from foreign sources.

B. BREEDER FISSION POWER REACTOR

In the 1970 vanadium forecast (National Materials Advisory Board, 1970), there was a substantial projected use of an appropriate thin-walled tubing for canning the fissionable material. There was an unresolved choice between a stainless steel, a nickel alloy or a vanadium alloy. Since that time, the evidence has ruled against using the vanadium alloys. The technical problem has to do with the absorption of oxygen from molten sodium at the level of oxygen attainable by cold trap methods. The resultant oxygen absorption by vanadium leads to unacceptable embrittlement.

TABLE 21 Representative Tokamak Demonstration Plant Parameters

Parameter	Value		
Major Radius (meters)	6.01		
Aspect Ratio (A)	3.0		
Plasma D Elongation (κ)	1.65		
Maximum Toroidal Field (tesla)	8.5		
Superconductor	NbTi		
Average Plasma (β_t, %)	8		
Plasma Safety Factor (q)	3		
Thermal Power (MW)	1,500		
Plasma Current [(I_p) MA]	13.3		
Maximum OH Field (tesla)	5.5		
Coolant	Lithium		
Structural Material*	Vanadium Alloy	vs.	Stainless Steel
Electric Power (MW)	460		403
Maximum Structural Temperature (°C)	650		500
Plant Availability Factor (%)	86		81
Wall Lifetime (years)	3.3		1.7
Direct Capital Cost ($ million)	650		580
Total Capital Cost ($ million)**	1,040		930
Direct Cost of Power ($/KWE)	1,390		1,440

NOTE: Based on data from Stacey and Abdou, 1978.

* Possible future consideration may also include Ti-6Al-4V alloy.

** Including contingency, engineering and interest.

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Chapter Seventeen

VANADIUM IN CHEMICAL AND RELATED INDUSTRIES

There is a large and growing body of technical literature which describes a multitude of uses for vanadium compounds. However, most of these uses either are not commercial or are insignificant in size. The vanadium literature is essentially of little value in determining exact consumption in chemical applications. Significant present uses consist of catalysts taken as a group, ceramic pigments, and electronic uses (mainly in the red phosphor component of color television tubes). It has been reported that vanadium compounds are used in some special refractories in Europe, but apparently this application is of negligible size in the U. S. All chemical uses together amount to approximately 7 to 11 percent of total U. S. consumption of vanadium, with the balance going to metals or alloys.

A. CATALYTIC APPLICATIONS

Estimated chemical usage of vanadium for the period 1971-1975 shown in Table 22 is based in large part on private communications from a number of industrial specialists in each area (plus selected industrial statistics from the Department of Commerce and appropriate literature sources). Table 24 at the end of this chapter gives projected future consumption figures.

It should be noted that the figures do not agree well with statistics previously published by the Bureau of Mines, but overall totals are of roughly the same order of magnitude as Bureau of Mines figures for the sum of chemical uses plus other miscellaneous and unspecified uses. The figures represent apparent U. S. demand; i.e., shipments plus imports minus exports, taking into account any changes in inventories. Note also that the figures represent gross vanadium usage or purchases, uncorrected for external losses (losses net of any internal recovery), or any salvaged wastes which are shipped to vanadium producers.

Over the time period covered by Table 22, there have been some significant changes within each industry. In particular, there has been increasing effort to reduce

TABLE 22 Estimated U.S. Consumption of Vanadium in Chemical and Related Uses

Use	Vanadium Consumption (short tons)				
	1971	1972	1973	1974	1975
Sulfuric Acid Catalyst	70	100	100	170	190
EPDM Rubber Catalyst	45	67	88	92	74
Adipic Acid Catalyst	71	81	85	82	73
Maleic Anhydride Catalyst	10	11	12	12	10
All Other Catalysts	5	5	5	5	5
Total Catalysts	201	264	290	361	352
Ceramic Pigments	65	65	65	73	56
Electronic and Miscellaneous	12	15	19	21	16
Total Consumption	278	344	374	455	424

NOTE: Based in a large part on private communications from industrial specialists and selected industrial statistics (see text for details).

or eliminate vanadium discharges in process effluents. Consequently, the amounts of vanadium recovered for recycling have increased from an initial rather low level in 1970. In most of the applications, significant quantities of spent catalysts or process wastes are now recovered and either reused or returned to primary vanadium producers for reworking. The magnitude of this recovery is not known, but gains are still being made and it is likely that growth in overall net usage will be rather small in the period 1976-1980 because of this increasing recovery.

