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Vanadium Recycling in the United States in 2004

By Thomas G. Goonan

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FOREWORD

As world population increases and the world economy expands, so does the demand for natural resources. An accurate assessment of the Nation's mineral resources must include not only the resources available in the ground but also those that become available through recycling. Supplying this information to decisionmakers is an essential part of the USGS commitment to providing the science that society needs to meet natural resource and environmental challenges.

The U.S. Geological Survey is authorized by Congress to collect, analyze, and disseminate data on the domestic and international supply of and demand for minerals essential to the U.S. economy and national security. This information on mineral occurrence, production, use, and recycling helps policymakers manage resources wisely.

USGS Circular 1196, "Flow Studies for Recycling Metal Commodities in the United States," presents the results of flow studies for recycling 26 metal commodities, from aluminum to zinc. These metals are a key component of the U.S. economy. Overall, recycling accounts for more than half of the U.S. metal supply by weight and roughly 40 percent by value.

Marcia K. McNutt
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CONVERSION FACTORS

Multiply	By	To obtain
	<i>Mass</i>	
kilogram (kg)	2.205	pound avoirdupois (lb)
metric ton (t, 1,000 kg)	1.102	short ton (2,000 lb)

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ABSTRACT

As one of a series of reports that describe the recycling of metal commodities in the United States, this report discusses the flow of vanadium in the U.S. economy in 2004. This report includes a description of vanadium supply and demand in the United States and illustrates the extent of vanadium recycling and recycling trends.

In 2004, apparent vanadium consumption, by end use, in the United States was 3,820 metric tons (t) in steelmaking and 232 t in manufacturing, of which 17 t was for the production of superalloys and 215 t was for the production of other alloys, cast iron, catalysts, and chemicals. Vanadium use in steel is almost entirely dissipative because recovery of vanadium from steel scrap is chemically impeded under the oxidizing conditions in steelmaking furnaces. The greatest amount of vanadium recycling is in the superalloy, other-alloy, and catalyst sectors of the vanadium market. Vanadium-bearing catalysts are associated with hydrocarbon recovery and refining in the oil industry.

In 2004, 2,850 t of vanadium contained in alloy scrap and spent catalysts was recycled, which amounted to about 44 percent of U.S. domestic production. About 94 percent of vanadium use in the United States was dissipative (3,820 t in steel/4,050 t in steel+fabricated products).

INTRODUCTION

Vanadium-containing mineral deposits are found in many parts of the world, usually associated with other elements, such as iron, phosphorus, and uranium. Vanadium is also recovered from petroleum-refining residues, vanadiferous slag from iron and steelmaking operations that process materials with high vanadium contents, and wastes such as dusts collected in air-pollution-control devices and systems. In addition, vanadium is being recycled by processing of spent catalysts and nonsteel vanadium-containing alloys. In 2004, world vanadium production from ores, concentrates, petroleum-refining residues, and slag was 51,900 metric tons (t) of contained vanadium. The principal producing countries (in descending order of amount produced) were South Africa,

45 percent; China, 31 percent; Russia, 21 percent; and other countries, 3 percent (Magyar, 2007b).

This report describes a snapshot of the flow through the U.S. economy of vanadium (contained in various forms) in 2004, which is shown in figure 1. It identifies sources and distribution of the U.S. vanadium supply and describes recycling trends. The selection of 2004 for the year of the study was made so that this report would be consistent with some other chapters in U.S. Geological Survey Circular 1196; although the chapters in this series were prepared during a long time period, the subject years were limited to 1998, 2000, and 2004. Vanadium recycling did not change significantly between 2004 and 2010, when this report was written. For completeness, the section on the vanadium industry structure and table 2 reflect the situation at the end of 2008, figure 6 shows prices through 2010, and figure 7 shows values through 2007.

The leading source of vanadium for the production of semifabricated and manufactured vanadium-containing products is vanadium pentoxide (V_2O_5), which is separated and recovered as a byproduct from such sources as ores of aluminum, iron, phosphate, and uranium; petroleum-refining residues; and recycled spent-catalyst scrap.

In 2004, the U.S. steel industry reported vanadium consumption of about 3,820 t of vanadium (contained mostly in ferrovanadium), which was about 94 percent of total U.S. reported vanadium consumption. Vanadium-containing steel alloys generally contain less than 1 percent vanadium. Steel scrap processing occurs mostly in electric arc furnaces under oxidizing conditions, where vanadium is readily oxidized and is chemically redistributed to the slag and airborne dust. The vanadium concentration in such slag is not sufficient for economic recovery. Vanadium is recovered from the dust.

The remaining 6 percent of U.S. reported consumption of vanadium (232 t) was used to manufacture superalloys, other alloys (many for aerospace applications), and chemicals (for catalyst, ceramic, electronic, glass, and metallurgical applications). Vanadium-containing alloys and spent catalysts are the primary source of recyclable vanadium. More than 2,700 t of vanadium is annually recovered in the United States from spent catalysts (Vanadium Technology Partnership, 2009). Vanadium recovery from alloys is generally undertaken by

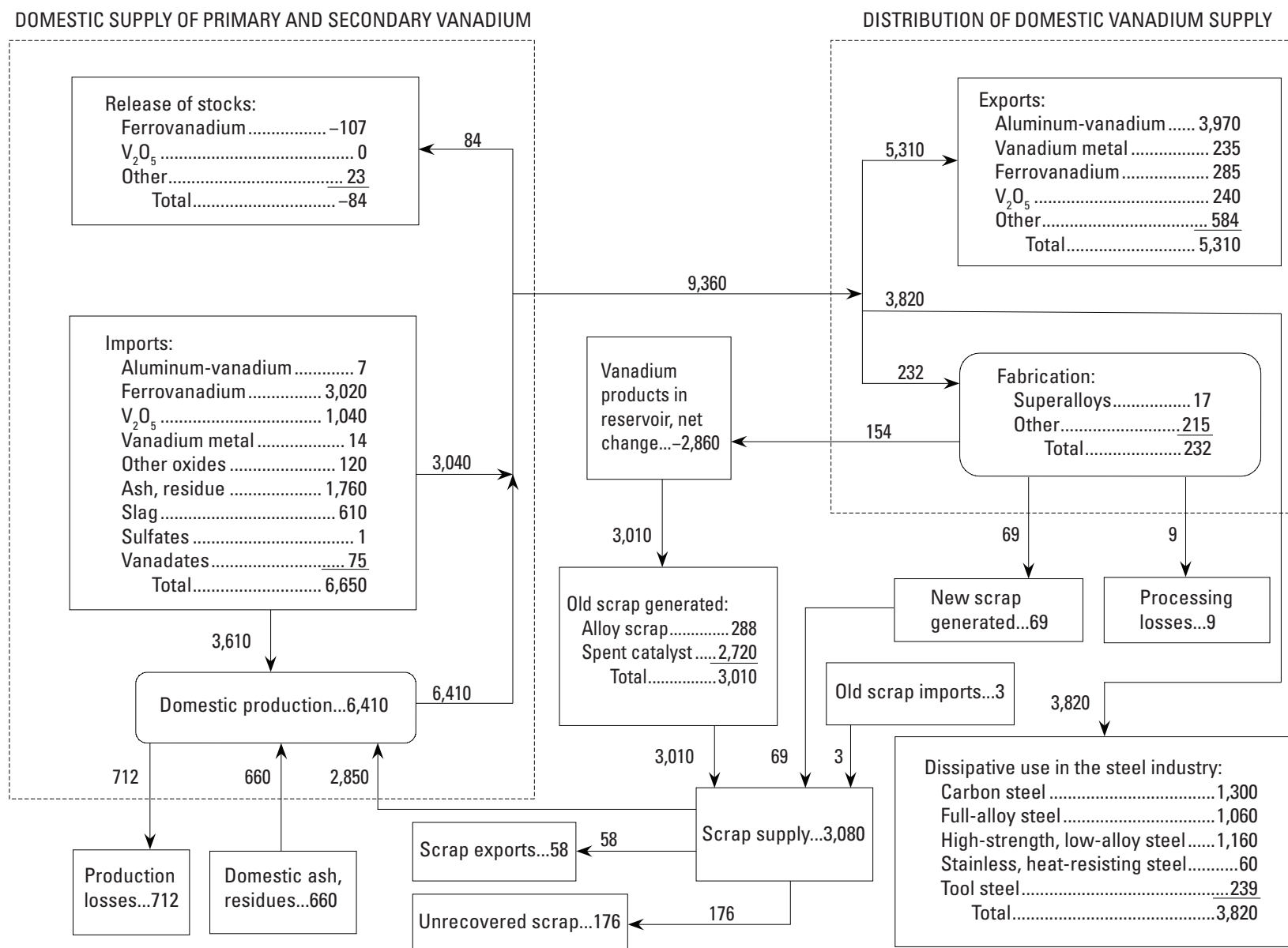


Figure 1. Diagram showing the flow of vanadium contained in various forms in the United States in 2004. Values are in metric tons of contained vanadium. The addition of the parts may not equal the totals owing to independent rounding. Data have been rounded to three significant figures. Stocks refer to producer stocks. There are no Government stocks involved. V₂O₅, vanadium pentoxide. Sources: GoldInsider (2006), Matos and Magyar (2006), Magyar (2007b), Vanadium Technology Partnership (2009).

