VANADIUM COMPOUNDS

1. Introduction

Vanadium is widely dispersed in the earth's crust at an average concentration of ~ 150 ppm. Deposits of ore-grade minable vanadium are rare. Vanadium is ordinarily recovered from its raw materials in the form of the pentoxide, but sometimes as the sesquioxide or sodium and ammonium vanadates. These initial compounds have catalytic and other chemical uses (see Catalysis). For such uses and for conversion to other vanadium chemicals, granular V_2O_5 usually is made by decomposing ammonium metavanadate. For metallurgical uses, which represent $\sim 90\%$ of vanadium consumption, some oxides are prepared for conversion to master alloys by fusion and flaking to form glassy chips. The preparation and application of alloying materials are described elsewhere (see Vanadium and vanadium alloys). Vanadium–aluminum master alloy is made for alloying with titanium metal. A part of such vanadium-rich raw materials as slags, ash, and residues is smelted directly to master alloys or to alloy steels. Figure 1 shows the prevailing process route (1).

Possibly because of price and performance competition from chromium, titanium, and other transition elements, only about a dozen vanadium compounds are commercially significant; of these, vanadium pentoxide is dominant.

2. Physical Properties

Some properties of selected vanadium compounds are listed in Table 1. Detailed solubility data are available (3), as are physical constants of other vanadium compounds (4). Included are the lattice energy of several metavanadates and the magnetic susceptibility of vanadium bromides, chlorides, fluorides, oxides, and sulfides (5).

Vanadium, a typical transition element, displays well-characterized valence states of 2–5 in solid compounds and in solutions. Valence states of -1 and 0 may occur in solid compounds, eg, the carbonyl and certain complexes. In oxidation state 5, vanadium is diamagnetic and forms colorless, pale yellow, or red compounds. In lower oxidation states, the presence of one or more *3d* electrons, usually unpaired, results in paramagnetic and colored compounds. All compounds of vanadium having unpaired electrons are colored, but because the absorption spectra may be complex, a specific color does not necessarily correspond to a particular oxidation state. As an illustration, vanadium(IV) oxy salts are generally blue, whereas vanadium(IV) chloride is deep red. Differences over the valence range of 2–5 are shown in Table 2. The structure of vanadium compounds has been discussed (6,7).

3. Chemical Properties

The chemistry of vanadium compounds is related to the oxidation state of the vanadium. Thus, V_2O_5 is acidic and weakly basic, VO_2 is basic and weakly acidic, and V_2O_3 and VO are basic. Vanadium in an aqueous solution of vanadate salt occurs as the anion, eg, $(VO_3)^-$ or $(V_3O_9)^{3-}$, but in strongly acid solution, the cation $(VO_2)^+$ prevails. Vanadium(IV) forms both oxyanions $(V_4O_9)^{2-}$ and oxycations $(VO)^{2+}$. Compounds of vanadium(III) and (II) in solution contain the hydrated ions $[V(H_2O)_6]^{3+}$ and $[V(H_2O)_6]^{2+}$, respectively.

Coordination compounds of vanadium are mainly based on six coordination, in which vanadium has a pseudooctahedral structure. Coordination number 4 is typical of many vanadates. Coordination numbers 5 and 8 also are known for vanadium compounds, but numbers < 4 have not been reported. The coordination chemistry of vanadium has been extensively reviewed (8–12) (see Coordination compounds).

Aqueous pentavalent vanadium is readily reduced to the tetravalent state by iron powder or by SO_2 gas. A stronger reducing agent, eg, zinc amalgam, is needed to yield divalent vanadium. Divalent and trivalent vanadium compounds are reducing agents and require storage under an inert atmosphere to avoid oxidation by air.

3.1. Interstitial and Intermetallic Compounds. In common with certain other metals, eg, Hf, Nb, Ti, Zr, Mo, W, and Ta, vanadium is capable of taking atoms of nonmetals into its lattice. Such uptake is accompanied by a change in the packing pattern to a cubic close-packed structure. Carbides, hydrides, and nitrides so formed are called interstitial compounds. Their composition is determined by geometrical packing arrangements rather than by valence bonding. As all possible vacant lattice sites need not be filled, the compositions display a range of nonmetal content up to the theoretical limit. A range for the vanadium nitride compound is $VN_{0.71-1.00}$. Compounds corresponding to V_2C [12012-17-8], VC, and $VH_{1.8}$ [12713-06-3] have been formed. Vanadium borides also are known. In VB [12045-27-1], the boron atoms form a zigzag chain; whereas, in VB_2 [12007-37-3], the interstitial boron atoms are linked in a layer of hexagons.

Large-atomed nonmetals, eg, Si, Ge, P, As, Se, and Te, form compounds with vanadium that are intermediate between being interstitial and intermetallic. The interstitial and intermetallic vanadium compounds are very hard crystalline solids (9–10 on Mohs' scale), have high melting points (2000–3000°C), and generally are resistant to attack by mineral acids. Except for carbides that are used in impure form, eg, in making alloy steels, this group of compounds is little used. Vanadium disilicide, VSi_2, which is made by the reaction of vanadium pentoxide with silicon metal at ~1200°C, has limited use as a refractory material (see Refractories). Preparation of vanadium nitride from the reaction of vanadium oxides with ammonia was investigated by the U.S. Bureau of Mines (13). In subsequent studies, the nitrides were to be converted to vanadium metal.

