Vanadium

By Harold A. Taylor, Jr.[1]

Domestic demand for vanadium was still weak in 1972, compared to the high of 1969, although it was stronger than last year. Overseas demand was also weak but becoming stronger. Domestic production, expressed as vanadium pentoxide recovered, did not change significantly from last year because the production decrease resulting from the shutdown of the Rifle mill was balanced by increases in output at other facilities. Exports of both ferrovanadium and vanadium ores and oxides were much smaller than in 1971, while imports of ferrovanadium were much larger. The Government sold all of its surplus vanadium pentoxide in May.

Legislation and Government Programs.—The General Services Administration (GSA) sold all its excess vanadium pentoxide, 5.6 million pounds, to three metal trading firms in May. A condition of sale was that the material could not be sold abroad as vanadium pentoxide. It must be converted to another vanadium product in this country in the event of export. The material sold consisted of 87 lots, the vanadium pentoxide contents of which ranged between 85% and 90%.

As of December 31, 1972, the Government had an inventory of 2,800 short tons of vanadium, the entire quantity in the national stockpile. Of this total, 1,200 tons was held as ferrovanadium and 1,600 tons was held as vanadium pentoxide.

Table 1.—Salient vanadium statistics

(Short tons of contained vanadium)

	1968	1969	1970	1971	1972
United States:					
Production:					
Ore and concentrate:					
Recoverable vanadium [1]	6,483	5,577	5,319	5,252	4,887
Value thousands	$23,143	$26,334	$34,923	$37,690	$30,867
Vanadium pentoxide recovered	6,149	5,906	5,594	5,293	5,248
Consumption	5,495	6,154	5,134	4,802	5,227
Exports:					
Ferrovanadium and other vanadium alloying materials (gross weight)	278	644	2,155	676	269
Vanadium ores, concentrates, oxides, and vanadates	463	258	973	260	176
Imports (general):					
Ferrovanadium (gross weight)	626	449	21	89	578
Ores and concentrates	31	--	--	--	--
World production	13,331	18,581	20,171	18,571	19,949

[1] Measured by receipts of uranium and vanadium ores and concentrates at mills, plus vanadium recovered from ferrophosphorus derived from domestic phosphate rock.

DOMESTIC PRODUCTION

The principal domestic source of vanadium continued to be the Colorado Plateau uranium-vanadium ores, but by an even more slender margin than in 1971. Both Arkansas vanadium ore and Idaho ferrophosphorus supplied an increased amount of vanadium. Most of the producing facilities processed such materials as vanadium-bearing oil residues, spent catalysts, vanadium-bearing residues from titanium dioxide production, and foreign vanadium-containing slags. Vanadium obtained by processing imported vanadium-

[1] Physical scientist, Division of Ferrous Metals.

Table 2.—Recoverable vanadium of domestic origin produced in the United States, by State

(Short tons of contained vanadium)

State	1968	1969	1970	1971	1972
Colorado	3,492	W	W	W	W
Utah	563	W	257	226	188
Other States [1]	2,428	W	W	W	W
Total	6,483	5,577	5,319	5,252	4,887

W Withheld to avoid disclosing individual company confidential data; included in total.
[1] Includes Arizona 1968–69, Arkansas 1968–72, Idaho 1968–72, New Mexico 1968–72, South Dakota 1970, and 1972.

containing slags was not included in the recovered vanadium pentoxide figures shown in tables 1 and 4.

Most of the vanadium obtained from domestic uranium-vanadium ores in 1972 was recovered at the Rifle mill of Union Carbide Corp. The Soda Springs, Idaho, plant of Kerr-McGee Corp. and the Hot Springs, Ark., plant of Union Carbide Corp. recovered vanadium from byproduct ferrophosphorus obtained in elemental phosphorus production. The Hot Springs, Ark., plant also recovered vanadium from Arkansas vanadium ore. Other producers of vanadium pentoxide or ammonium metavanadate from domestic ores and/or residues included the Edgemont, S. Dak., mill of Susquehanna-Western, Inc., the Wilmington, Del., plant of The Pyrites Co., Inc., the Texas City, Tex., plant of Gulf Chemical & Metallurgical Corp., and the Moab, Utah, mill of Atlas Corp.