the industries that provide the other alloying element. For example, the aluminum industry may recover vanadium from aluminum-vanadium alloys.

In 2004, the U.S. vanadium supply, net of stock increases, was 9,360 t of vanadium. The sources for this supply included imports (6,650 t of vanadium) and recycled materials (3,510 t of vanadium), less production losses (712 t of vanadium). In 2004, this supply was distributed as follows: 3,820 t was consumed by the U.S. steel industry; 232 t was consumed in the production of cast iron, vanadium alloys, and vanadium chemicals; and 5,310 t was contained in exported material.

The amount of vanadium contained in imported product assemblies that embody vanadium-containing alloys, steel alloys, and other products is not known. In 2004, the U.S. vanadium metals product reservoir theoretically generated 288 t of vanadium as old alloy scrap and 2,720 t of vanadium contained in spent catalysts for a total of 3,010 t of vanadium in old scrap generated. Recycling efficiency for 2004 was calculated to be 94 percent. The recycling rate was 70 percent, and the new-to-old-scrap consumption ratio was 2:98. Salient statistics for U.S. vanadium scrap in 2004 are summarized in table 1.

Some generalizations that can be made about vanadium scrap handling in the United States (Magyar, 2005b) include the following:

- Vanadium use in steel alloys, especially in alloys having low vanadium concentrations (less than 1 percent), is essentially dissipative, because the vanadium separates to the slag and dust-collection system during scrap remelting and is discarded with the slag or dust.
- The principal focus of vanadium recycling is catalyst material, which is recycled into new catalyst materials.
- Probably a few alloys having high vanadium concentrations can be economically vacuum arc remelted; however, little information is available.

GLOBAL GEOLOGIC OCCURRENCE OF VANADIUM

The abundance of vanadium in the Earth's crust is about 160 parts per million (ppm), and that in seawater is about 0.0014 ppm. Among 65 minerals that contain vanadium, the most common vanadium minerals include patronite (VS_4), vanadinite [$\text{Pb}_5(\text{VO}_4)_3\text{Cl}$], and carnotite [$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$] (Barbalace, 2007). Vanadium is also found in bauxite, phosphate rock, and certain iron ores and is present in the form of organic complexes in some carbon-containing deposits, such as coal, crude oils (particularly those of Venezuela), oil shale, and tar sands (Spectrum Laboratories Inc., 2007).

The role of vanadium during the formation of fossil fuels is obscure. The ratio of vanadium to nickel in crude oil is a

Table 1. Salient statistics for U.S. vanadium scrap in 2004.

[Values are in metric tons of contained vanadium, unless otherwise specified. Definitions for selected terms are in the appendix]

Old scrap:	
Generated ¹	3,010
Consumed ²	2,780
Value of scrap consumed	\$20,800,000
Recycling efficiency ³	94 percent
Supply ⁴	3,010
Unrecovered ⁵	176
New scrap consumed ⁶	69
New-to-old-scrap ratio ⁷	2:98
Recycling rate ⁸	70 percent
U.S. net imports of scrap ⁹	54
Value of U.S. net imports of scrap	\$1,190,000

¹Vanadium content of products theoretically becoming obsolete in the United States in 2004. Dissipative uses were excluded.

²Vanadium content of products that were recycled in the United States in 2004.

³Defined as (old scrap consumed plus old scrap exported) divided by (old scrap generated plus old scrap imported, adjusted for stock changes, which, in this case, are unknown).

⁴Old scrap generated plus old scrap imported.

⁵Old scrap supply minus old scrap consumed minus old scrap exported, adjusted for stock changes, which, in this case, are unknown.

⁶New scrap includes prompt industrial scrap but excludes home scrap.

⁷Ratio of quantities consumed, in percent.

⁸Fraction of the vanadium apparent supply that is scrap on an annual basis. It is defined as (consumption of old scrap plus consumption of new scrap) divided by apparent supply, measured in weight and expressed as a percentage.

⁹Trade in scrap is assumed to be principally in old scrap. Net exports are exports of old scrap minus imports of old scrap.

function of the oxidation-reduction potential (Eh), the hydrogen ion activity (pH), and the sulfide activity of the environment in which the source rocks of the crude oil were deposited. The two metals form stable metallo-organic complexes in the high-molecular-weight fractions of crude oil (Lewan, 1984).

VANADIUM INDUSTRY STRUCTURE

The world vanadium industry has undergone many ownership changes in recent years. Table 2 shows the status of the industry at the end of 2008. The principal vanadium recyclers in the United States are Gulf Chemical and Metallurgical Corporation, Freeport, Tex.; Metallurg Vanadium Corporation, Cambridge, Ohio; and Stratcor, Inc., Hot Springs, Ark.

Table 2. Vanadium industry structure in 2008.

[---, unknown; NA, not applicable; V₂O₅, vanadium pentoxide. Sources: Highveld Steel and Vanadium Corporation Limited (2005), Evraz Group S.A. (2007), Tamlin and Smith (2007), Aurox Resources Limited (2009), Gulf Chemical and Metallurgical Corporation (2009), Metallurg Vanadium Corporation (2009), Precious Metals Australia Ltd. (2009), Strategic Minerals Corporation (2009), Xstrata (2009a,b), Zhuyu Group (2009a,b)]

Entity	Location	Interest, in percent	Annual capacity, in metric tons of V ₂ O ₅	Business function or source of vanadium
AMG Advanced Metallurgical Group N.V.	Wayne, Pa., United States	NA	---	Corporate governance. ¹
Metallurg Vanadium Corporation	Cambridge, Ohio, United States	100	---	Catalyst recycling.
Aurox Resources Limited	Perth, Western Australia, Australia	NA	9,900	Corporate governance.
Balla Balla	Balla Balla, Western Australia, Australia	100	9,900	Ore, developing mine.
Eramet Group	Paris, France	NA	---	Group governance.
Gulf Chemical and Metallurgical Corporation	Freeport, Tex., United States	100	---	Catalyst recycling.
Bear Metallurgical Company	Butler, Pa., United States	100	---	Catalyst recycling.
Fort Saskatchewan Plant	Fort Saskatchewan, Alberta, Canada	100	---	Catalyst recycling.
Evraz Group, S.A.	Luxembourg, Luxembourg	NA	22,300	Group governance.
Highveld Steel and Vanadium Corporation	Witbank, Mpumalanga Province, South Africa	81	11,000	Slag from steel and iron.
Nikom	Mnisek pod Brdy, Czech Republic	100	---	Manufacturing ferrovanadium.
Strategic Minerals Corporation	Danbury, Conn., United States	73	11,300	Corporate governance.
Stratcor, Inc.	Hot Springs, Ark., United States	100	5,500	Catalyst recycling.
Butler Plant ²	Butler, Pa., United States	100	6,400	Catalyst recycling.
Vametco Minerals Corporation	Brits, North West Province, South Africa	100	4,800	Slag from steel and iron.
Windimurra Vanadium, Ltd.	Perth, Western Australia, Australia	90	8,100	Ore, developing mine.
Xstrata PLC	Zug, Switzerland	NA	13,400	Corporate governance.
Rhovan	Brits, South Africa	74	10,000	Slag from steel and iron.
Swazi Vanadium	Maloma, Swaziland	100	3,400	Residues from coal.
Zhuyu Group	Chengdu, Sichuan, China	NA	10,600	Group governance.
Chengde Xinxin Vanadium and Titanium Stock Company, Ltd.	Chengdu, Sichuan, China	100	7,100	Slag from steel and iron.
Panzhihua New Steel and Vanadium Company, Ltd.	Panzhihua, Sichuan, China	100	3,500	Slag from steel and iron.

