NATIONAL INVENTORY OF SOURCES AND EMISSIONS OF VANADIUM (1972)

Pollution Data Analysis Division

Air Pollution Programs Branch

Air Pollution Control Directorate

APCD 75-3

September 1975

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ABSTRACT

Atmospheric emissions of vanadium from various sectors of the Canadian economy have been estimated for the year 1972. The data presented in this report are summarized in Table 1. Total vanadium emissions to the atmosphere in 1972 are estimated at 2065 tons, of which 97.2% was emitted through the use of petroleum products. Heavy fuel oil combustion is the largest single source of vanadium emissions, accounting for 94.1% of the total. On a geographic basis, eastern Canada accounts for over 90% of the total vanadium emissions, with 64% coming from the Province of Quebec. This situation results primarily from the combustion of significant quantities of high-vanadium-content, Venezuelan heavy oil.

Although most emissions have been estimated using available Canadian data, it was sometimes necessary to rely on information from the United States. These estimates may require modification as further data for Canadian sources become available.

RÉSUMÉ

On a évalué pour 1972 les émissions atmosphériques de vanadium pour différents secteurs de l'économie canadienne. Le tableau 1 donne un résumé des données présentées dans le présent rapport. On a estimé les émissions totales de vanadium dans l'atmosphère à 2065 tonnes dont 97.2% provenait de l'utilisation de produits du pétrole. La combustion d'huile lourde constitue la principale source particulière d'émissions de vanadium, fournissant 94.1% du total. Sur une base géographique l'est du Canada a été responsable de plus de 90% des émissions totales de vanadium, avec environ 64% provenant de la Province de Québec. Cette situation a été causée en grande partie par la combustion de quantités significatives d'huile lourde Vénézuélienne à teneur élevée en vanadium.

Quoique la plupart des émissions ont été évaluées à l'aide de données canadiennes, il a parfois été nécessaire de se baser sur de l'information des Etats-Unis. On aura peut-être à modifier ces chiffres lorsqu'on disposera de données portant sur des sources canadiennes d'émissions.

TABLE 1 SUMMARY OF VANADIUM EMISSIONS BY PROVINCE AND SECTOR, 1972 (Tons)

	Province												
Sactor	Nfld .	P.E.1.	N.S.	N.B.	Quo	Ont.	Man.	Sask.	Alta .	B.C.	Y-NWT	Total Canada	% Total
Natural amissions 1	_1	_1	1	_1	_1	_1	_1	_1	_1	_1	_1	_1	_1
Racovary of variadium pantoxida and farrovariadium production	-	-	-	-	0.25	0.87	-	-	-	-	-	1.12	0.12
Production of steels containing variation	-	-	0.29	-	0.29	0,90	0.04	-	-	0.01	-	1.51	0.07
Iron ora pallatizing	2.15	-	-	-	1.67	1.93	-	-	-	-	-	5.75	0.28
Primary iron and steel production	-	-	7.93	-	0.18	1.54	=	-	-	0.05	-	9.70	0.47
Nonintegrated steel	4				• o.	17 🕶					-	0.17	0.01
Iron foundries	-				 0.	23					-	0.23	0.01
Primacy aluminum	-	-	-	-	0.60	-	-	-	-	0.01	-	0.61	0.03
Primary copper and nicket	-	-	-	-	0.82	1.73	1.44	-	-	-	-	3.99	0.19
Primary load and zinc	-	-	-	0.01	0.01	0.01	-	-	-	0.13	-	0.16	0.01
Coal combustion	0.01	0.03	1.64	1.08	3.52	5.35	1.74	5.56	10.46	0.15	-	29.54	1.42
Coal cleaning	_	-	0.01	-	-	-	-	-	0.01	0.03	-	0.05	n eg .
Matallurgical coke	-	-	_2	-	_2	0.15	-	_2	-	_2	-	0.18	0.01
Heavy fuel oil combustion	72.73	27.00	284.87	229.51	1269.43	43.86	1.28	0.99	1.00	13.01	0.21	1943.89	94.08
Patroleum coke combustion	-	0.62	6.71	6.23	47.99	0.42	-	0.09	0.06	1.16	-	63.28	3.0€
Degradation of road oils						. 95 🚤	_				-	0.95	0.05
Waste oil burning	•				O	. 34	-	-	-	-	-	0.34	0.02
Erosion of asphalt ¹	_1	_1	-1	_1	_1	_1	_1	_1	-1	-1	_1	_1	_1
Abrasives manufacture	-	-	-	-	1.55	0.44	-	-	-	-	-	1.99	0.10
Cament manufactura	-	-	-	-	0.15	0.21	0.05	-	0.08	0.07	-	0.56	0.00
Waste incineration	◄				 0	. 55 🔫						0.55	0.00
Miscellaneous sources	~				→ 0	.15 🔫					→	0.15	0.0
TOTAL ³	74.89	27.65	301.43	236.83	1326.46	57.41	4.55	6.64	11.61	14.62	0.21	2064.72	
% TOTAL	3.63	1.34	14.60	11,47	64.24	2.78	0.22	0.32	0.56	0.71	0.01		