The figures given include no allowances for vanadium consumed in exports of vanadium chemicals or catalysts. So far as can be determined, this is not a significant factor except for sulfuric acid and maleic anhydride catalysts. The U. S. is apparently a net exporter of sulfuric acid and maleic anhydride catalysts, so actual consumption for these end uses will be possibly 20 to 30 percent higher than shown. The U. S. appears to be a net importer of catalysts for production of phthalic anhydride, but this use is insignificant in terms of vanadium consumption.

Other trends within each major use category are discussed in following paragraphs.

Consumption of sulfuric acid catalyst on an average is essentially evenly divided between initial charges to new acid plants and replacements or additions to catalyst in existing plants. Consumption is highly cyclical, varying with the general level of business and with the supply-demand relationship for fertilizers, which consume more than 50 percent of all sulfuric acid produced. Growth rate was quite high in the period 1971-1975, due to a combination of fertilizer capacity increases and a need to increase acid plant conversion efficiencies to meet tight new emission limits. It is likely that smoothed future growth rates will approximate four to five percent per year, with some inevitable peaks and valleys.

Platinum catalysts are the only known practical alternates to vanadium catalyst, but were abandoned in the past because of their greater susceptibility to poisoning and degradation, plus the greater cost of losses in service. There are no developments now in view which might reduce the need for vanadium in sulfuric acid catalysts. Should raw material supplies become tight, platinum undoubtedly would be more difficult to obtain than vanadium.

The use of vanadium in sulfuric acid catalysts must be considered a critical application because sulfuric acid is a basic commodity for much of the chemical and related industries, as well as phosphatic (and other) fertilizers. The vanadium source for sulfuric acid catalysts is typically either ammonium metavanadate or granular V_2O_5 obtained by roasting ammonium vanadate. Fused V_2O_5 is not a desirable raw material because it is difficult to convert to a soluble form. In the event of an emergency, it could probably be used by providing a special hydrolysis treatment. It is also possible that red cake (sodium polyvanadate) might be used with special treatment and/or changes in catalyst formulation.

Vanadium compounds which are soluble in organics are used as catalysts for the co-polymerization of ethylene and propylene to make a special type of rubber which has desirable properties for many automotive and industrial uses. This rubber is designated as EPDM, short for ethylene propylene diene monomer. It is used in tires to a minor extent, and this might well increase with further development work. EPDM rubber consumption is increasing rapidly, with a temporary decrease noted in the depressed year 1975.

The main vanadium compounds used are vanadium tetrachloride (VCl_4) and vanadium oxytrichloride ($VOCl_3$), the latter representing approximately 80 to 85 percent of consumption. The vanadium appears to end up in waste water from the rubber process and is said to be either precipitated as an unsoluble sludge or otherwise removed to prevent stream pollution. The amount recovered for return to primary vanadium producers is unknown.

Vanadium apparently is specifically required to obtain desired EPDM rubber properties. In other organic polymerizations, titanium and chromium are used as similar Ziegler-Natta type catalysts and vanadium is less desirable. In simple terms, vanadium favors trans-isomers and titanium or chromium favor the cis-isomers, although other factors may also be significant.

Since one of the main uses of EPDM rubber is in automotive applications, future consumption will undoubtedly fluctuate widely with the cyclic automobile industry. Growth rate in the period 1971-1975 was quite high, as can be seen from Table 22. It is expected that average growth rates in future years will be approximately as follows:

1976 to 1980 - 9 percent per year
1981 to 1985 - 7 percent per year
1986 to 1990 - 5 percent per year

However, if usage of EPDM rubber in tires increases substantially, these forecasts could well be low.

In the production of adipic acid (a major chemical intermediate), ammonium metavanadate is used as a source of vanadium to catalyze the liquid phase nitric acid oxidation of cyclohexanone or cyclohexanol to adipic acid. Adipic acid in turn is used to produce Nylon 6/6, plasticizers, polyester urethanes, and other smaller volume products. Nylon 6/6 is by far the biggest end product, accounting for about 85 to 90 percent of all adipic acid use. Adipic acid is a relatively mature product, and future growth rates are expected to average about four to five percent per year.