Union Carbide shut down its mine and milling operations at Rifle, Colo., on August 1 and began transferring its vanadium milling circuit to Uravan. It was estimated that installation of the circuit at Uravan would take about 9 to 10 months, and meanwhile the Rifle mill will be maintained on a standby status. Vanadium liquor produced at the new Uravan operation will be shipped to Rifle where ammonium metavanadate will be precipitated, vanadium oxide produced, and the product stored for shipment. Management cited the following reasons for the shutdown and transfer: the depressed uranium prices caused by delay in nuclear powerplant construction, the diminished ore reserves and relatively low ore grades, and the increased cost caused by meeting new regulations concerning radon daughter exposure in underground mines.

Atlas Corp. began preparations to resume production of vanadium from Colorado Plateau ores. Its plans included the reinstallation of a vanadium recovery circuit at its Moab mill. However, the circuit will not be entirely completed until late 1975 or early 1976. Ongoing exploration has revealed a large deposit of uranium-vanadium ore worth an estimated $30 to $50 million located on leased properties in the Sage Plains area of Utah. In addition, the company signed an agreement to buy all the American Metals Climax (AMAX) uranium-vanadium properties in the Uravan minerals belt of Utah and Colorado, estimated to be worth another $30 to $50 million, and finalized the sale in early 1973. The company expects to be in a strong position to process ores on a toll basis and to bid for uranium-vanadium ore reserves.

Table 3.—Mine production and recoverable vanadium of domestic origin produced in the United States

(Short tons of contained vanadium)

Year	Mine production [1]	Recoverable vanadium [2]
1968	7,105	6,483
1969	5,737	5,577
1970	5,793	5,319
1971	5,547	5,252
1972	4,699	4,887

[1] Measured by receipts of uranium and vanadium ores and concentrates at mills, vanadium content.
[2] Recoverable vanadium contained in uranium and vanadium ores and concentrates received at mills, plus vanadium recovered from ferrophosphorus derived from domestic phosphate rock.

Table 4.—Production of vanadium pentoxide in the United States [1]

(Short tons)

Year	Gross weight	V_2O_5 content
1968	12,105	10,976
1969	12,120	10,542
1970	11,035	9,986
1971	10,492	9,448
1972	10,410	9,367

[1] Includes vanadium pentoxide and metavanadate produced directly from all domestic sources, plus small byproduct quantities from imported chromium ores.

The Pyrites Co., a subsidiary of Rio Tinto-Zinc Corp., Ltd., placed its new vanadium facility at Wilmington, Del., in partial operation, and was producing ammonium metavanadate by the end of the year. Plans called for production of fused flake vanadium pentoxide later; feed is expected to consist largely of residues.

CONSUMPTION AND USES

Total domestic consumption of vanadium, as reported for all end-use categories in table 6, rose almost 9% in 1972. The marked increase in consumption in alloy steels and the decrease in consumption in carbon steel reflected a change in reporting. The old category for alloy steel (excluding stainless and tool) was subdivided into the following new categories: full alloy steel, high-strength low-alloy steel, and electric steel (special steel for use in electrical equipment). Under the revised reporting, some material that formerly appeared in the categories for carbon steel or miscellaneous and unspecified now appears in the new alloy steel categories.

Union Carbide Corp. announced a new steel additive, trademarked Nitrovan, containing 78% to 80% Vanadium, 6% to 7% nitrogen, and 10% to 12% carbon. It was designed for use in vanadium-nitrogen high-strength steels, especially the "killed" grades. Nitrovan was said to have the advantages of dissolving quickly and mixing uniformly in the steel, and having a higher purity than the premium grades of ferrovanadium.

Table 5.—Consumption and consumer stocks of vanadium materials in the United States

(Short tons of contained vanadium)

Type of material	1971		1972	
	Consumption	Ending stocks	Consumption	Ending stocks
Ferrovanadium [1]	4,171	544	4,493	623
Oxide	143	24	189	56
Ammonium metavanadate	35	9	47	8
Other [2]	453	68	498	101
Total	4,802	645	5,227	788

[1] Includes other vanadium-iron-carbon alloys.
[2] Consists principally of vanadium-aluminum alloy, plus relatively small quantities of other vanadium alloys and vanadium metal.