¹ Unknown

 $^{^{2}\}mathrm{Emissions}$ from this province are aggregated into a "balance of Canada" value of $^{0.03}$ ton

³ Because emissions from some sectors are not broken down into provinces, the provincial totals are incomplete and do not sum to the Canada total shown.

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1 INTRODUCTION

1.1 Scope

The purpose of this report is to identify and quantify sources of atmospheric emissions of vanadium in Canada for the year 1972. Information contained in this report was obtained from scientific publications, from Canadian industry, and from discussions with individuals. The vanadium emissions determined from these data are the best approximations possible and provide an indication of the magnitude of the emission situation in Canada.

1.2 Occurrences of Vanadium

Vanadium occurs in many small deposits across Canada, as shown in Figure 1 (1). Of these, the major deposits are located at Quadra Island, British Columbia; Beaverlodge, Saskatchewan; Mine Centre and Mattawa, Ontario; and St. Georges, Newfoundland. Vanadium usually occurs in association with other minerals such as (1):

- titanium, iron, manganese, chromium;
- uranium, thorium;
- copper, (lead and zinc);
- bitumens (Athabasca tar sands); and
- phosphates

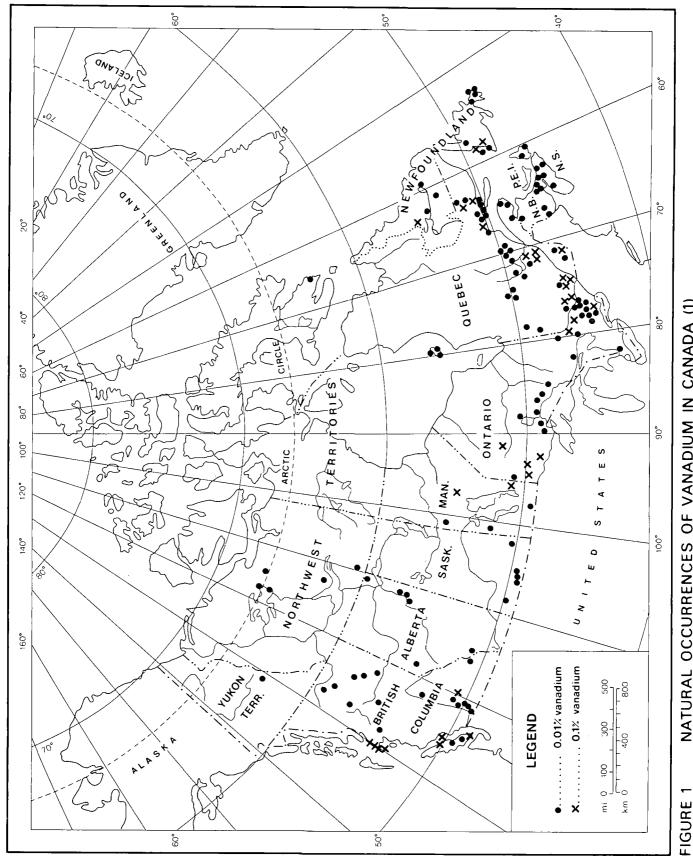
None of the Canadian deposits is rich enough to make recovery economical and vanadium used in Canada is imported, either as ferrovanadium or as vanadium-containing raw materials, or recovered as a by-product from other processes.