In the adipic acid process, approximately 80 to 90 percent of the vanadium used as a catalyst is recovered and returned to process. Net consumption to make up for losses is approximately 0.25 pounds of ammonium vanadate per 1,000 pounds of adipic acid produced. This figure is used in conjunction with published data on adipic acid production to calculate the figures given in Table 22.

Efforts to increase vanadium recovery are in progress, and it appears possible that losses might conceivably be reduced to about 0.10 to 0.15 pounds of ammonium vanadate per 1,000 pounds of adipic acid. In forecasting future consumption of vanadium, this possibility has <u>not</u> been taken into account.

Solid catalysts based on vanadium are used for the vapor phase partial oxidation of benzene or n-butane to maleic anhydride. Maleic anhydride in turn is used as a raw material to produce unsaturated polyester resins, agricultural chemicals, lubricant additives, copolymers and other miscellaneous chemical products. Approximately 55 to 60 percent of maleic acid usage is in polyester resins and 10 to 15 percent in agricultural chemicals.

Forecast overall growth rate for maleic anhydride is approximately seven percent per year, with a possibility of higher growth if polyester resins increase at the high rates which some observers expect. In addition, there appears to be a trend toward production of maleic anhydride from n-butane rather than traditional benzene, which in turn might cause some small temporary increases in catalyst consumption in the form of initial catalyst charges to new or modified plants, as well as some continued increase in vanadium usage in service. To summarize, forecast consumption of vanadium for maleic anhydride catalysts, as given in this report, is probably conservative.

There is an extensive body of patents on various types of vanadium catalysts for maleic anhydride (or phthalic anhydride, an analogous product). In most cases, the preferred source of vanadium appears to be ammonium metavanadate. There seems to be no reasonably efficient substitute for vanadium in this use.

There are a great number of literature and patent references to other types of vanadium catalysts for different chemical and related uses. However, the uses shown in Table 23 appear to be the only ones which are now significant or are likely to be so in the near future.

Phthalic anhydride is currently made either by fluid bed catalytic oxidation of naphthalene or by oxidation of o-xylene in fixed bed catalytic reactors. Any new plants built will undoubtedly be of the fixed bed type, and it is possible that fluid bed units will eventually be shut down because of unfavorable economics for the use of naphthalene. Fixed bed units are almost entirely based on German technology (BASF or von Heyden) and their catalyst is imported into the U. S. The fixed bed catalyst contains only about 0.3 percent vanadium and has a relatively long life, so vanadium usage in it is quite small (much less than one ton per year). The estimated total usage rate given in Table 23 is based largely on catalyst consumption in fluid bed plants, which currently accounts for about 30 percent of installed phthalic anhydride capacity. Future consumption of vanadium probably will decrease.

Miscellaneous liquid phase polymerizations have not been identified in depth. The consumption figure given in Table 23 is essentially based on estimated usage of vanadium acetyl acetonate, $V(OC_5H_7O)_3$, and vanadium trichloride, VCl_3. Of these two compounds, vanadium acetyl acetonate is predominant, at an estimated 90 percent of total usage. In most large-volume organic polymerizations (EPDM rubber excepted) titanium and chromium compounds are preferred to vanadium. Consumption in this field is expected to increase rather slowly.

TABLE 23 Miscellaneous Catalysts Using Vanadium

Catalytic Reaction	Current Annual Vanadium Usage (short tons)	Compounds Used or Percent Vanadium in Catalyst
Phtalic Anhydride	1	~ 2% (Fluid Bed)
Miscellaneous Organic Polymerizations (Soluble Vanadium Compounds)	2	Vanadium Acetyl Acetonate Vanadium Trichloride
Miscellaneous Organic Polymerizations and Oxidations (Vapor Phase)	1	--
Miscellaneous Organic Oxidations (Soluble Vanadium Compounds)	1	Vanadium Naphthenate (plus others cited)
Total Vanadium Usage	5	

NOTE: Estimated values are based on private communications from industrial specialists and calculations from the end product produced using the catalyst (see text for details).

Miscellaneous liquid phase organic oxidations have not been identified in depth. Some reported applications in this field are production of aniline black dyes (largely for textile use), printing inks, vegetable oil drying, and paints. Experts indicate that all of these uses are quite minor in terms of total usage. The consumption figure given in Table 23 has been derived from estimated production of vanadium naphthenate, which contains approximately three percent vanadium. This general field of use is considered to be essentially static, or low growth rate.