¹Governance means corporate functions, as opposed to production operations.

²The Butler Plant was formerly owned by Bear Metallurgical Company.

WORLD PRODUCTION

China, Russia, and South Africa accounted for more than 97 percent (50,200 t) of the world's contained vanadium produced from concentrates, ores, petroleum-refining residues, and slag in 2004 (fig. 2). An estimated 40 percent of China's production was from vanadiferous slag. Russian and South African production was almost entirely from vanadiferous slag. Australia's production capacity exceeded 3,000 t of vanadium per year, but actual production in 2004 was 150 t due to poor market conditions. Japan reported 560 t of vanadium production from petroleum-refining residues (Magyar, 2007b, table 7).

PRODUCTION PROCESSES

This section of the report describes the details of the many vanadium production processes, which taken together (fig. 3) transform vanadium-containing materials into value-added products.

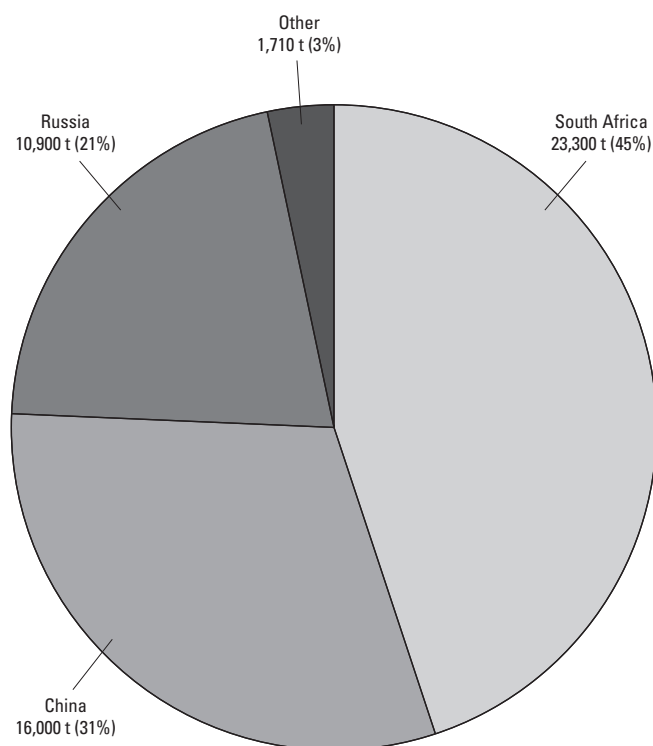


Figure 2. Pie chart showing world production of vanadium from concentrates, ores, petroleum-refining residues, and slag by country in 2004. Values are in metric tons (t) of contained vanadium (rounded to three significant figures) and percentage of total production (rounded to zero decimal places). Production for U.S. and European producers is not included, being withheld from reporting. Data from Magyar (2007b, table 7).

VANADIUM RECOVERY PROCESSES

Vanadium can be recovered from mineral deposits, particularly as a byproduct of bauxite, phosphate, and uranium processing; however, these are not the most important sources. Vanadium is recovered in large quantities from slag that is collected from the processing of vanadiferous magnetite ores where iron and steel are the principal products. The processing of gas and petroleum products is also an important source of vanadium, which is recovered both from the raw material (ashes and residues) and from the recycling of vanadium-bearing catalysts used in the process (fig. 4).

Vanadium-bearing catalysts are used in hydrocarbon processing to remove nickel and vanadium from the process stream. The material recovered (residue) is processed for the metal content, and the spent catalysts are recycled. A typical spent catalyst contains 5 to 16 percent sulfur, 1 to 8 percent molybdenum, 1 to 13 percent vanadium, 1 to 3 percent nickel, 10 to 30 percent carbon, and 20 to 30 percent aluminum (Wernick and Themelis, 1998).

The principal vanadium recovery processes include acid and caustic leaching and salt roasting. The intermediate products from these processes are vanadic acid and vanadium pentoxide (V_2O_5).

ACID LEACH PROCESS

The acid leach process (using sulfuric acid) treats spent catalysts, uranium-vanadium ore, and vanadium-bearing boiler residues and fly ash. The products of the process are both vanadic acid and V_2O_5 . The purpose of acid leaching is to dissolve vanadium-bearing compounds into a solution. The solution may contain other soluble elements, in which case, it must be further treated with vanadium-selective solvent extraction chemicals to separate the vanadium products (Ye, 2006, p. 14).

CAUSTIC LEACH PROCESS

The caustic leach process (using sodium-based alkali) treats ores, spent-catalysts, and vanadium-bearing boiler bottom and fly ash. The product of the process is V_2O_5 . The purpose of caustic leaching is to selectively dissolve vanadium-bearing compounds into a solution from which V_2O_5 can be extracted (Ye, 2006, p. 14).

SALT ROAST PROCESS

The vanadium winning process once used at the Windimurra Mine in Western Australia is illustrative of the salt roast process. Vanadiferous titanomagnetite ore processed at the mine had a grade of 0.47 percent V_2O_5 (Raja, 2007). Prior to salt roasting, the vanadiferous titanomagnetite ore was smelted into a pig iron that contained about 0.5 to 1 percent vanadium. The pig iron was transferred to steelmaking furnaces, where oxidation removed carbon to