Internationally, major mineable deposits of vanadium exist in the southwestern United States, Finland, and South Africa, usually in association with titaniferous magnetites.

There are more than one hundred vanadium-bearing minerals in addition to those mentioned above, of which the principal mineable are: patronite, carnotite, uvanite, tyuyamunite, hewettite, roscoelite, uranyl potassium vanadate, mottramite, descloizite, pucherite, and sulvanite. Environmentally, the occurrence of vanadium in petroleum and coal is important because the combustion of these fuels constitutes the major source of vanadium emissions to the atmosphere. Vanadium has a strong affinity for carbonaceous materials, as exemplified by anomalous concentrations in black shales, asphalt, coal, tar sands and graphite.

1.3 Properties of Vanadium

Vanadium, atomic number 23, is found in Group V of the periodic table of elements, between phosphorus and arsenic. It is a soft, steel-grey, ductile, lustrous metal, with a melting point of 1919 °C (2), and is resistant to salt water corrosion.



NATURAL OCCURRENCES OF VANADIUM IN CANADA (1)

Vanadium comprises about 0.011% by weight of the earth's crust (3) and is the twenty-second element in order of abundance, with an average distribution of 150 parts per million. It is found in small deposits in scattered locations, in association with many minerals, principally uranium and titaniferous magnetite. Chemically, the most important compounds are vanadium pentoxide (V_2O_5) and ammonium metavanadate (NH_4VO_3) which are used as catalysts in the production of many industrial chemicals, and in the catalytic cracking of petroleum.

Some of the physical properties of vanadium are listed in Table 2.

TABLE 2 PHYSICAL PROPERTIES OF VANADIUM METAL (2)

Atomic number	23
Atomic weight	50.95
Reported isotopes	46, 47, 48, 49, 50, 51, 52, 53, 54
Crystal structure (to 1550 °C)	Body-centered cubic
Density	6.11 g/cc
Melting point	1919 ± 2 ℃
Boiling point	3000 ℃
Specific heat (20 ° - 100 °C)	0.120 cal/g
Latent heat of fusion	4 kcal/mole
Latent heat of vaporization	106 kcal/mole
Enthalpy	1.26 kcal/mole
Entropy	7.05 cal/mole/ °C
Thermal conductivity (100 °C)	0.074 cal/sq cm/ °C/cm
Electrical resistance (20 °C)	24.8 microhm-cm
Modulus of elasticity	18 - 19 X 10 ⁶ psi
Shear modulus	6.73 X 10 ⁶ psi
Poisson ratio	0.36

1.4 Uses of Vanadium

About 80% of all vanadium consumed in industrial applications is used in steel making, 8% in the production of nonferrous alloys, and 1% in the manufacture of iron castings. The balance, about 11%, is used in nonmetallurgical applications. These figures are based on 1968 United States vanadium consumption figures, outlined in Figure 2 (4). It is reasonable to assume that this also represents the Canadian situation in 1972.

Table 3 lists the different types of steels and other metals which contain vanadium as an alloying element.