Table 6.—Consumption of vanadium in the United States by end use

(Short tons of contained vanadium)

End use	1972
Steel:	
Carbon	630
Stainless and heat resisting	30
Full alloy	1,088
High-strength low-alloy	2,062
Electric	W
Tool	620
Cast irons	60
Superalloys	17
Alloys (excludes steels and superalloys):	
Cutting and wear resistant materials	W
Welding and alloy hard-facing rods and materials	11
Nonferrous alloys	353
Other alloys [1]	20
Chemical and ceramic uses:	
Catalysts	147
Other [2]	W
Miscellaneous and unspecified	189
Total	5,227

W Withheld to avoid disclosing individual company confidential data, included in "Miscellaneous and unspecified."
[1] Includes magnetic alloys.
[2] Includes pigments.

STOCKS

In addition to the consumers' stocks reported in table 5, producers' stocks of vanadium as fused oxide, precipitated oxide, metavanadate, metal, alloys, and chemicals totaled 3,640 short tons of contained vanadium at yearend 1972, compared with 3,775 tons at yearend 1971.

PRICES

The dealer price quoted by Metals Week for export merchant technical-grade vanadium pentoxide remained at the late 1971 level of $1.50 per pound of contained V_2O_5 throughout the whole of 1972. The quote for domestic 98% fused vanadium pentoxide, applying to metallurgical markets, also was unchanged at $1.50 per pound of contained V_2O_5. The price for technical-grade, air-dried vanadium pentoxide, used by the chemical industry, stayed at $2.21 per pound of contained V_2O_5, f.o.b. plant, from 1971 through the end of 1972.

GSA sold all its excess vanadium pentoxide in May for bids ranging between $1.14 and $1.18 per pound of contained vanadium pentoxide.

There were small changes in some of the ferrovanadium prices in 1972. The price for U.S. standard grade ferrovanadium was $4.12 per pound of contained vanadium f.o.b. shipping point until July 1, when it rose to $4.19 for the rest of the year. On July 1 the price of Carvan also rose, in this instance from the $3.48 per pound of contained vanadium that existed since 1971 to the $3.66 that continued through the end of 1972. The price for Ferovan remained unchanged during 1972 at $3.68 per pound of contained vanadium.

FOREIGN TRADE

During 1972 exports of both ferrovanadium and vanadium ores, concentrates, and oxides varied irregularly from month to month, usually at a low level. The declared value for exports of ores, concentrates, and technical-grade oxides averaged

Table 7.—U.S. exports of vanadium, by country

(Thousand pounds and thousand dollars)

Destination	Ferrovanadium and other vanadium alloying materials containing over 6% vanadium (gross weight)				Vanadium ore, concentrates, pentoxide, vanadic acid, vanadium oxide and vanadates (except chemically pure grade) (vanadium content)			
	1971		1972		1971		1972	
	Quantity	Value	Quantity	Value	Quantity	Value	Quantity	Value
Argentina	9	30	--	--	--	--	--	--
Australia	5	13	--	--	127	360	101	216
Austria	--	--	74	129	--	--	--	--
Belgium-Luxembourg	--	--	--	--	20	49	--	--
Brazil	8	23	221	596	48	217	--	--
Canada	450	1,178	--	--	16	21	--	--
Chile	2	5	2	5	--	--	--	--
Colombia	--	--	--	--	121	633	--	--
Czechoslovakia	--	--	--	--	--	--	--	--
Dominican Republic	(1)	1	--	--	12	29	(1)	1
France	80	234	--	--	2	6	117	247
Germany, West	9	12	--	--	--	--	--	--
India	172	493	18	34	57	208	--	--
Israel	4	9	--	--	--	--	--	--
Italy	--	--	--	--	27	88	--	--
Japan	312	772	29	57	29	86	--	--
Korea, Republic of	6	9	--	--	--	--	--	--
Mexico	137	300	95	231	24	50	31	73
Netherlands	132	391	--	--	--	--	--	--
Spain	--	--	17	42	--	--	102	219
Switzerland	25	20	81	162	--	--	--	--
United Kingdom	--	--	--	--	37	87	--	--
Total	1,351	3,490	537	1,256	520	1,834	351	756

[1] Less than ½ unit.