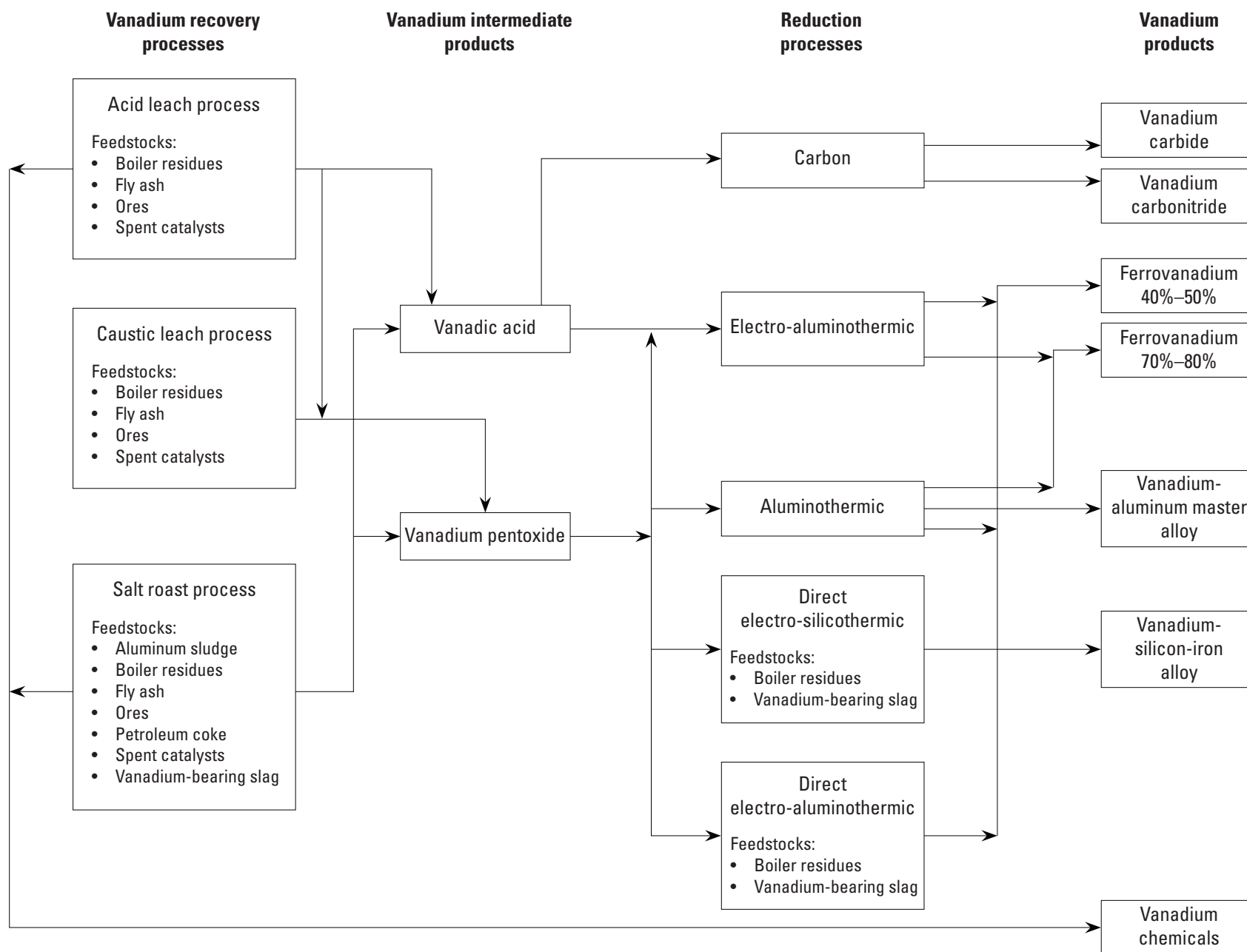


Figure 3. Diagram showing the production flows of vanadium from source through placement into end-use service. Modified from Hilliard (1994, fig. 1).

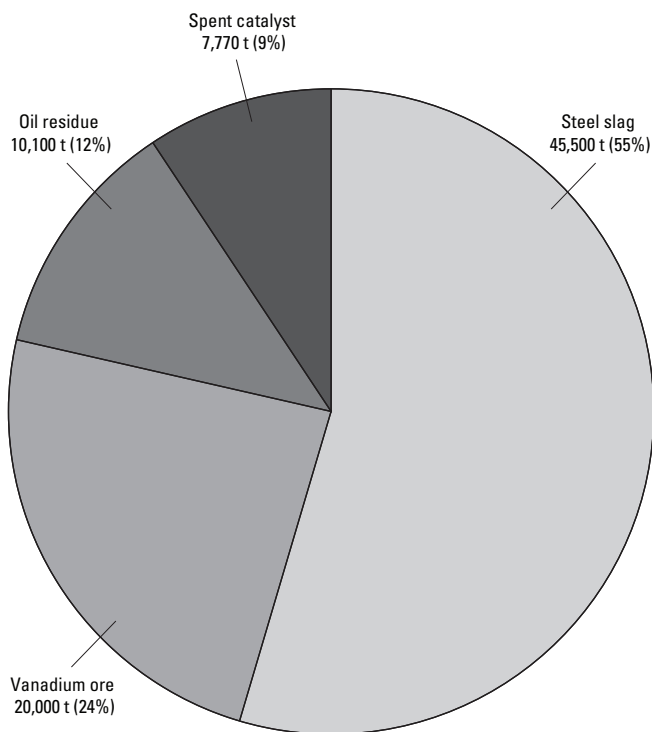


Figure 4. Pie chart showing world production of vanadium by source of vanadium in 2004. Values are in metric tons (t) of contained vanadium pentoxide and percentage of total. Data from Bunting (2004, fig. 10).

make steel and transferred about 90 percent of the vanadium from the metal (steel) to the steelmaking slag as $\text{FeO} \cdot \text{V}_2\text{O}_3$. The steelmaking slag was crushed and milled, and the magnetic particles (entrained iron from the melt/slag interface) were magnetically separated. The slag was mixed with sodium sulfate or sodium carbonate and heated in a kiln (salt roasted in an oxidizing environment), producing a calcine that contained sodium vanadate. The calcine was cooled, and water was used to leach the sodium vanadate. The resulting solution was treated with ammonium sulfate to precipitate ammonium polyvanadate. The precipitate was dewatered and heated to drive off the ammonia and to leave V_2O_5 (Raja, 2007).

The salt roast process can be used for feedstocks other than ore and slag, such as aluminum sludge, boiler bottom and fly ash, petroleum coke, and spent catalysts.

VANADIUM REDUCTION PROCESSES

The most used vanadium products are ferrovanadium (steel industry), vanadium carbides and carbonitrides (abrasives industry), and vanadium-aluminum master alloys (aerospace industry). These products are obtained from the reduction of V_2O_5 and vanadic acid by using different reductants and processes.

ALUMINOTHERMIC REDUCTION, DIRECT ELECTRO-ALUMINOTHERMIC REDUCTION, AND ELECTRO-ALUMINOTHERMIC REDUCTION

Aluminothermic reduction, for the processing of V_2O_5 into ferrovanadium, begins with mixing pure V_2O_5 , aluminum, iron cuttings, lime, fluorspar, and a priming mixture (either sodium nitrate and aluminum powder and turnings or fused barium pentoxide and aluminum/magnesium powder), which is ignited by red hot iron or electric spark. The resulting product is ferrovanadium having a vanadium content up to 97 percent (Raja, 2007). Aluminothermic vanadium reduction, without the presence of iron, can be used to make vanadium-aluminum master alloys, which will be processed by others into aluminum-titanium-vanadium alloys for application in the aerospace industry.

Direct electro-aluminothermic reduction is accomplished in an electric smelting furnace. Aluminum is added to vanadium-containing slag to produce ferrovanadium alloys having vanadium contents ranging from 40 to 50 percent.

Electro-aluminothermic reduction differs from direct electro-aluminothermic reduction by the nature of the feedstocks to each. The former handles purer feedstocks (V_2O_5 and vanadic acid), and the latter handles impure vanadium-containing materials (directly).

CARBON REDUCTION

Carbon is a common reductant used for converting metal oxides to metals. In the case of vanadium, which is a carbide-forming element, carbon reduction of vanadic acid yields vanadium carbide or vanadium carbonitride, alloys containing up to 6 percent carbon, which are used in the manufacture of high-carbon steel (limited application) (Raja, 2007).

DIRECT ELECTRO-SILICOTHERMIC REDUCTION

The best method for bulk production of vanadium-silicon-iron alloy is the direct electro-silicothermic reduction of V_2O_5 . The process is carried out in an electric smelting furnace. The raw materials required are melted V_2O_5 , ferro-silicon, soft iron cuttings, and lime. The silicon content of the alloy is carefully controlled by incrementally adding aluminum to the slag that is generated in the electric smelting furnace. The amount of the aluminum addition controls the vanadium flux across the interface of the slag (floating on top of the alloy melt) and the alloy (melt beneath the slag). The resulting vanadium-silicon-iron alloy is used in the steel industry, usually as a ladle addition, to control steel composition with regard to the final vanadium and silicon content of the steel (Raja, 2007).

U.S. VANADIUM DEMAND

Vanadium pentoxide is the starting point for the development of products that have commercial application.

Figure 5 shows vanadium metal demand by end use in the United States in 2004.

In 2004, 94 percent of vanadium metal demand in the United States was for steelmaking end uses. About 87 percent of the steelmaking use was fairly evenly split among the production of three classes of common steel alloys (carbon, full-alloy, and high-strength, low-alloy steel). Stainless and heat-resisting steel and tool steel accounted for 7 percent of the vanadium demand in 2004. Superalloys, other alloys, and chemicals accounted for about 5 percent of total U.S. vanadium demand in 2004. Vanadium chemicals, which made up less than 1 percent of U.S. vanadium demand in 2004, include catalysts, dietary supplements, dyes, glass, pigments, and plastic.

PRICES

Historically, the price of vanadium has shown peaks and valleys, with long periods of low prices followed by brief price spikes. Large vanadium producers (which produce byproduct and coproduct vanadium) are generally supply inelastic, and they continue to produce through periods of low vanadium demand (GoldInsider, 2006).