3.2. Vanadium Oxides. Vanadium pentoxide (V_2O_5) is intermediate in behavior and stability between the highest oxides of titanium, ie, TiO_2, and of chromium, ie, CrO_3. It is thus less stable to heat than TiO_2 and more heat-stable than CrO_3. Also, V_2O_5 is more acidic and a stronger oxidant than TiO_2, but less so than CrO_3. An excess of aluminum is capable of reducing V_2O_5 to a V–Al alloy, but only calcium can reduce the oxide to vanadium metal. Solubility in water is 0.1–0.8 g/100 g H_2O and is lowest for crystals solidified from the molten state. The pentoxide readily dissolves in both acids and alkalies. In strongly alkaline solutions (pH >13), simple mononuclear vanadate ions are present. In strongly acid solutions, the main species is the dioxyvanadium(V) cation $(VO_2)^+$. More complex ions are present in solutions of intermediate strength alkali or acid; these include $(VO_3)^-$, $(HVO_4)^{2-}$, $(V_3O_9)^{3-}$, $(V_4O_{12})^{4-}$, $(V_{10}O_{28})^{6-}$, and others.

Vanadium(IV) Oxide. Vanadium(IV) oxide (vanadium dioxide, VO_2) is a blue-black solid, having a distorted rutile (TiO_2) structure. It can be prepared from the reaction of V_2O_5 at the melting point with sulfur or carbonaceous reductants such as sugar or oxalic acid. The dioxide slowly oxidizes in air. Vanadium dioxide dissolves in acids to give the stable $(VO)^{2+}$ ions and in hot alkalies to yield vanadate(IV) species, eg, $(HV_2O_5)^-$.

Vanadium(III) Oxide. Vanadium(III) oxide (vanadium sesquioxide, V_2O_3) is a black solid, having the corundum (Al_2O_3) structure. It can be prepared by reduction of the pentoxide or ammonium metavanadate by natural gas, hydrogen or carbon. Air oxidation proceeds slowly at ambient temperatures, but oxidation by chlorine at elevated temperatures to give $VOCl_3$ and V_2O_5 is rapid.

Vanadium(II) Oxide. Vanadium(II) oxide is a nonstoichiometric material with a gray-black color, metallic luster, and metallic-type electrical conductivity. Metal—metal bonding increases as the oxygen content decreases, until an essentially metal phase containing dissolved oxygen is obtained (14).

3.3. Vanadates. Ammonium metavanadate and, to a lesser extent, potassium and sodium metavanadates, are the main vanadates of commercial interest. The pure compounds are colorless crystals. Vanadates(V) are identified as the meta (MVO_3), ortho (M_3VO_4), and pyro ($M_4V_2O_7$) compounds, and the nomenclature commonly used is that applied to the phosphates (M is univalent). Orthovanadates contain discrete tetrahedral $(VO_4)^{3-}$ anions. The pyrovanadates also contain discrete ions $(V_2O_7)^{4-}$ and have two VO_4 tetrahedra sharing a corner. The metavanadate structure is different for the anhydrous and hydrated salts. In the anhydrous salts KVO_3 and NH_4VO_3, the vanadium atoms are four-coordinate, with VO_4 tetrahedra linking through two oxygen atoms. In the hydrated form, $KVO_3 \cdot H_2O$, the vanadium atoms are five coordinate, with three shared oxygen atoms per vanadium and two terminal oxygen atoms.

3.4. Vanadium Halides and Oxyhalides. Known halides and oxyhalides of vanadium, their valences, and their colors are listed in Table 3. Only vanadium(V) oxytrichloride ($VOCl_3$) and the tetrachloride (VCl_4) have appreciable commercial importance. The trichloride (VCl_3) is of minor commercial interest. The absence of pentavalent vanadium halides, other than the fluoride, is attributed to the relative weakness of the fluoride–fluoride bond compared with analogous bonds in other halides. Even VCl_4 is somewhat unstable, and VBr_4 decomposes at $-23°C$. The halides and oxyhalides have been well characterized (6).

Vanadium(V) Oxytrichloride. Vanadium(V) oxytrichloride ($VOCl_3$) is readily hydrolyzed and forms coordination compounds with simple donor molecules, eg, ethers, but is reduced by reaction with sulfur-containing ligands and molecules. It is completely miscible with many hydrocarbons and nonpolar metal halides, eg, $TiCl_4$, and it dissolves sulfur.