Table 8.—U.S. imports of ferrovanadium, by country
(Thousand pounds and thousand dollars)

Country	1971			1972		
	Gross weight	Vanadium content	Value	Gross weight	Vanadium content	Value
General imports:						
Austria	--	--	--	255	207	648
Belgium-Luxembourg	--	--	--	44	36	113
Canada	--	--	--	14	11	38
Germany, West	177	137	439	549	411	1,194
Norway	--	--	--	140	67	197
Sweden	--	--	--	68	55	164
Switzerland	--	--	--	85	50	151
Total	177	137	439	1,155	837	2,505
Imports for consumption:						
Austria	--	--	--	255	207	648
Belgium-Luxembourg	--	--	--	44	36	113
Canada	--	--	--	14	11	38
Germany, West	138	110	360	386	282	817
Norway	--	--	--	56	26	76
Sweden	--	--	--	68	55	164
Switzerland	--	--	--	85	50	151
Total	138	110	360	908	667	2,007

$1.21 per pound of contained vanadium pentoxide in 1972, compared with $1.98 in 1971. The declared value for exports of ferrovanadium averaged $2.34 per pound of alloy, compared with $2.58 in 1971.

No imports classified as vanadium ore and concentrate were received in 1972. Imports of vanadium-bearing materials such as ashes and slags, which are classified as metal-bearing residues, were estimated to be about 2.8 million pounds of contained vanadium in 1972, compared with 4.0 million pounds in 1971. Most of these materials originated in the Republic of South Africa and Chile.

WORLD REVIEW

Besides those listed in table 9, several other nations produced relatively minor amounts of vanadium, usually from secondary, waste, or byproduct sources. Japan and Canada both produced vanadium from several such sources, as did West Germany. While the world market for vanadium was not strong in 1972, it was better than in 1971.

Australia.—The Julia Creek, Queensland, vanadiferous oil shale project was expected to be set back because of technical problems relating to vanadium extraction. A special research program to solve these problems was anticipated to take at least 2 years. The project is a joint venture of the Oil Shale Corp., Australian Aquitaine Petroleum, and Pacminex Pty.[2]

Ferrovanadium Corp. N.L. announced the discovery of gold in its vanadium-bearing titanomagnetite-titanomartite ore body. Later in the year, it announced that it had commissioned a leading engineering group to make a feasibility study of the deposit.

Finland.—Rautaruukki Oy, Finland's vanadium producer, revealed plans for opening a new mine and vanadium pentoxide operation at Mustavaara, 125 miles north of their present source of vanadium at Otanmäki. The operation was designed to produce about 1,850 short tons of contained vanadium annually from 1.76 million tons of ore. The deposit was estimated to contain 44 million tons of ore, and is to be mined as an open pit.

France.—According to French trade statistics, France imported 855 short tons of vanadium pentoxide (not including other vanadium oxides) in 1971, of which 476 tons came from Finland, 171 tons from West Germany, 138 tons from the Netherlands, and the balance from other sources. The camparable import figure for 1970 was 1,483 short tons, of which 622 tons came from West Germany, 410 tons from

[2] Metal Bulletin (London). Julia Creek Setback. No. 5729, Sept. 1, 1972, p. 18.

Finland, 396 tons from the Netherlands, and the balance from other sources.

Germany, West.—According to the trade statistics of West Germany, imports of vanadium-bearing slags and residues totaled 33,800 short tons (gross weight) in 1972, 5,720 tons of this from Belgium-Luxembourg, 1,835 tons from France, 1,050 tons from the Soviet Union, 415 tons from other European and Israeli sources, and the balance from unspecified sources. For comparison, the imports of vanadium-bearing slags and residues totaled 24,240 short tons in 1971, 3,800 tons of this from Belgium-Luxembourg, 1,350 tons from France, 840 tons from other European and Israeli sources, and the balance from unspecified sources.