Other vapor phase polymerizations or oxidations using vanadium catalysts appear to use negligible quantities of vanadium at the present time. At one time, it was thought that vanadium catalysts might be used on a large scale for oxidation of automobile exhaust gases. However, this application does not now appear practical, and the chance of any significant development in the future appears remote. It is possible that vanadium catalysts or compounds may find application in some other gaseous emission abatement processes.

It is known that vanadium catalysts have promise as agents for vapor phase polymerizations of ethylene and propylene (U.S. Patents 3,784,539 [Mullikin and Ort, 1975]; 3,925,338 [Ort, 1975]; and 3,956,225 [Ort, 1976]). This use may become commercialized in the future. It is also known that vanadium catalysts have promise as agents for reacting ammonia and oxygen with propylene to form acrylonitrile, and for similar conversion of p-xylene to terephthalonitrile. Other so-called ammoxidations over vanadium catalysts may have commercial potential. Vanadium catalysts for hydrodesulfurization of crude oils are described in Chapter 4, Section B, but this use (when commercialized) will be likely to recover vanadium from crudes rather than consuming it.

It has also been reported that vanadium compounds are promising in new processes for fixing atmospheric nitrogen.

To summarize, miscellaneous catalyst uses are now small, with low foreseeable growth rates in present applications, and, in some cases, declines. However, there are some promising applications on the horizon which could cause growth. For prediction purposes, it has been assumed that overall growth rate will approximate four to five percent per year, with one or two new or growing catalysts compensating for those which decline or become obsolete.

B. INORGANIC COMPOUNDS APPLICATIONS

Vanadium has substantial use as a component of inorganic pigments used in ceramic floor and wall tiles and in porcelain enamel household fixtures and appliances. It is used in primary zirconia-vanadate blues and yellows, which in turn are blended to form greens and a number of intermediate colors, such as turquoise, gold, etc. The original U. S. patents issued to Harshaw Chemical Company (Patent Nos. 2,441,447 [Seabright, 1948] and 2,623,833 [King and Tesar, 1952]) have now expired, and these pigments are produced by a considerable number of manufacturers.

In earlier years, tin vanadate was also used as a ceramic pigment. However, the relatively high cost of tin has now made this pigment essentially obsolete. Over the past five to seven years, production of vanadium blue pigment has declined because more intense shades of the same general type have been developed which have substantially increased pigmenting efficiency. There are no known substitutes for vanadium in the production of these specific ceramic colors.

Overall growth rate would apparently have been substantial over the 1971-1975 period except for these changes in technology. Because of the changes, estimated vanadium consumption (Table 24) shows low averaged growth, even allowing for the depressed year 1975.

Future consumption will undoubtedly fluctuate widely, varying with the general level of business and the number of new housing starts (or formation of new households). Color preferences of consumers will also be a factor and some observers report that the popularity of white is increasing. Average growth rate in the future is expected to be approximately three percent per year, in part because of changing age distribution within the U. S. population.

Some literature references report that vanadium oxides are used as a coloring agent (or ultraviolet radiation screening agent) in glass. However, this appears to be a very minor use, if still practiced at all. One major glass manufacturer reports no usage for this purpose.

Vanadium consumption in electrical applications, refractory materials and biological applications is currently not large, but this general area appears to be a promising and exciting field for new developments. The future cannot be clearly foretold, but there are enough different new

TABLE 24 Present and Projected U.S. Chemical Consumption of Vanadium

	Vanadium Consumption (short tons contained V)				
	1970	1975*	1980	1985	1990
Catalysts					
Sulfuric Acid Catalyst	60	190	140	180	230
EPDM Rubber Catalyst	46	74	140	200	250
Adipic Acid Catalyst	59	73	110	135	170
Maleic Anhydride Catalyst	9	10	16	23	30
All Other Catalysts	4	5	6	8	10
Total Catalysts	178	352	412	546	690
Ceramic Pigments	65	56	85	100	115
Electronic and Miscellaneous	9	16	40	80	160
Total Consumption	252	424	537	726	965

NOTE: Estimated values are based to a large part on private communications from industrial specialists (see text for details).

* The year 1975 does not fit normalized trend lines.

applications being studied to suggest that at least some of them will be successful and that average growth rate in this category will be substantial.