Vanadium(IV) Chloride. Vanadium(IV) chloride (vanadium tetrachloride, VCl_4) is a red-brown liquid, is readily hydrolyzed, forms addition compounds with donor solvents, eg, pyridine, and is reduced by such molecules to trivalent vanadium compounds. Vanadium tetrachloride dissociates slowly at room temperature and rapidly at higher temperatures, yielding VCl_3 and Cl_2. Decomposition also is induced catalytically and photochemically. This instability reflects the difficulty in storing and transporting it for industrial use.

Vanadium(III) Chloride. Vanadium(III) chloride (vanadium trichloride, VCl_3) is a pink-violet solid, is readily hydrolyzed, and is insoluble in nonpolar solvents but dissolves in donor solvents, eg, acetonitrile, to form coordination compounds. Chemical behavior of the tribromide (VBr_3) is similar to that of VCl_3.

3.5. Vanadium Sulfates. Sulfate solutions derived from sulfuric acid leaching of vanadium ores are industrially important in the recovery of vanadium from its raw materials. Vanadium in tetravalent form may be solvent-extracted from leach solutions as the oxycation complex $(VO)^{2+}$. Alternatively, the vanadium can be oxidized to the pentavalent form and solvent extracted as an oxyanion, eg, $(V_3O_9)^{3-}$. Pentavalent vanadium does not form simple sulfate salts.

Vanadium(IV) Oxysulfate. Vanadium(IV) oxysulfate pentahydrate (vanadyl sulfate), ($VOSO_4{\cdot}5H_2O$) is an ethereal blue solid and is readily soluble in water. It forms from the reduction of $V_2\ O_5$ by SO_2 in sulfuric acid solution. Vanadium(III) sulfate [13701-70-7] [$V_2(SO_4)_3$] is a powerful reducing agent and has been prepared in both hydrated and anhydrous forms. The anhydrous form is insoluble in either water or sulfuric acid. Vanadium(II) sulfate heptahydrate ($VSO_4{\cdot}7H_2O$) is a light red-violet crystalline powder that can be prepared by electrolytic reduction of $VOSO_4$. The powder is oxidized by air and dissolves in water to give a red-violet solution.

4. Manufacture

Primary industrial compounds produced directly from vanadium raw materials are principally 98 wt % fused pentoxide, air-dried (technical-grade) pentoxide, and technical-grade ammonium metavanadate (NH_4VO_3). Much of the fused and air-dried pentoxides produced at the millsite is made by thermal decomposition of ammonium vanadates. Prior to 1960, the main vanadium mill products were fused technical-grade pentoxide (black cake) containing 86–92 wt % V_2O_5 and air-dried technical-grade pentoxide (red cake) containing 83–86 wt % V_2O_5, both being high in alkali content. An historical review of the manufacture of vanadium compounds until 1960 is available (15). Some milling practices for the production of primary vanadium compounds from ores have been reviewed (16).

Vanadium raw materials are processed to produce vanadium chemicals, eg, the pentoxide and ammonium metavanadate (AMV) primary compounds, by salt roasting or acid leaching. Interlocking circuits, in which unfinished or scavenged material from one process is diverted to the other, are sometimes used. Such interlocking to enhance vanadium recovery and product grade became more feasible in the late 1950s with the advent of solvent extraction.

4.1. Salt Roasting. Iron ore concentrate, uranium–vanadium ores, ferrophosphorus from manufacture of elemental phosphorus, vanadiferous shale, and assorted slag, ash, fumes, residues, and depleted catalysts, singly or in combination, are suitable feed for the salt-roast process. Sometimes, substitution of sodium carbonate for part or all of the salt results in improved vanadium recovery. The presence of calcium and magnesium carbonates is deleterious, because these form vanadates that are insoluble in water. Interference from calcium carbonate can be ameliorated by acidulating the ore with sulfuric acid before roasting or by adding pyrite to the charge, which results in formation of calcium sulfate that is innocuous in salt roasting. Calcium vanadates, present in a salt-roast calcine, can be dissolved by acid leaching the calcine. Limestone of low magnesium content must be added to the charge when salt roasting ferrophosphorus to combine with the phosphate that forms.

The ore is ordinarily ground to pass through a ~1.2-mm (14-mesh) screen, mixed with 8–10 wt % NaCl and other reactants that may be needed, and roasted under oxidizing conditions in a multiple-hearth furnace or rotary kiln at 800–850°C for 1–2 h. Temperature control is critical because conversion of vanadium to vanadates slows markedly at ~800°C, and the formation of liquid phases at ~850°C interferes with access of air to the mineral particles. During roasting, a reaction of sodium chloride with hydrous silicates, which often are present in the ore feed, yields HCl gas. This is scrubbed from the roaster off-gas and neutralized for pollution control, or used in acid-leaching processes at the mill site.

Hot calcine from the kiln is water-quenched or cooled in air before being lightly ground and leached. Air cooling allows back reactions, which adversely affect vanadium extraction for some ores. Leaching and washing of the residue is by percolation in vats or by agitation and filtration. Extraction of vanadium is 65–85%. Vanadium solution from water leaching of the calcine has a pH of 7–8 and a vanadium content of ~30–50 g V_2O_5/L. If the water-leach residue is leached subsequently with sulfuric acid solution, as for uranium extraction, as much as 10–15 wt % more vanadium may dissolve. Originally, such acid-leached vanadium precipitated from the uranium solvent extraction raffinate as an impure sludge that was recycled to the salt-roast kiln. The vanadium generally is recovered from the uranium raffinate by solvent extraction (see Uranium and uranium compounds).