TABLE 3 STEELS AND OTHER METALS CONTAINING VANADIUM (4-7)

	Vanadium	
•	Concentration	
Type	(%)	Properties/Uses
High strength, low alloy		
steels (HSLA)	0.10 - 0.25	Construction
Carbon steels containing		
vanadium	0.1 - 0.5	General quality improvement
High-speed and tool steels	1 – 4	Cutting
Cold work tool steels	0.2 - 0.3	Punches, chisels
Hot work tool steels	0.4 - 2.0	Forming, bending
Chromium/Manganese alloys	0.1 - 0:5	Heavy equipment, high impact
Stainless steels containing		
vanadium	0.3	Corrosion resistance
Cast iron containing vanadium	0.08 - 0.20	High impact resistance
Nonferrous alloys containing		
vanadium	2.5 – 85	Stabilizer with titanium, improves hot and cold workability

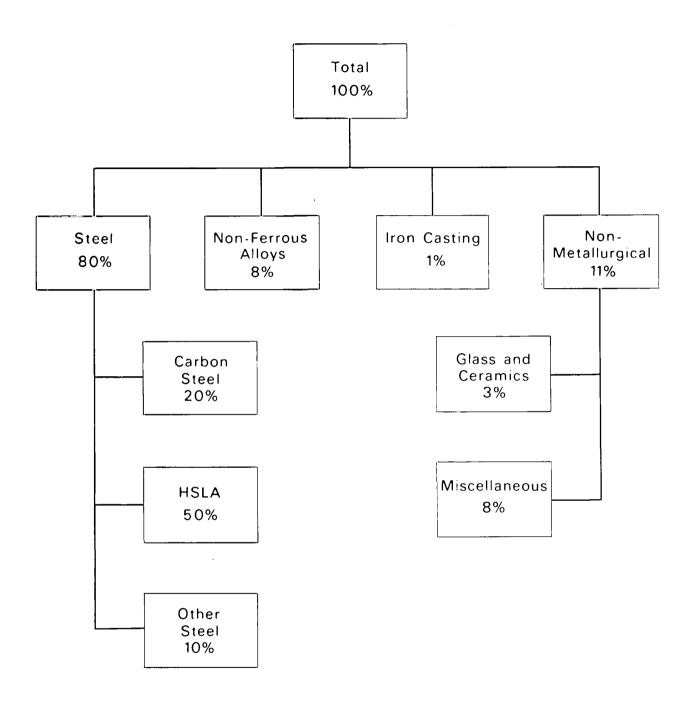


FIGURE 2 VANADIUM FLOW IN THE UNITED STATES, 1968: (4)

^{&#}x27;It is assumed that a similar situation prevailed in Canada in 1972.

In steel, vanadium is used to reduce and control the grain size, imparting toughness, greater tensile strength, better impact and wear resistance and hardness at elevated temperatures. The largest quantity of vanadium used is in the production of high-strength low-alloy steels (HSLA). These accounted for about 50% of the overall vanadium consumption in the United States in 1968 (Figure 2). These types of steels are estimated to account for about 55% of Canadian vanadium consumption in 1972 (8), reflecting the similar situation prevailing in both countries. In addition to the vanadium consumed for HSLA steel production, from 15%-20% is used in carbon steel production and 10% in the manufacture of specialty steels.

The manufacture of nonferrous alloys accounts for nearly 8% of total vanadium consumption. Vanadium improves the tensile strength and corrosion resistance of these materials at elevated temperatures. Vanadium is preferred over other metals because of its low melting temperature and density. In most cases the metal is alloyed with titanium or aluminum.

In the production of iron castings, vanadium is used to improve casting properties. This application accounts for about 1% of total vanadium consumption. Combined with chromium, molybdenum and nickel, it improves tensile strength, hardness and other high-temperature properties.

In the United States some vanadium is used as fuel cladding for liquid-metal cooled, fast-breeder nuclear reactors, because of its high creep strength and great resistance to neutron damage. No fast-breeder reactors are used in Canada and their implementation is unlikely in the near future (9).

Nonmetallurgical processes account for approximately 11% of total vanadium consumption. The glass and ceramics industry uses vanadium as a colourant or glaze (about 3% of overall consumption). Miscellaneous applications, accounting for about 8% of total vanadium consumption, include its use in the manufacture of catalysts for the production of sulphuric acid, phthalic and maleic anhydride, adipic acid, plastic, rubber and nylon. Vanadium is also used in the catalytic cracking of petroleum and in colour film processing to tone the green shades of silver bromide.