Figure 6 shows market prices for vanadium pentoxide for the period 1960 through 2010. For the period, the constant

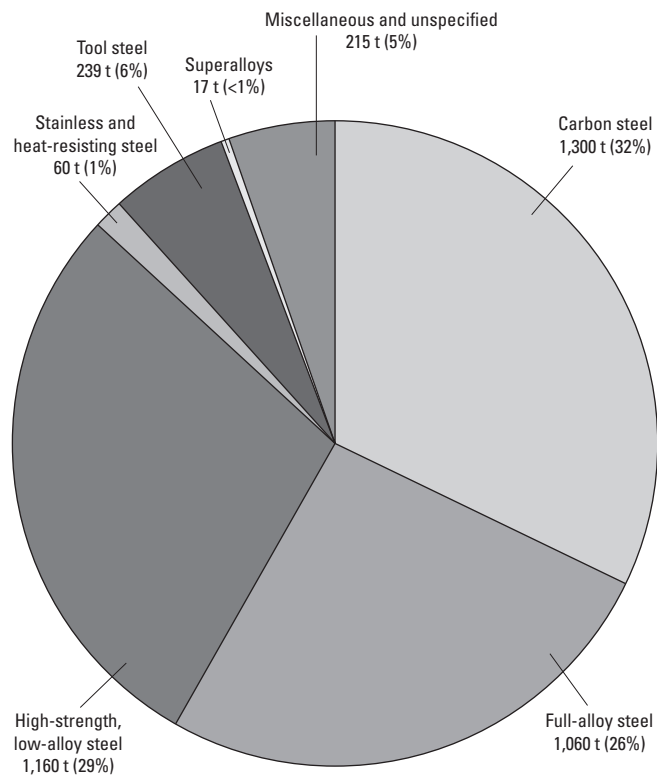


Figure 5. Pie chart showing vanadium metal demand by end use in the United States in 2004. Values are in metric tons (t) of contained vanadium and percentage of total. Data from Magyar (2007b, table 2).

dollar price of vanadium pentoxide showed several peaks and valleys and declined by about 1.13 percent per year, on average. During the same period, reported U.S. consumption of vanadium in the United States increased by about 0.10 percent per year.

Ashes and residues from petroleum processing may contain as much as 34 percent V_2O_5 . Slag from iron and steel-making in countries processing vanadium-containing ore may contain between 6 and 24 percent V_2O_5 . Figure 7 shows the unit values (based on values of imports for consumption) of V_2O_5 contained in ashes and residues and slag and the market price of V_2O_5 as a salable product for the years 1990 through 2007.

Figure 7 illustrates expected relationships, such as (1) the value of V_2O_5 contained in source materials is less than the value of purified V_2O_5 and (2) the relative values track the market. One unexpected observation is that, in 1999 and thereafter, the value of V_2O_5 contained in ashes and residues exceeded the value of V_2O_5 contained in slag.

The principal vanadium scrap that is actually recycled is catalyst scrap. Companies that process this type of scrap make offers to buy it and make contracts for supply; however, there is no compilation of prices enabling one to determine an industry-wide vanadium scrap price for a given moment in time.

SOURCES AND DISPOSITION OF VANADIUM SCRAP

There are two necessary conditions for recycling to occur—a supply of material and the ability to collect, process, and recover the desired material at a profit. Many materials dissipate with use and cannot be recycled; for example, the vanadium content of the bulk of steel alloys is lost to the slag or dust that develops when those alloys are recycled for their iron content. The slag (containing the vanadium) that develops when these alloys are recycled may be recovered for use as some type of aggregate, but the vanadium content is lost. It is possible to recover vanadium in some tool steels, which can contain up to 5 percent vanadium, if the tool steel is recycled by melting under vacuum or is otherwise processed under reducing conditions. The amount of tool steel so processed is undocumented, and this is not a large business sector.

Vanadium-bearing catalysts lose economic utility with use but little or none of their mass. These are candidates for recycling, and there is a ready supply. Spent-catalyst recyclers recover not just vanadium but also aluminum, cobalt, molybdenum, nickel, and platinum-group metals. Avoidance of the cost of disposing of spent catalysts as a hazardous waste is also a driver of catalyst recycling.

In 2004, about 3,010 t of vanadium (contained in old scrap) was generated from the vanadium-product reservoir in

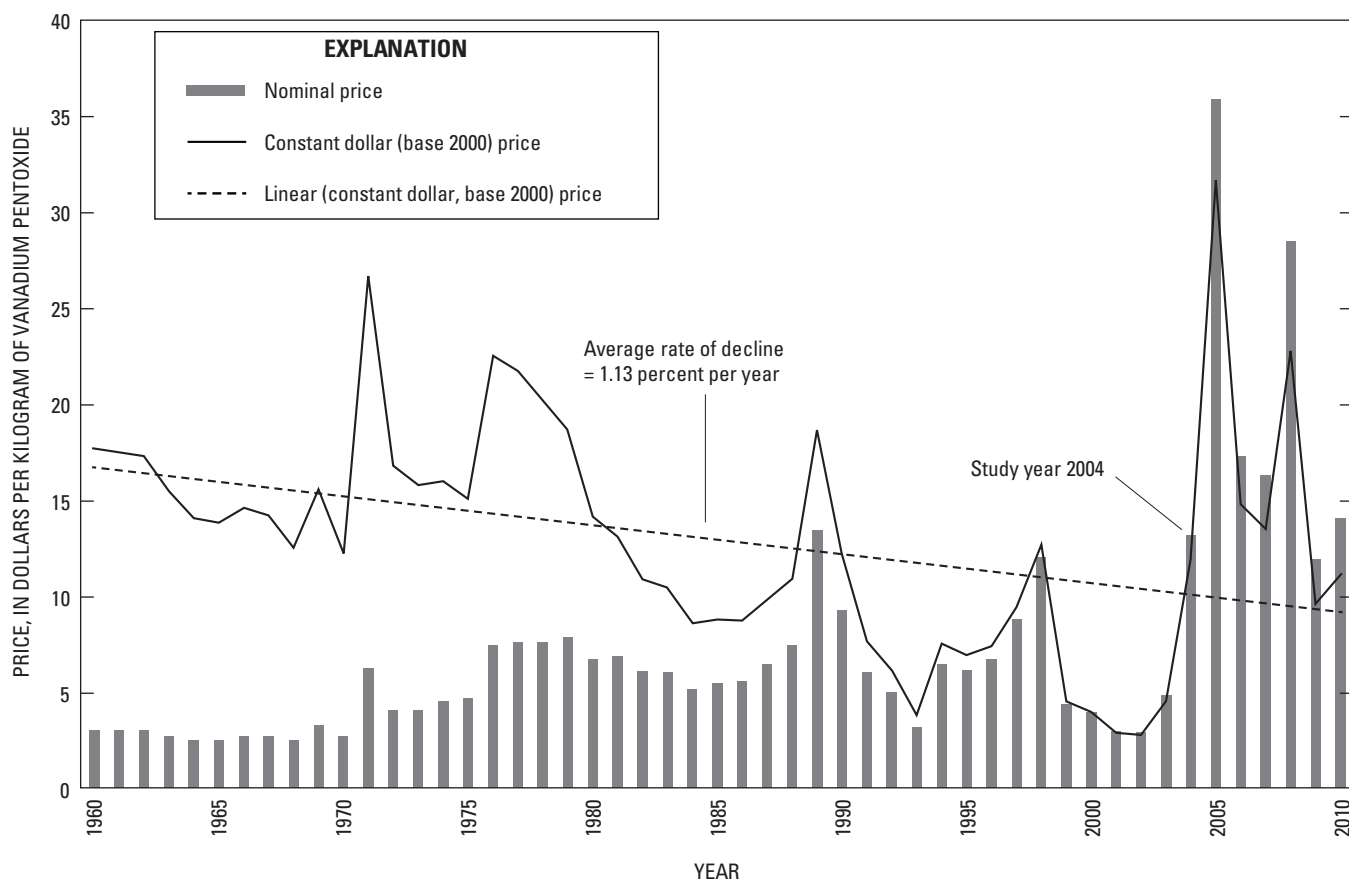


Figure 6. Graph showing vanadium pentoxide (V_2O_5) prices, in nominal and constant dollars, in the United States in 1960 through 2010. Values are in dollars per kilogram of V_2O_5 . For the years 1960 through 1998, the nominal price is taken as the producer price for V_2O_5 as extracted from Metal Bulletin and reported by U.S. Geological Survey publications (see sources below). Constant dollars are based on discounting nominal dollar prices using the Consumer Price Index (2000 basis). Sources: Reese (1999a), Magyar (2003, 2004, 2005a, 2007a, 2008, 2009), U.S. Department of Labor, Bureau of Labor Statistics (2010).

the United States; this amount consisted of 288 t of vanadium alloys and 2,720 t of spent catalysts. In addition, roughly 69 t of vanadium was recovered as new scrap.