In the period 1971-1975, vanadium consumption in refractory materials and biological uses was apparently negligible. The major electrical use was as the red phosphor component of color television tubes ($YVO_4 \cdot Eu$). Small additional amounts of vanadium were reportedly used as color modifying agents in mercury vapor lamps, as well as (presumably) in fluorescent lamps or specialty electronic devices.

Growth rate of color television tubes has been significant in recent years and this rate is expected to continue at least until 1980. Imports of color television sets are increasing, but there is also a growing demand for rebuilt or replacement tubes. About 1980, it is expected that other applications in electronics or refractory materials may become important, and that high growth will continue until 1990.

Some of the promising electrical or electronic applications currently being studied are:

1. Use of V_3Ga as a superconductor.
2. Use of VO_2 as a thermally or optically activated resistor/conductor.
3. Use of vanadate glasses as electro-optical or other switches.
4. Use of vanadium as a doping agent for semi-conductors or semi-conductive glasses.
5. Use of vanadium electrodes for special fuel cells or other similar applications.
6. Use of rare earth vanadites as special magnetic materials.

Although some of these uses may require only small amounts of vanadium even if successful, the future potential for large superconducting electric motors, generators and cables, and for fuel cells appears to be substantial.

In the refractory materials field, it is reported that vanadium borides, carbides, nitrides, and silicides have good refractory properties. A mixture of V_2O_5 and BeO reportedly makes a strong, low porosity refractory body. In Germany it is reported that approximately 5 percent V_2O_5 is added to silicon carbide refractories to increase their resistance to oxidation at high temperatures. It has also been reported that vanadium is being used in some cermets. This general area appears to be an interesting field for research and possible future applications.

In the biological area, it is reported that minor amounts of vanadium are being used in some medications for heart disease. Some marine organisms are known to utilize vanadium as a critical ingredient of body chemistry, which suggests that other biological applications will be found. However, this general field cannot be considered of any real significance in relation to vanadium consumption.

Forecasts of future use are shown in Table 24 based on individual growth rates described in preceding paragraphs. Obviously, there is considerable uncertainty in forecasting more than five years ahead, since changes in technology may occur which are not now visualized. For planning purposes, it is probably desirable to add an uncertainty factor of at least plus or minus 15 or 20 percent to the overall totals shown; a trivial amount.

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Chapter Eighteen

ENVIRONMENTAL EFFECTS OF VANADIUM

Dispersion of vanadium in combined form occurs predominantly by airborne dust and fume. Soluble vanadium salts could occur in ground waters near plants which leach salt roasted minerals and slags, from plants which pickle wrought products containing appreciable amounts of vanadium, and from plants using or handling ammonium vanadate. However, there have been no reports of ground water contamination.

Vanadium-containing dust or fumes could be deposited in the environs of industrial plants which produce ferrovanadium or aluminothermic vanadium but there have been no documented air samplings that indicate that present air management facilities are inadequate. By far the bulk of airborne vanadium-containing particles derives from combustion of coal and certain residual oils used as fuels. Vanadium is present in small amounts in many coal resources and particularly in South American crude oils. The vanadium traces are concentrated in the ash which is substantially airborne, part of which is discharged from stacks. A recent article (McMullen and Faoro, 1977) reports atmospheric vanadium concentrations in the range of 0.01 to 1.0 micrograms per cubic meter in northeastern states, attributed primarily to combustion of oil-containing vanadium.

Airborne vanadium exists as oxides and sub-oxides. Quoting from an earlier National Academy of Sciences publication (1974):

> "In man, the principal toxic effects of vanadium have been observed in industrial workers exposed on the job to relatively high concentrations of various vanadium compounds. In general, these exposures have been to several milligrams per cubic meter (of air) or higher. In these circumstances, direct irritation of the tracheobronchial tree results, with cough, sputum, tightness in the chest, wheezing, and eye, nose and throat irritation. Some workers thus exposed also exhibit weakness, neurasthenia, and

> slight anemia, which suggests chronic toxic effects from absorption. Several workers have demonstrated an apparent increased sensitivity to vanadium compounds after a rather heavy initial exposure whereas other workers seem to develop some adaptation to exposure."

A recently proposed standard for work environment (National Institute for Occupational Safety and Health, 1977) is 0.05 milligrams per cubic meter for vanadium compounds, or 1 milligram per cubic meter for elemental vanadium or vanadium carbides. This document also contains considerable background information.