Other miscellaneous uses of vanadium include the production of insecticides, permanent magnets, drying agents in paints and varnishes, aerospace equipment, jet engines, aircraft frames and chemical process equipment as well as the removal of sulphur from coke oven gas, the killing of fermentation microbes and textile printing. Vanadium is also used in the treatment of wounds and anemia and for boosting appetite (4,5,10-12).

1.5 Vanadium Processing

In the United States, vanadium is obtained from domestic ore deposits using various processing methods. The most common is the roasting and leaching of vanadium-bearing uranium ores and refinement of the liquor to produce a product that is 90% vanadium pentoxide (13). Figure 3 is a flow diagram of this process.

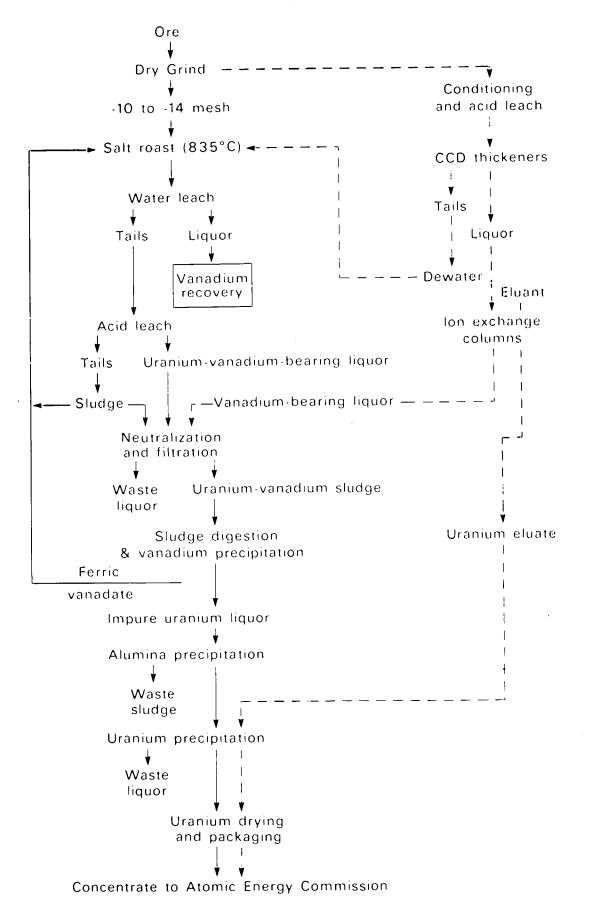


FIGURE 3 WATER-ACID LEACHING AND ION EXCHANGE PROCESS USED IN THE UNITED STATES FOR RECOVERY OF VANADIUM (13)

In Canada, in 1972, vanadium was recovered in the form of vanadium pentoxide at a plant operated by Masterloy Products Limited near Ottawa, Ontario. This plant processed petroleum residue fly ash from thermoelectric power stations and from sodium fluorovanadate, which is precipitated from the Aluminum Company of Canada, Limited's bauxite leaching circuit at its alumina plant in Arvida, Quebec. Difficulties encountered in obtaining raw material sources resulted in the shutdown of Masterloy's vanadium pentoxide recovery plant in June 1973. Vanadium du Quebec Limited, in St. Louis de Terrebonne, Quebec, also produced limited quantities of vanadium pentoxide in 1972. The company obtained vanadium from the by-products of other processes, such as heavy oil boiler fly-ash residue from Hydro-Quebec's Tracy power station.

The only plant in Canada that produced ferrovanadium in 1972 was the Masterloy plant. The ferrovanadium was produced by aluminothermic reduction of vanadium pentoxide. Although the vanadium pentoxide recovery unit ceased operations in 1973, Masterloy continues to process significant quantities of ferrovanadium using imported raw materials.

2 EMISSIONS

2.1 Natural Emissions

Natural vanadium emissions account for only a minor portion of the total emissions in urban areas (14). In rural areas, most of the vanadium enters the atmosphere from natural weathering. Under certain conditions, vanadium may also be leached and transported by water to be deposited in clay minerals (15).