OLD SCRAP

In the United States, the primary source of vanadium is spent catalysts from chemical processing plants, and each year about 2,700 t of vanadium is recycled from spent catalysts (Vanadium Technology Partnership, 2009). Also, other industries with priorities other than vanadium (aluminum, steel) would be the most likely recyclers of vanadium from vanadium-containing alloys, recovering it in pyrometallurgical operations under non-oxidizing conditions.

The leading vanadium-catalyst recyclers in the United States are Gulf Chemical and Metallurgical Corporation, Freeport, Tex. (with subsidiary plants in Butler, Pa., and Fort Saskatchewan, Canada); Metallurg Vanadium Corporation, Cambridge, Ohio; and Stratcor, Inc., Hot Springs, Ark. These plants service the tar sands processing industries of Canada

and the oil refining industries along the Gulf of Mexico Coast. Other industries use vanadium-containing catalysts; for example, the food industry uses catalysts for carbolic and sulfuric acid production and for fat hydrogenation.

In 2004, 11 percent of world vanadium production was from residues and ashes associated with processing of carbon-based fuel (coal, petroleum, tar sands), and 8 percent was attributable to recycling of vanadium from spent catalysts, most of which were used to catalyze the production of the residues. The U.S. fraction of world production from these sources, which was processed by the companies named above, has been withheld to preserve company confidentiality.

Old scrap recycling efficiency is defined as the amount of old scrap recovered and reused relative to the amount available to be recovered and reused; that is, [consumption of old scrap (COS) plus exports of old scrap (OSE)] divided by [old scrap generated (OSG) plus imports of old scrap (OSI) plus a decrease in old scrap stocks (OSS) or minus an increase in OSS], measured in weight and expressed as a percentage.

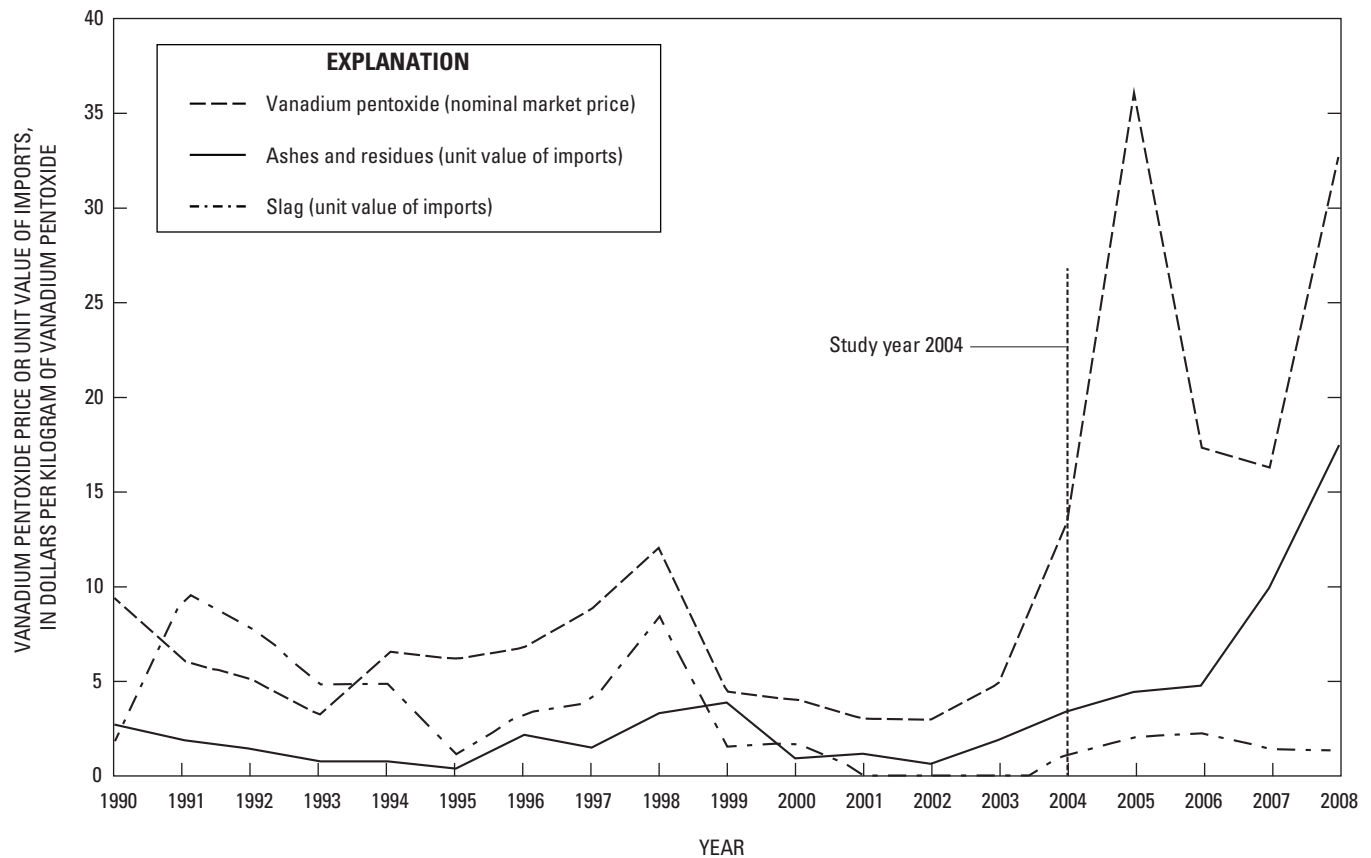


Figure 7. Graph showing unit values of vanadium pentoxide (V_2O_5) contained in ashes and residues and slag and the market price of V_2O_5 as a salable product for the years 1990 through 2007. Unit values are based on reported values of imports for consumption. The nominal price of V_2O_5 is taken as the producer price for V_2O_5 as extracted from Metal Bulletin and reported by U.S. Geological Survey publications: Hilliard (1994, 1995, 1996, 1997, 1998), Reese (1999a,b, 2000, 2001, 2002, 2003), Magyar (2003, 2004, 2005a, 2007a, 2008, 2009), and Polyak (2009).

In 2004, the domestic old scrap recycling efficiency for vanadium metal was about 94 percent. The specific values for the calculation follow: $[2,780 \text{ t (COS)} + 58 \text{ t (OSE)}]$ divided by $[3,010 \text{ t (OSG)} + 3 \text{ t (OSI)} + 0 \text{ (assumed value for decrease in OSS)}]$.

The recycling rate is that fraction of annual apparent vanadium supply that is derived from scrap. It is defined as [consumption of old scrap (COS) plus consumption of new scrap (CNS)] divided by apparent vanadium supply (AS), measured in weight and expressed as a percentage. In 2004, the recycling rate for vanadium was estimated to be 70 percent of apparent vanadium supply.

The new-to-old-scrap ratio in the United States is the ratio of the percentage of vanadium contained in new scrap recovered to the percentage of vanadium contained in old scrap recovered. In 2004, the new-to-old-scrap ratio was estimated to be 2:98, with spent catalysts prevailing as the source of vanadium in old scrap. This ratio for vanadium is low compared to that for other metals; for example, aluminum, 60:40

(Plunkert, 2006, table 1); copper, 76:24 (Goonan, 2010, table 1); and nickel, 12:88 (Goonan, 2009, table 1).