A more detailed discussion of symptoms is given by Browning (1961):

> "SYMPTOMS
>
> "<u>Respiratory</u>.--Nasal catarrh or nose bleeding, observed in gas turbine workers by Browne (1955), in boiler cleaners by Thomas and Stiebris (1956) and in process workers by Symanski (1939) has been a prominent initial symptom. This, with soreness of the throat and chest, is described by Williams (1952) as belonging to a primary group of symptoms with an onset between a half and one hour after starting work. Dry cough, wheezing and dyspnoea on exertion appear after a period of 6-24 hours.
>
> "Bronchitis, mainly of an acute nature, is considered by Sjoberg (1956) to be a prominent symptom, lasting from a few days to more than 2 months. He also observed (Sjoberg, 1950) cases of bronchopneumonia and lobar pneumonia, probably of combined chemical and bacterial origin (vanadium pneumonitis) and one case of pleurisy.
>
> "The question of emphysema as a sequel of the bronchitis due to vanadium has occasioned some diversity of opinion. It was suggested by Symanski (1939), and Wyers (1946) reported one case. In a follow-up by Sjoberg (1956), however, among 36 workers examined 8 years after their original exposure, there was no evidence of either pneumoconiosis or emphysema, although 6 still

had bronchitis with rhonchi resembling asthma and bouts of dyspnoea. X-ray appearances have in some cases (e.g. Williams) shown no abnormality, but Wyers described some where there was reticulation.

"Gastro-intestinal.--Some of the patients described by Thomas and Stiebris (1956) complained of nausea, vomiting and abdominal pain, but Symanski found no evidence of gastro-intestinal disturbance.

"Kidney injury.--Dutton's findings of blood and casts in the urine have not been confirmed by the majority of observers, but one man in Wyers' series had hyaline and granular casts. Vanadium has been demonstrated in the urine of workers suffering from clinical symptoms of vanadium poisoning. Thomas and Stiebris found 0.07 mg. per l. in the most severely affected, and Williams found 0.07-0.4 mg. per l., also in the clinically most severe cases.

"Skin and conjunctival irritation.-- Both eyes and skin are liable to irritation by the dust or by contact with the acid solutions of vanadium pentoxide. Some eczematous lesions were noted by Sjoberg (1951) and in 3 cases there was an allergic response to patch tests with sodium vanadate. Intense itching of the skin and, in some cases, generalized urticaria were particularly prominent in the series examined by Thomas and Stiebris, who remark that it is possible that sulphur compounds present may further increase the severity of the symptoms.

"Nervous disorders.-- Several observers have reported tremor of the hands and nervous depression. Wyers remarked that the fine tremor of the fingers might affect the arms of workers with prolonged exposure.

"Discoloration of the tongue.--A greenish-black discoloration of the tongue is a characteristic manifestation of the toxic action of vanadium. That it is not merely a deposit of the metal or its salts on the surface of the tongue is shown by the fact that though it

> disappears within 2 to 3 days with cessation of exposure, it cannot be removed by cleaning. Wyers suggested that it might be due to the reduction of the pentoxide to trioxide, and to the formation of green salts by the action of ptyalin and bacteria in the mouth; he regarded it as evidence of exposure rather than intoxication. In the only case observed by Sjoberg, a man employed in scraping an iron plate on which a mixture of sulphuric acid and the sulphates of vanadium, manganese and iron had leaked, the colour was light greyish-green, and he assumed that in this case the discoloration was caused by precipitation of quadrivalent vanadium hydroxides.
>
> "Cardiac symptoms.-- Palpitation on exertion has been fairly commonly reported, and Wyers thought it to be an effect of vanadium on the cardiac nerve supply. Sjoberg (1951) found 3 cases of extra-systole, and stated that the possibility of pathological changes in the heart due to vanadium cannot be ruled out."

Another comprehensive reference is by T. G. Faulkner Hudson (1964). It should be noted that there is no evidence that suggests lethality is involved with vanadium ingestion. Nor is there evidence that vanadium is linked with carcinogenesis.

Inquiries and discussions with industrial management involved in vanadium processing and use indicate that there exist no serious problems in the industry's ability and willingness to comply with environmental regulations. Better recycling technology and more efficient utilization of vanadium materials should make for an even better capability within the industry to readily comply with concerns relating to environmental impact.

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