It has been reported that approximately 10¹⁰ tons of the earth's crust is eroded yearly (16). Because Canada occupies about 6% of the world's land mass and the vanadium content of the earth's crust is 0.011% (3), the release of vanadium due to natural weathering can be estimated at 66 000 tons per year. Only a small fraction of this, which cannot be quantified, may eventually enter the atmosphere.

2.2 Emissions from the Processing of Vanadium

2.2.1 Recovery of Vanadium Pentoxide and Ferrovanadium Production. The plant operated by Vanadium du Quebec Limited used an uncontrolled propane-fired furnace in the recovery of vanadium pentoxide from heavy oil boiler fly-ash residues in 1972. Emissions of vanadium to the atmosphere from this source are estimated at 0.25 ton (17).

Masterloy Products, which recovered vanadium pentoxide from heavy oil fly-ash and from sodium fluorovanadate in the slag produced by Alcan at Arvida, produced an estimated 350 000 lb of ferrovanadium in 1972 (18). Because Canadian demand exceeded supply, it is reasonable to assume that 1972 operation at the Masterloy plant was close to capacity.

There are no emission factors for ferrovanadium production by an aluminothermic reduction process, as used by Masterloy. Emission factors for ferrovanadium production by electric furnaces do exist

but are not applicable (4). An estimated controlled emission factor of 40 lb particulate/ton product has been used. This factor includes an uncontrolled handling loss of 10 lb particulate/ton product and a potential process loss of 250 lb particulate/ton product controlled to about 88% (18).

The vanadium content of particulates emitted during the thermit reaction has been estimated at approximately 20% while that of particulates emitted as handling losses (almost exclusively vanadium pontoxide) should be about 39% (18). With the above assumptions, vanadium emissions from the Masterley plant in 1972 are estimated at 0.87 ton.

2.2.2 Production of Steels Containing Vanadium. The production of specialty steels containing vanadium is usually carried out in electric furnaces. Emissions generated during steel making consist of fume and dust emitted from the furnace during charging and refining.

The rate of particulate emissions from electric arc furnaces has been estimated at 14 lb/ton of steel with oxygen lancing (12). With an overall industry control efficiency estimated to be about 25% this results in a controlled emission factor of 10.5 lb particulate/ton of steel (12). Assuming that vanadium is present in particulate emissions in the same proportion that it is present in the melt, the controlled vanadium emission factor becomes 10.5 lb/ton of vanadium consumed.

The provincial consumption of ferrovanadium as an alloying material in carbon and alloy steels, and the average vanadium content of 71.9% in ferrovanadium were used to calculate emissions on a provincial basis, as listed in Table 4 (8, 19). Total emissions in 1972 are estimated at 1.51 tons.

2.3 Emissions from the Iron and Steel Industry

2.3.1 Iron Ore Pelletizing. The pelletizing process involves the formation of a 'green', unbaked pellet or ball which is then hardened by heating. It is an agglomerating process usually carried out in a traveling grate, shaft-furnace, or grate-kiln system.

Particulate emissions from this source are indicated to be 3.2 lb/ton of product (20). With the vanadium content of the ore at about 0.03% (4) and an overall industry control efficiency of 50% (12), a controlled vanadium emission factor of 0.48 lb/1000 tons of pellets produced can be calculated. Vanadium emissions from iron ore pelletizing are estimated at 5.75 tons in 1972, (Table 5).

2.3.2 Primary Iron and Steel Production. Potential vanadium emission sources in the production of iron include the blast furnace, the electric smelting furnace and the sintering process. In steel making, potential sources are the open hearth furnace, the basic oxygen furnace, the electric furnace and the scarfing operation.