Recovery of Vanadium from Salt-Roast Leach Solution. When recovery of vanadium as sodium red cake was practiced, the leach solution pH was adjusted to 2.7 by adding sulfuric acid. Any vanadium not already in the pentavalent form was oxidized by addition of sodium chlorate, and the solution was boiled for 2–8 h to precipitate substantially all of the vanadium as shotlike particles of sodium red cake. Although melting and flaking converted the highly alkaline red cake to black cake suitable for most metallurgical uses, extensive purification, usually by conversion to ammonium metavanadate, was required to prepare compounds for catalytic and chemical use. The process routes favored for recovering vanadium from the leach solution are solvent extraction and precipitation of ammonium vanadates or vanadic acid. Sometimes both solvent extraction and direct precipitation are used in integrated circuits.

For solvent extraction of pentavalent vanadium as a decavanadate anion, the leach solution is acidified to ~pH 3 by addition of sulfuric acid. Vanadium is extracted in about four countercurrent mixer–settler stages by a 3–5 wt % solution of a tertiary alkyl amine in kerosene. The organic solvent is stripped by a soda ash or ammonium hydroxide solution, and addition of ammoniacal salts to the rich vanadium strip liquor yields ammonium metavanadate. A small part of the metavanadate is marketed in that form and some is decomposed at a carefully controlled low temperature to make air-dried or fine granular pentoxide, but most is converted to fused pentoxide by thermal decomposition at ~450°C, melting at 900°C, then chilling and flaking.

For solvent extraction of a tetravalent vanadium oxyvanadium cation, the leach solution is acidified to ~pH 1.6–2.0 by addition of sulfuric acid, and the redox potential is adjusted to −250mV by heating and reaction with iron powder. Vanadium is extracted from the blue solution in about six countercurrent mixer–settler stages by a kerosene solution of 5–6 wt % di-2-ethylhexyl phosphoric acid (EHPA) and 3 wt % tributyl phosphate (TBP). The organic solvent is stripped by a 15 wt % sulfuric acid solution. The rich strip liquor containing ~50–65 g V_2O_5/L is oxidized batchwise initially at pH 0.3 by addition of sodium chlorate; then it is heated to 70°C and agitated during the addition of NH_3 to raise the pH to 0.6. Vanadium pentoxide of 98–99% grade precipitates, is removed by filtration, and then is fused and flaked.

For direct precipitation of vanadium from the salt-roast leach liquor, acidulation to ~pH 1 without the addition of ammonia salts yields an impure vanadic acid; when ammonium salts are added, ammonium polyvanadate precipitates. The impure vanadic acid ordinarily is redissolved in sodium carbonate solution, and ammonium metavanadate precipitates upon addition of ammonium salts. Fusion of the directly precipitated ammonium salts can yield high purity V_2O_5 for the chemical industry. Amine solvent extraction is sometimes used to recover 1–3 g/L of residual V_2O_5 from the directly precipitated tail liquors.

Other Developments. Recovery of vanadium from a dolomitic shale by salt roasting, acid leaching, and amine solvent extraction has been reported (17). A patent was issued for recovery of vanadium-bearing solution from silica containing titaniferous magnetic ore by roasting a mixture of ore, a sodium salt, and cryolite at <1350°C for 30 min to 2 h and then leaching the calcine (18). Roasting of iron ores with limestone to form calcium vanadate [14100-64-2] and leaching of the vanadate with ammonium carbonate or bicarbonate solution have also been patented (19). A patent was granted for heating a mixture of slag and sodium carbonate in a converter at 600–800°C in the presence of oxygen to solubilize the vanadium, leach with water, and recover vanadium from the leach solution (20). Another patent for vanadium recovery from slag calls for an oxidizing roast, followed by leaching of the calcine with phosphoric acid to dissolve the vanadium, and recovery of vanadium from the leach solution (21). A patent was issued for recovering a vanadium redcake directly from Orimulsion fuel ash (Orimulsion is a stabilized bitumen emulsion from the Orinoco basin in Venezuela that can be used as a substitute for fuel oil in power generation) (22).

4.2. Acid Leaching. Direct acid leaching for vanadium recovery is used mainly for vanadium–uranium ores and less extensively for processing spent catalyst, fly ash, and boiler residues. Although V_2O_5 in spent catalysts dissolves readily in acid solutions, the dissolution of vanadium from ores and other feed materials requires leaching for ~14–24 h in strong, hot, oxidizing sulfuric acid solutions. Ore is ground to ~0.60 mm(28 mesh) and is leached at 50–55 wt % solids and 75°C in a series of about four agitated tanks. Enough sulfuric acid and sodium chlorate are added to the first tank in the series to maintain ~70 g/L of free acid in the second tank and a terminal redox potential of at least −430mV. Such intensive leaching conditions dissolve ~75% of the vanadium and 95% of the uranium. Excess acid in the leach liquor, after liquid–solids separation, is neutralized by reaction with fresh ore. A second liquid–solids separation produces a clarified leach liquor of ~ pH 1 for solvent extraction. Vanadium is recovered from the uranium solvent-extraction raffinate.