Luxembourg.—Continental Alloys began installing slag roasting facilities at its works at Dommeldange and hoped to begin operation some time during 1973. The plant was designed to have a capacity of about 2,000 tons of fused flake vanadium pentoxide product per year, and to consume South African vanadiferous slag barged to the plant by way of the inland waterway system. Already existing facilities at the same location will convert the fused flake product into ferrovanadium.[3]

Mozambique.—The Cia. do Urânio de Moçambique has submitted a feasibility study for a vanadium slag-producing iron and steel works to the Portuguese Government. The proposed plant would be built in the Tete district by mid-1975 and would use local vanadium-bearing titanomagnetite ore and coal, while electricity would come from the Cabora Bassa power complex now under construction. The process route would involve electric reduction and LD steelmaking.[4]

South Africa, Republic of.—The vanadium-bearing slag output of Highveld Steel and Vanadium Corp., Ltd., totaled 31,072 short tons in the fiscal year ending June 30, 1972, compared to 31,736 short tons in the previous fiscal year. Although the gross weight declined, the actual output of vanadium pentoxide in the slag was the highest to date because of an increase in the proportion of vanadium in the iron. The problem with electrode failure in the iron furnaces was solved, so that the plant was able to operate at 95% of rated capacity after the end of February. The fifth prereduction kiln was commissioned on schedule in February 1972.

The company's Vantra Division produced vanadium pentoxide at a substantially lower rate in this fiscal year than last year because of the poor market for vanadium. Because of this reduced production, the Vantra Division began using ore from the Mapochs mine in April 1972, resulting in the temporary closure of the Kennedy's Vale mine and in the indefinite postponement of operations in the new Northam mine.

United Kingdom.—Imports of ferrovanadium were 197 tons (gross weight) in 1971, with 137 tons coming from Austria

[3] Metal Bulletin (London). New Continental Alloys Roaster. No. 5723, Aug. 8, 1972, p. 13.
[4] Metal Bulletin (London). Mozambique Steelworks Planned. No. 5671, Feb. 1, 1972, p. 27.

Table 9.—Vanadium: World production from ores and concentrates, by country

(Short tons of contained vanadium)

Country	1970	1971	1972 p
Chile e	610	660	720
Finland (in vanadium pentoxide product)	1,450	1,222	1,312
France e [1]	100	100	100
Norway e	1,190	1,160	1,200
South Africa, Republic of:			
Content of pentoxide and vanadate products	2,665	e 2,470	e 3,370
Content of vanadiferous slag product e	r 4,800	r 4,060	4,860
Total	7,465	6,530	8,230
South-West Africa, Territory of: (in lead-vanadate concentrate) e	660	730	600
U.S.S.R. (in slag exports) [2]	3,377	2,917	e 2,900
United States (recoverable vanadium)	5,319	5,252	4,887
Total	r 20,171	r 18,571	19,949

e Estimate. p Preliminary. r Revised.
[1] Byproduct from bauxite.
[2] Partial figure representing only that vanadium contained in exported slags; does not include vanadium produced for domestic consumption in any form or for export in any form except slag.

and the balance from three other sources. These imports were only a fraction of the 1970 total of 1,308 tons, 524 tons of which came from Austria, 216 tons from Norway, 195 tons from Sweden, and the balance from six other sources.

TECHNOLOGY

As in the last several years, much of the research on vanadium in 1972 centered on vanadium metal as a possible structural material for fast-breeder reactors, and on vanadium extraction from raw materials. There was an investigation of the purification of vanadium metal by an electrotransport technique. A pair of studies were made which have implications concerning the strength of vanadium metal, specifically concerning allotropy in vanadium and deformation mechanisms of vanadium. Three investigations were reported concerning carbon, nitrogen, and oxygen impurities in vanadium metal, and two interesting new processes for extracting vanadium were patented.