OLD SCRAP GENERATED

The U.S. Geological Survey estimated that 288 t of vanadium contained in old alloy scrap and 2,720 t of vanadium contained in spent catalysts were generated in 2004 as end-of-life material from the in-service reservoir of vanadium products in the United States. The development of the estimate for the alloy fraction is shown in table 3, which has data for the distribution of vanadium metal to the superalloys sector and the other-alloys sector with yearly variance included; an estimate for average life of products within each sector; and an assumption (in conformance with common practice) that the Gaussian distribution (a normal-like distribution; see appendix) closely approximates the actual decay of economic utility.

In table 3, the method for estimating old alloy scrap generated is shown completely for the superalloys sector and

Table 3. The development of the estimate for old alloy scrap generated in the United States in 2004.

[Years in column 1 are nominal years. Values for alloys placed in service and old scrap generated, columns 2, 4, 5, and 7, are in metric tons (t) of contained vanadium. Gaussian factors in columns 3 and 6 are unitless. The estimates for old scrap generated (through 2003, and available for 2004), by sector, are at the bottom of the table. The author estimates the average life of superalloys and other alloys at 10 years. Placed-in-service data are derived, using estimates for material recovery in semifabrication and manufacturing processes, from apparent consumption data reported by Matos and Magyar (2006). NA, not available]

Year	Superalloys			Other alloys		
	Placed in service (t)	Gaussian factor	Old scrap generated (t)	Placed in service (t)	Gaussian factor	Old scrap generated (t)
1985	7	0.0000	0	524	0.0001	0
1986	5	0.0001	0	445	0.0003	0
1987	4	0.0004	0	465	0.0014	1
1988	4	0.0022	0	526	0.0051	3
1989	18	0.0088	0	576	0.0151	9
1990	20	0.0271	1	423	0.0366	15
1991	8	0.0649	0	254	0.0731	19
1992	7	0.1213	1	318	0.1198	38
1993	7	0.1765	1	224	0.1611	36
1994	8	0.2000	2	232	0.1778	41
1995	10	0.1765	2	225	0.1611	36
1996	11	0.1213	1	281	0.1198	34
1997	11	0.0649	1	361	0.0731	26
1998	72	0.0271	2	363	0.0366	13
1999	6	0.0088	0	290	0.0151	4
2000	29	0.0022	0	285	0.0051	1
2001	78	0.0004	0	311	0.0014	0
2002	6	0.0001	0	241	0.0003	0
2003	6	0.0000	0	132	0.0001	0
2004	NA	NA	11	NA	NA	277

the other-alloys sector. The Gaussian distribution is a device that is overlain on a series of historical consumption data to estimate the contribution of old scrap (having experienced decay of utility in service) for a given year of service life. For this analysis, the historical sector consumption data from Matos and Magyar (2006) were transformed by the author into placed-in-service estimates. The average life estimates for the sectors were made by the author.

It is estimated that 11 t of vanadium metal contained in old alloy scrap was theoretically generated in 2004 by the superalloy sector from material that had been placed in service during the period 1985 through 2003. The average life for the sector was assumed to be 10 years, and the data spread (distribution about the average) was assumed to be 8 years. In like manner, the consumption dataset for the other-alloys sector was superimposed with a Gaussian distribution to esti-

mate the vanadium contribution from that sector (for 2004, 277 t of vanadium). The total estimate was 288 t of vanadium for both sectors.

Uncertainties in the estimate for old scrap theoretically generated can arise from several factors, including the following:

- Average life and spread (distribution about the average) are estimates.
- The datasets for sector consumption of vanadium metal are underestimated by the amount of vanadium metal contained in net imports of finished goods that contain semifinished materials containing vanadium.
- The datasets may be underreported as is.
- The Gaussian distribution, while useful, may not be the best distribution to apply.

OLD SCRAP UNRECOVERED

Old scrap unrecovered could be in several places. It could be abandoned in place (hibernating) pending suitable economic incentives (scrap prices) to warrant collection and processing. It might have been placed in landfills, which would potentially conserve it for a time of better prices. It might have been dissipated during use. Lastly, the method for estimating old scrap generated might be wrong.

In figure 1, the arrow directed to “Unrecovered [old] scrap” is the amount that would close the material balance after summing inputs and outputs. It is, therefore, an artifact of the materials flow accounting process. Vanadium contained in unrecovered old scrap in 2004 was estimated to be 176 t.

OLD SCRAP RECOVERED AND REUSED

Old scrap recovered and reused for metals is generally based on data that are reported to the U.S. Geological Survey; however, no such reports are received for vanadium metal. Therefore, the author’s estimate consists of two parts. First, the author assumes that 20 percent of the vanadium alloy scrap was returned to U.S. vanadium production (the low number is in deference to known concerns about the quality of vanadium alloy scrap for use in demanding aerospace applications). Secondly, the estimate for catalyst use is taken from Vanadium Technology Partnership (2009).

NEW SCRAP

Figure 1 shows 69 t of vanadium returning to the U.S. scrap supply in 2004. New scrap is generated from semifabrication of superalloys and other alloys and from the assembly of these alloys into end-use items such as airframes and engines. In 2004, new scrap generated from semifabrication and manufacturing (taken together and reported as “Fabrication” in fig. 1) was estimated to contain about 10 t of vanadium, and new scrap from assembly-manufacturing, about 60 t of vanadium—a total of about 69 t, as shown in figure 1.

PROCESSING OF VANADIUM SCRAP

The collection and handling of new vanadium-containing metal scrap are fairly straightforward. New scrap is generated during semifabrication and manufacturing operations and consists of items such as clippings, stampings, and turnings. These are usually segregated by material specification and returned to controlled-atmosphere induction furnace operations, where the scrap is matched and melted into a product having the desired chemistry. Some new scrap enters the open market, but the major portion is returned to U.S. producers of steel or aluminum alloys through purchase agreements.

Old (obsolete) scrap originates when products that are within the reservoir of products in service undergo decay of

economic utility. In the past, old vanadium scrap has had a tendency to hibernate because the stringency of vanadium metal and alloy specifications deterred its use. In recent years, more old scrap has been recovered, but reporting is not reliable.

VANADIUM SCRAP TRADE

Vanadium contained in various forms and mixtures flows through the international scrap trade. The vanadium content of the U.S. scrap trade in 2004 was 58 t of vanadium in exports and 3 t of vanadium in imports; thus, net exports contained 54 t of vanadium. Figure 8 shows countries that were sources of vanadium-containing old scrap imported by the United States in 2004. Figure 9 shows the country-by-country data for vanadium scrap exports.

OUTLOOK

Although vanadium prices show volatility over the long run (1960–2010), this volatility has more to do with the management of production capacity than the availability of vanadium supply sources. There are large vanadium ore reserves in Australia, which seem to be always on the brink of development. Vanadium contained in titaniferous magnetite

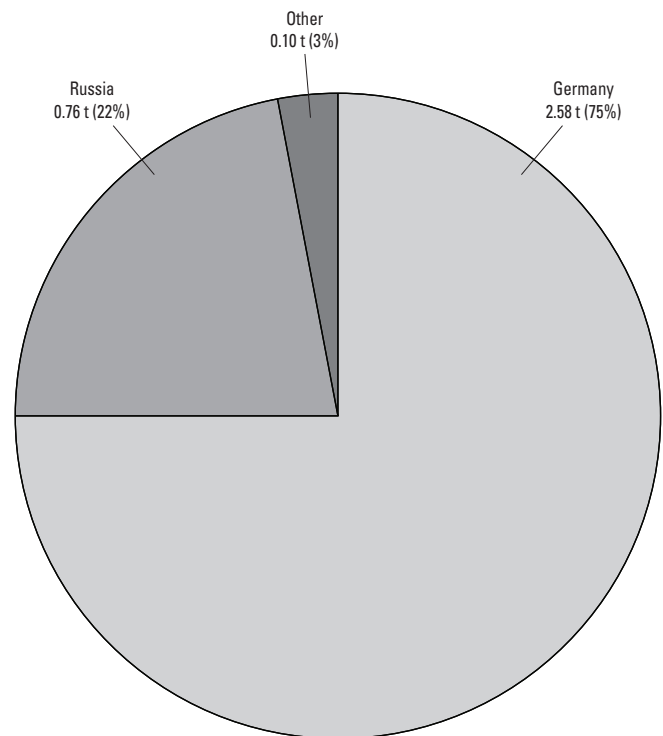


Figure 8. Pie chart showing estimated U.S. imports of old vanadium scrap by country in 2004. Values are in metric tons (t) and percentage of total imports. Derived from data in Magyar (2007b).

iron ores, which are a major source of byproduct vanadium through slag processing, may be under stress as a reliable source in the future because these ores, which derive their economic utility from the iron content, are relatively expensive to process compared to the typically higher grade ores processed elsewhere in the world. When these deposits are depleted or become uncompetitive in the iron market, then they will not be processed just for the vanadium content.