For vanadium solvent extraction, iron powder can be added to reduce pentavalent vanadium to tetravalent and trivalent iron to divalent at a redox potential of -150mV. The pH is adjusted to 2 by addition of NH_3, and an oxyvanadium cation is extracted in four countercurrent stages of mixer–settlers by a diesel oil solution of EHPA. Vanadium is stripped from the organic solvent with a 15 wt % sulfuric acid solution in four countercurrent stages. Addition of NH_3, steam, and sodium chlorate to the strip liquor results in the precipitation of vanadium oxides, which are filtered, dried, fused, and flaked (23). Vanadium can also be extracted from oxidized uranium raffinate by solvent extraction with a tertiary amine, and ammonium metavanadate is produced from the soda ash strip liquor. Fused and flaked pentoxide is made from the ammonium metavanadate (24).

4.3. Australian Vanadium–Uranium Ore.

A calcareous carnotite ore at Yeelirrie, Australia, is ill-suited for salt roasting and acid leaching. Dissolution of vanadium and uranium by leaching in sodium carbonate solution at elevated temperature and pressure has been tested on a pilot-plant scale (25).

4.4. Halides and Oxyhalides.

Vanadium(V) oxytrichloride is prepared by chlorination of V_2O_5 mixed with charcoal at red heat. The tetrachloride (VCl_4) is prepared by chlorinating crude metal at 300°C and freeing the liquid from dissolved chlorine by repeated freezing and evacuation. It now is made by chlorinating V_2O_5 or $VOCl_3$ in the presence of carbon at ~ 800°C. Vanadium trichloride (VCl_3) can be prepared by heating VCl_4 in a stream of CO_2 or by reaction of vanadium metal with HCl.

5. Production

The bulk of world vanadium production is derived as a by-product or coproduct in processing iron, titanium, and uranium ores, and, to a lesser extent, from phosphate, bauxite, and chromium ores, spent catalysts and the ash, fume, or coke from burning or refining petroleum. Total world production of V_2O_5 was ~ 85 t (190×10^6 lb) in 2004.

Essentially no U.S. production, 9 t (20×10^6lb in 2004), of primary vanadium compounds has been as by-products or coproducts of uranium or of ferrophosphorus derived from smelting Idaho phosphates. However, a uranium/vanadium producer did start up in 2005. Essentially all of the 2004 U.S. production was from processing petroleum residues, and spent catalysts. The only domestic commercially mined ore, for its sole production of vanadium, is Arkansas brookite. It has contributed significantly to domestic supply since ~ 1969, however, it has not been mined since 1992 (26).

Most foreign vanadium is obtained as a coproduct of iron and titanium. South Africa, Norway, and Finland are suppliers. Chile produces slag from an iron operation. Australia had the world's largest vanadium operation, but it shut down in 2003 after only a few years of operation. Russia and the People's Republic of China produce slag and pentoxide from iron–titanium ores.

6. Economic Aspects and Specifications

Prices are only published in the *London Metal Bulletin* and *Ryan*'s *Notes*. In September 2005, the following equivalent prices per kilogram of V and V_2O_5, respectively, were reported by the *London Metal Bulletin.* (27): \$46.00–52.00, on the basis of FeV containing 70–80% V, and \$22.05–25.80, based on minimum oxide of 98% V_2O_5. For the same period, *Ryan*'s *Notes* reported a price range equivalent to \$41.90–44.10 per kilogram of V for FeV (28).

Product data issued by a producer of vanadium catalysts include the following specifications. Vanadium(III) acetylacetonate, $V(C_5H_7O_2)_3$ 98.0 wt % min, $VO(C_5H_7O_2)_2$ 2 wt % max, must be maintained under inert atmosphere (nitrogen containing <10 ppm O_2 is recommended). Vanadium oxytrichloride, $VOCl_3$ 95.0 wt% min, V^{5+} 28.5 wt% min, Cl 60.5–61.5 wt% Fe 0.06 wt% max, must be maintained under inert atmosphere (N_2 containing <10 ppm O_2); exposure to moisture in air results in formation of HCl and HVO_3. Vanadium tetrachloride, vanadium(IV) 22.5 wt% min, vanadium(V) 3.0 wt% max, free $Cl_2\sim$ 3.0 wt%, chloride 73.0 wt%; store under inert atmosphere and away from heat; reacts vigorously with water.