Electrotransport was demonstrated to be an effective method of reducing interstitial impurities in vanadium metal to a total amount less than 5 weight ppm.[5] The technique of electrotransport involves heating a cylindrical rod by internal electrical resistance to cause migration of the impurities towards the cathode end upon application of a high density electric current.

Both polycrystalline and single crystal vanadium metal were strained in tension at low temperatures, varying both the strain and the temperature, to study the deformation mechanism. A change of rate-controlling mechanism occurred at approximately 200 K. The predominant controlling mechanism seemed to be the interaction between dislocations and interstitial impurities at temperatures between 200 and 293 K. Single crystals developed mechanical twins when deformed at 77 and 120 K.[6]

The possibility of allotropy in vanadium at subambient temperatures was investigated by measuring electrical resistivity and elastic constants, and by X-ray diffractometry. While some previous workers have proposed a low-temperature allotropic form on the basis of anomalies in various properties, no evidence of allotropy was found in the temperature range 77 to 300 K.[7]

Using transmission electron microscopy on thin foils doped with carbon, the precipitation of carbon from a supersaturated solid solution in vanadium was investigated. It was found to precipitate initially as a finely dispersed carbide which became coarser with age.[8] The precipitation rate must largely depend on the rate of carbon diffusion.[9]

Other investigations disclosed that the precipation of $V_{16}N$ occurs homogeneously in vanadium-nitrogen alloys but requires long-range diffusion of nitrogen,[10] and, contrary to the conclusions of some investigators, the scavenging action of titanium for oxygen in vanadium-titanium alloys is apparently not a function of titanium concentration.[11]

One of the new processes patented in 1972 involved the extraction of vanadium from calcium-containing vanadium ore. Vanadium can be extracted from high-calcium ores and oil shales by slurrying the calcined ore in highly alkaline water, treating the slurry with carbon monoxide to precipitate waste calcium carbonate, contacting the vanadium-enriched solution with a basic anion exchange resin, and then stripping the adsorbed vanadium from the resin with a sodium chloride solution.[12] Another patent provided for

[5] Carlson, O. N., F. A. Schmidt, and D. G. Alexander. Electrotransport Purification and Some Characterization Studies of Vanadium Metal. Met. Trans., v. 3, No. 5, May 1972, pp. 1249–1254.

[6] Wang, C. T., and D. W. Bainbridge. The Deformation Mechanism for High-Purity Vanadium at Low Temperatures. Met. Trans., v. 3, No. 12, December 1972, pp. 3161–3165.

[7] Westlake, D. G., S. T. Ockers, M. H. Mueller, and K. D. Anderson. Reexamination of Vanadium for Allotropy. Met. Trans., v. 3, No. 7, July 1972, pp. 1711–1713.

[8] Diercks, D. R. and C. A. Wert. An Electron Microscopy Study of Carbide Precipitation in Vanadium. Met. Trans., v. 3, No. 7, July 1972, pp. 1699–1708.

[9] Mosher, D. R., D. R. Diercks, and C. A. Wert. Precipitation of Carbon from Solid Solution in Vanadium. Met. Trans., v. 3, No. 12, December 1972, pp. 3077–3080.

[10] Potter, D. and C. Altstetter. Precipitation of $V_{16}N$ in Vanadium. Materials Sci. and Eng., v. 9, No. 1, January 1972, pp. 43–46.

[11] Hasson, D. F. and R. J. Arsenault. Scavenging in Vanadium-Titanium Alloys. J. Less-Common Metals, v. 27, No. 3, June 1972, pp. 417–418.

[12] Hass, F. C. (assigned to Oil Shale Corp.). Vanadium Recovery Process. U.S. Pat. 3,656,936, Apr. 18, 1972.

vanadium recovery from ore leach solutions or other aqueous acidic solutions by contacting the solution with a specified fluorinated beta-diketone dissolved in kerosene or isooctane, and then stripping the vanadium-rich organic phase with a strong mineral acid.[13]

[13] Lucid, M. F. (assigned to Kerr-McGee Corp.). Extraction of Vanadium and Copper with Fluorinated Beta-Diketones. U.S. Pat. 3,700,416, Oct. 24, 1972.