The fact that vanadium is found in petroleum and tar sands ensures that there will be vanadium coproduction from those sources and continued recycling of the vanadium-bearing catalysts that help to separate vanadium from the hydrocarbons. Vanadium supply, while subject to the volatility of short-term bottleneck challenges, is not constrained by lack of resources or reserves.

On the demand side, the superior strength-to-weight characteristic of vanadium-treated steel ensures that vanadium will continue to serve its leading use as a steel alloying element on a worldwide basis. The demand for steel will govern the demand for vanadium.

Titanium-vanadium alloys (vanadium content at 5 to 6 percent), are used extensively in the growing aerospace sector. New-generation commercial aircraft will contain much larger quantities (70 to 90 t of alloy per plane) of this alloy than previous generations (Tamlin and Smith, 2007). The

commercialization of vanadium is only about 60 years old. Research directed at new uses will likely expand the vanadium market, and the present uses in steel strengthening and high-temperature alloy performance are not likely to diminish.

It is expected that vanadium recycling from spent catalysts will continue and perhaps increase as more North American hydrocarbon resources (which contain vanadium) are utilized. If the price of V_2O_5 were to increase due to supply pressure of some kind, then steps could be taken to recover vanadium from steelmaking slag, which is now the greatest avenue for dissipative losses of vanadium.

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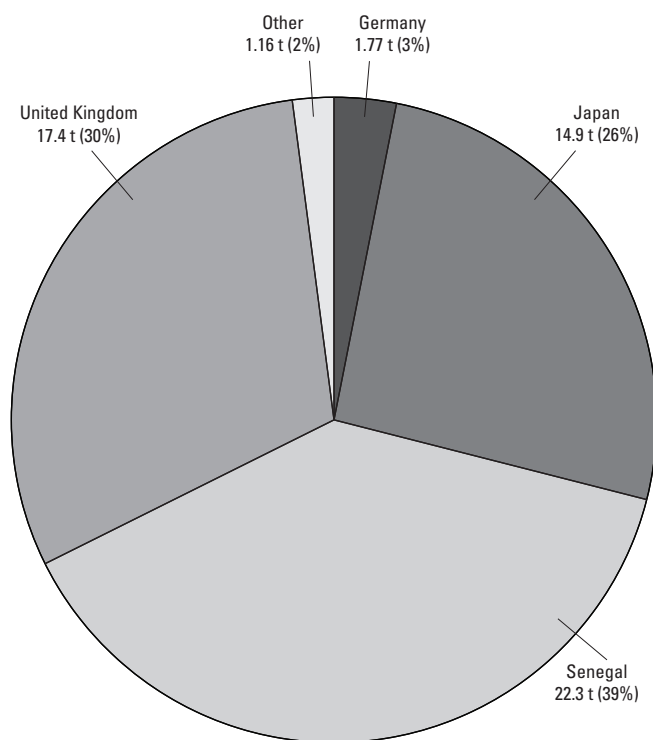


Figure 9. Pie chart showing estimated U.S. exports of old vanadium scrap by country in 2004. Values are in metric tons (t) and percentage of total exports. Derived from data in Magyar (2007b).

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APPENDIX—DEFINITIONS

apparent consumption. Primary refined production plus secondary production (old scrap) plus imports minus exports plus adjustments for Government and industry stock changes. For vanadium, no Government stocks exist.

apparent supply. Apparent consumption plus secondary production (new scrap).

Gaussian distribution. A statistical tool that is used by analysts of alloy life cycles to spread end-of-life estimates about the average value to a selected number of years.

hibernating scrap. Material at the end of its service life that could be recovered and recycled if prices and other economic factors warranted.

home scrap. Scrap generated as process or runaround scrap and consumed in the same plant where generated. It does not enter into trade and is not considered in this study.

hydrometallurgy. A process of separating desired metals from aqueous solutions.

master alloys (of vanadium). Alloys containing more than 10 percent by weight vanadium. They serve as an intermediate material source in the manufacture of other placed-in-service alloys or as deoxidants and desulfurizers. The vanadium content ranges between 30 and 90 percent in master alloys.

new scrap (prompt scrap). Scrap that is produced during the manufacture of metals and articles for both intermediate and ultimate consumption, including all defective finished or semifinished articles that must be reworked, and that is obtained from a facility separate from the recycling refiner, smelter, or processor. Examples of new scrap are borings, castings, clippings, drosses, skims, and turnings. Excluded from new scrap is home scrap that is generated as process scrap and used in the same plant.

new-to-old-scrap ratio. New scrap consumption compared with old scrap consumption in the United States, measured in weight and expressed as a ratio of new scrap to old scrap; for example, 2:98.

nominal price. The price at the time of sale.

obsolete (end-of-service-life). Material removed from service either because it is no longer serviceable or for any other reason.

old scrap. Scrap including (but not limited to) metal articles that have been discarded after serving a useful purpose. Typical examples of old scrap are electrical wiring, lead-acid batteries, silver from photographic materials, metals from shredded cars and appliances, used aluminum beverage cans, spent catalysts, and tool bits. "Old scrap" is also referred to as postconsumer scrap and may originate from industry or the general public. Expended and obsolete materials used dissipatively, such as paints and fertilizers, are not included.

old scrap exports. The amount of old scrap exported from the United States in a subject year.

old scrap generated. The metal content of obsolete products from the U.S. product reservoir that theoretically becomes available for recycling in a subject year. This definition excludes dissipative uses.

old scrap imports. The amount of old scrap imported to the United States in a subject year.

old scrap recovered and used. Equals old scrap reported as recovered.

old scrap recycling efficiency. The amount of old scrap recovered and reused relative to the amount available to be recovered and reused. Defined as [consumption of old scrap (COS) plus exports of old scrap (OSE)] divided by [old scrap generated (OSG) plus imports of old scrap (OSI) plus a decrease in old scrap stocks (OSS) or minus an increase in old scrap stocks], measured in weight and expressed as a percentage:

$$\frac{\text{COS} + \text{OSE}}{\text{OSG} + \text{OSI} + \text{decrease in OSS or - increase in OSS}} \times 100$$

old scrap unrecovered. Scrap that might have been abandoned in place (hibernating scrap), sent to a landfill, or dissipated during use. The amount of old scrap unrecovered is the difference between theoretical scrap generated and actual scrap collected and processed for sale to the global pool of manufacturers.

product reservoir. The stock of vanadium-bearing materials serving consumer needs. It is otherwise known as "in-service" stock.

pyrometallurgy. A process of separating desired metals from materials under conditions of high heat.

recycling. The process of recovering a metal in usable form from scrap or waste. Recovery products can be alloys, mixtures, or compounds that are useful. Vanadium can be recovered by recycling of alloys such as aluminum-vanadium, vanadium catalyst material, and tool steel scrap.

recycling rate. Fraction of the apparent metal supply that is scrap on an annual basis. It is defined as [consumption of old scrap (COS) plus consumption of new scrap (CNS)] divided by apparent supply (AS), measured in weight and expressed as a percentage:

$$\frac{\text{COS} + \text{CNS}}{\text{AS}} \times 100$$

scrap consumption. Scrap added to the production flow of a metal or metal product.

supply of recoverable vanadium. The sum of new (prompt) scrap, old scrap recovered, old scrap imports, and old scrap stock decrease. This supply serves the domestic and foreign demand for scrap.

vanadiferous slag. Slag processed during iron and steelmaking from iron ores with high vanadium content. The iron partitions to the metal bath, and the vanadium partitions to the slag as an oxide, thereby concentrating vanadium sufficiently to permit its economic recovery.