6.1. Energy Use in the Manufacture of Fused Pentoxide.

The energy required to produce fused pentoxide from a vanadium–uranium ore containing 1.3 wt% V_2O_5 and 0.20 wt% U_3O_8 is $\sim$360 MJ/kg (155,000 Btu/lb) (29). Treatment is assumed to be by salt roasting, water and acid leaching, uranium and vanadium solvent extraction, and production of fused pentoxide. Vanadium recovery from ore is $\sim$80%. The hypothetical carnotite ore selected for the energy estimation is relatively rich in vanadium and uranium. Processing of lower grade feed would require more energy per unit of product.

6.2. Imports and Exports.

The United States has long been a significant importer of vanadium slags, but imports of pentoxide were negligible until they rose quickly to 850 metric tons in 1974, and 2000 t in 1975 (mostly from the Republic of South Africa). By 2000 the primary U.S. supply of vanadium slags came from Mexico. Pentoxide imports then declined to 1400 t in 1980 with Finland being the main and South Africa the minor suppliers. In recent years, U.S. imports of ammonium and potassium vanadates and of other vanadium compounds have been 100–200 t/year, mainly from the United Kingdom, Germany, and the Republic of South Africa.

Annual U.S. exports of the pentoxide and other compounds were 1300–1400 t in 1978 and declined to 800–900 t in 1979 and 1980. The anhydrous pentoxide accounted for roughly three-fourths of the compounds exported.

6.3. U.S. Stockpile.

A U.S. government stockpile goal for vanadium pentoxide of 6985 t contained vanadium was announced on May 1, 1980. This is equivalent to 12,470 t of V_2O_5. At the time of the announcement, the stockpile contained only 491 t of vanadium in the form of the pentoxide (30). Physical requirements are that V_2O_5 be supplied as broken flake, all of a size to pass a 2.54-cm screen and not more than 5 wt% to pass a 4.7-mm screen. Packaging in polyethylene film inside 208-L steel drums and marking of the drums has been described in detail (31). In 1990, the pentoxide in this stockpile was reprocessed in Arkansas to a high purity granular form of V_2O_5, which is more suitable for producing titanium–vanadium–aluminum for aircraft applications.

7. Analytical and Test Methods

A delicate qualitative test for the presence of vanadium is the formation of brownish-red pervanadic acid upon addition of hydrogen peroxide to a solution of a vanadate. Although titanium reacts similarly, its color disappears when fluoride or phosphate ions are added (32). Quantitative determinations over a wide range of vanadium content are readily performed by induced coupled plasma or atomic absorption spectroscopy. Acetylene or nitrous oxide flames are ordinarily used. A highly sensitive atomic-absorption technique involving a carbon-filament atom reservoir has a detection limit of 100 pg V in a 1-μ/L sample. Volumetric, colorimetric, and spectrographic methods for vanadium are well-developed (33). Conversely, gravimetric methods are seldom used. X-ray absorption spectroscopy is a convenient means for identifying traces of vanadium in coal (34).

8. Health, Safety, and Environmental Considerations

The effect of vanadium compounds in the workplace and in ambient air on human health and safety has been extensively reviewed (35). In humans, toxic effects have been observed from occupational exposure to airborne concentrations of vanadium compounds that were probably several milligrams or more per cubic meter of air. Direct irritation of the bronchial passageways results from such exposure and is accompanied by coughing, spitting, wheezing, and eye, nose, and throat irritation. Some workers exhibit weakness, neurasthenia, and slight anemia, which suggests chronic toxic effect from vanadium absorption. Threshold limits for V_2O_5 in the air of the workplace have been established by OSHA as $0.05\,mg\,V_2O_5/m^3$ for respirable dust and fumes.

Oral vanadium toxicity in humans is minimal. Ingestion of 4.5 mg/day of vanadium has been without effect, but higher doses produce gastrointestinal distress and the greentongue associated with excessive inhalation of vanadium (36). The concentration of vanadium in vegetation varies from undetectable to 4 ppm in alfalfa and in animal tissues from 0.25 to slightly > 1 ppm. Drinking water contains up to 220 ppb [parts per billion (10^9)] of vanadium. Although contamination of water supplies by seepage from vanadium processing wastes seems possible, evidence of such contamination has not been found. Postulated to be an essential trace element for human well being, the function of vanadium and its limiting concentrations have yet to be established (37).

In the United States, the largest concentration of atmospheric vanadium occurs over eastern seaboard cities where residual fuels of high vanadium content from Venezuela are burned in utility boilers. Coal ash in the atmosphere also contains vanadium (38). Ambient air samples from New York and Boston contain as much as 600–1300 ng V/m^3, whereas air samples from Los Angeles and Honolulu contained 1–12 ng V/m^3. Adverse public health effects attributable to vanadium in the ambient air have not been determined. Increased emphasis by industry on controlling all plant emissions may have resulted in more internal reclamation and recycle of vanadium catalysts. An apparent drop in consumption of vanadium chemicals in the United States since 1974 may be attributed, in part, to such reclamation activities. A study published by the National Toxicity Program issued in 2002 (39) shows that there is some evidence of carcinogenicy in male rats, equivocal evidence of carcinogenicy in female rats and clear evidence of carcinogenicy in mice. This has led California to list V_2O_5 as a suspected human carcinogen in its Proposition 64.

9. Uses

Conversion of fused pentoxide to alloy additives is by far the largest use of vanadium compounds. Air-dried pentoxide, ammonium vanadate, and some fused pentoxide, representing ~10% of primary vanadium production, are used as such, purified, or converted to other forms for catalytic, chemical, ceramic, or specialty applications. The dominant single use of vanadium chemicals is in catalysts. Much less is consumed in ceramics and electronic gear, which are the other significant uses (see Batteries). Many of the numerous uses reported in the literature are speculative, proposed, obsolete, or in such small quantities as to be generally reported under such consolidated headings as miscellaneous or other.

The NRC Committee's estimates of catalyst use for 1972, 1974, and 1975 were 40–80% higher than the BOM's, and the former's estimates for overall use, including ceramics, electronics, and unspecified uses, were 3–39% higher. Data published by the BOM through 1980 show a precipitous decline in total annual use from ~311 t in 1974 to ~82 t in 1980. The decline appears to have been caused mainly by unfavorable business conditions and conservation efforts, but part of the apparent decline may stem from incomplete collection of data.

Catalytic uses result in little consumption or loss of vanadium. The need to increase conversion efficiency for pollution control from sulfuric acid plants, which require more catalyst, and expanded fertilizer needs, which require more acid plants, were factors in the growth of vanadium catalyst requirements during the mid-1970s. Use was about evenly divided between initial charges to new plants and replacements or addition to existing plants. The growth of vanadium use in catalysts since the 1990s can be attributed mainly to the consumption by the NO_x reduction catalyst producers for the SCR (selective catalytic reduction) process.

Minor uses of vanadium chemicals are preparation of vanadium metal from refined pentoxide or vanadium tetrachloride; liquid-phase organic oxidation reactions, eg, production of aniline black dyes for textile use and printing inks; color modifiers in mercury-vapor lamps; vanadyl fatty acids as driers in paints and varnish; and ammonium or sodium vanadates as corrosion inhibitors in flue-gas scrubbers.

Uses reported in the early literature, but which were insignificant in recent years at least in the United States, include refractories, V_2O_3 for coloring glass green, and V_2O_5 for ultraviolet screening in glass. Other developments include an expanded role as catalyst in such applications as vapor-phase polymerizations of ethylene and propylene, ammoxidations to form acrylonitrile and terephthalonitrile, and hydrodesulfurization of crude oils; V_3Ga [12024-15-6] as a superconductor; VO_2 as a thermal or light-activated resistor–conductor; vanadate glasses as electrooptical switches; rare-earth vanadites as magnetic materials; and addition of ~ 5 wt % V_2O_5 to silicon carbide refractories for increased oxidation resistance at high temperatures; the latter is reportedly being practiced in Germany (40). Recently, a lot of research has gone into the use of V_2O_5 for the treatment of diabetes, and a small amount of sodium metavanadate and vanadyl sulfate is used in vitamins for increasing metabolism rates.

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Table 1. **Physical Properties of Some Industrial and Other Selected Vanadium Compounds**[a]

Compound	CAS Registry-Number	Formula	Appearance	Mol wt	Density, g/cm^3	Mp, °C	Bp, °C	Solubility
vanadic acid, meta	[13470-24-1]	HVO_3	yellow scales	99.95				soluble in acid and alkali
ammonium metavanadate	[7803-55-6]	NH_4VO_3	white–yellowish or colorless crystals	116.98	2.326	200 dec		slightly soluble in H_2O
potassium metavanadate	[13769-43-2]	KVO_3	colorless crystals	134.04				soluble in hot H_2O
sodium metavanadate	[13718-26-8]	$NaVO_3$	colorless, monoclinic prisms	121.93		630		soluble in H_2O
sodium orthovanadate	[13721-39-6]	Na_3VO_4	colorless, hexagonal prisms	183.94		850–856		soluble in H_2O
sodium pyrovanadate	[13517-26-5]	$Na_4V_2O_7$	colorless, hexagonal prisms	305.84		632–654		soluble in H_2O
vanadium carbide	[12070-10-9]	VC	black cubic	62.95	5.77	2810	3900	insoluble in H_2O; soluble in HNO_3 with decomposition
vanadium nitride	[24646-85-3]	VN	black cubic	64.95	6.13	2320		soluble in aqua regia
vanadium(III) trichloride	[7718-98-1]	VCl_3	pink crystals, deliquescent	157.301	3.00	dec		soluble (deliquescent) in H_2O; soluble in methanol and ether
vanadium(IV) tetrachloride	[7632-51-1]	VCl_4	red-brown liquid	192.75	1.816	28±2	148.5	soluble (deliquescent) in H_2O; soluble in methanol, ether, and chloroform

vanadium(V) oxytrichloride	[7727-18-6]	$VOCl_3$	yellow liquid	173.30	1.829	−77±2	126.7	soluble (deliquescent) in H_2O; soluble in methanol, ether, acetone, and acid
vanadium(II) oxide	[12035-98-2]	VO	light green crystals	66.95	5.758	ignites		soluble in acid
vanadium(III) oxide	[1314-34-7]	V_2O_3	blue crystals	149.88	4.87	1970		soluble in HNO_3, HF, and alkali in presence of oxide
vanadium(IV) oxide	[12036-21-4]	VO_2	blue crystals	82.94	4.339	1967		soluble in acid and alkali
vanadium(V) oxide	[1314-62-1]	V_2O_5	yellow-red rhombohedra	181.88	3.357	690	1750 dec	slightly soluble in H_2O; soluble in acid and alkali
vanadium(IV) disilicide	[12039-87-1]	VSi_2	metallic prisms	107.11	4.42			soluble in HF
vanadium(III) acetylacetonate	[13476-99-8]	$V(C_5H_7O_2)_3$	brown crystals	348.27	0.9–1.2	178–190		soluble in methanol, acetone, benzene, and chloroform
biscyclopentadienylvanadium chloride	[12083-18-6]	$(C_5H_5)_2VCl_2$	pale green crystals	252.04		< 250 dec		soluble in methanol and chloroform

[a] Ref. 2.

Table 2. **Magnetism and Color of Vanadium Compounds**

Compound	CAS Registry Number	Vanadium valence	No. of *d* electrons	Magnetic moment, J/T × 10^{-23a}	Color
$VOCl_3$	[7727-18-6]	5	0	0	yellow
$VOSO_4\cdot 5H_2O$	[12439-96-2]	4	1	1.60	blue
$(NH_4)V(SO_4)_2\cdot 12H_2O$	[29932-01-2]	3	2	2.60	blue
$VSO_4\cdot 7H_2O$	[36907-42-3]	2	3	3.47	violet

[a] To convert J/T to $_B$, divide by 9.274×10^{-24}.

Table 3. **Vanadium Halides and Oxyhalides**

Vanadium valence	Formula	CAS Registry Number	Appearance[a]
		Halides	
V	VF_5	[7783-72-4]	white
IV	VF_4	[10049-16-8]	green
	VCl_4	[7632-51-1]	red-brown liquid
	VBr_4[b]	[13595-30-7]	magenta
III	VF_3	[10049-12-4]	green
	VCl_3	[7718-98-1]	red-violet
	VBr_3	[13470-26-3]	gray
	VI_3	[15513-94-7]	dark brown
II	VF_2	[13842-80-3]	blue
	VCl_2	[10580-52-6]	pale green
	VBr_2	[14890-41-6]	orange-brown
	VI_2	[15513-84-5]	red
		Oxyhalides	
V	VOF_3	[13709-31-4]	pale yellow
	$VOCl_3$	[7729-18-6]	yellow liquid
	$VOBr_3$	[13520-90-6]	deep red liquid
	VO_2F	[14259-82-6]	brown
	VO_2Cl	[13759-30-3]	orange
IV	VOF_2	[13814-83-0]	yellow
	$VOCl_2$	[10213-09-9]	green
	$VOBr_2$	[13520-89-3]	yellow-brown
III	$VOCl$	[13520-87-1]	brown
	$VOBr$	[13520-88-2]	violet

[a] At room temperature; solid unless identified as liquid.

[b] Decomposes at −23°C.

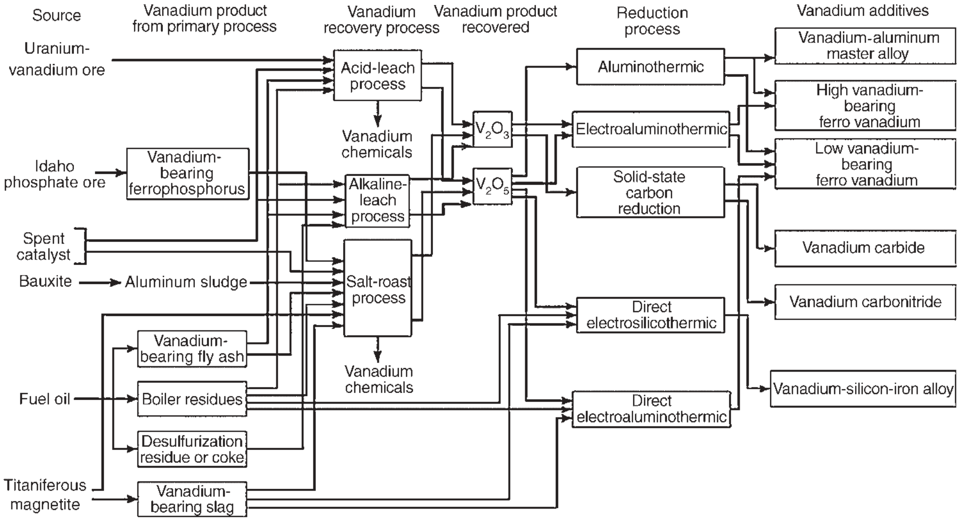

Fig. 1. Generalized flow sheet of minerals processing to vanadium products (1).