The blast furnace process removes impurities present in iron ore. Coke and limestone are charged to the furnace along with the ore and large amounts of particulates are produced. Vanadium enters the blast furnace from two known sources - the ore and the coke. The Appalachian coal, from which most of the coke used in iron making in Canada is derived, contains about 21 ppm of vanadium (4). The uncontrolled vanadium emission factor is 30 lb/1000 tons of pig iron produced and is based

TABLE 4	VANADIUM EMISSIONS FROM	THE PRODUCTION OF	VANADIUM EMISSIONS FROM THE PRODUCTION OF STEELS CONTAINING VANADIUM, 1972	1972
Province	Ferrovanadium consumption (19) (tons)	Vanadium content of ferrovanadium (tons)	Controlled emission factor (lb V/ton V consumed)	Vanadium emissions (tons)
Nova Scotia	7.1	51.1	10.5	0.27
Quebec	92	54.6	10.5	0.29
Ontario	238	171.1	10.5	06.0
Manitoba	11	7.9	10.5	0.04
British Columbia	m	2.2	10.5	0.01
TOTAL	399	286.9	10.5	1.51

TABLE 5 VANADIUM EMISSIONS FROM IRON ORE PELLETIZING, 1972

Provinco	Pellet production (21) (tons)	Controlled emission factor (Ib V/1000 tons) of product	Vanadium emissions (tons)
Newfoundland	8 943 200	0 . 48	2.15
Quebec	6 930 560	0.48	1.67
Ontario	8 106 560	0 . 48	1.93
Total	23 980 320	0 . 48	5.75

on an estimated vanadium content of 0.03% in the iron ore (22). Considering the emission control levels for each blast furnace operation in Canada, it is estimated that 5.46 tons of vanadium were released in 1972 from this source. This includes emissions of 0.20 ton due to vanadium in the coke.

The electric smelting furnace was used only to a limited extent in Canada in 1972. Pig iron production was about 0.7 million tons (23). The uncontrolled emission factor used is 2.2 lb vanadium/1000 tons of pig iron produced and reflects the fact that uncontrolled particulate emissions from an electric smelting furnace are about 15 times less than those from a blast furnace. It is estimated that 0.20 ton of vanadium was emitted from this type of furnace in 1972.

Vanadium emissions from the sintering process are based on an uncontrolled particulate emission factor of 42 lb/ton of sinter (24), the vanadium content of the particulate being 0.03% (4). With a production of close to 1.3 million tons in 1972 (23) and considering the control equipment in use, vanadium emissions from the sintering process are estimated at 0.27 ton.

In the open hearth furnace, steel is made from a mixture of scrap and pig iron. Emissions of metal oxides are continuous and vary during the charging, meltdown, hot-metal addition, ore and lime boil, working and tapping cycles. The uncontrolled vanadium emission factor used is 10 lb/1000 tons of steel produced (22) and takes into account the fact that all open hearth furnaces in Canada are oxygen lanced. Based on a production level of about 4.6 million tons in 1972 (23) and applying appropriate control levels, the vanadium emissions from this source are estimated at 3.49 tons.

The charge to a basic oxygen furnace consists of steel scrap, pig iron and sometimes alloying materials. The uncontrolled variadium emissions resulting from the molten mass are indicated to be

9 lb/1000 tons of steel produced (22). With a production level of about 6.5 million tons of steel in 1972 (23) and considering the control equipment used, vanadium emissions are estimated at 0.28 ton from this source.

Emissions from electric steel-making furnaces result from charging, refining, and pouring of the molten mass. Less than 0.1 million tons of steel was produced in electric arc furnaces by primary manufacturers in Canada in 1972 (23). The uncontrolled particulate emission factor for this type of furnace is 11 lb/ton of steel produced (24). The vanadium content of the particulates emitted is unknown but is estimated at 0.003% (4). With these base data, and considering the control equipment used, vanadium emissions from this source have been estimated at less than 0.01 ton in 1972.

The scarfing operation involves the removal of the oxide layer produced at the surface of the steel product. The uncontrolled vanadium emission factor used is 0.03 lb/1000 tons of steel scarfed and is based on a particulate emission factor of about 1 lb/ton (24) and a vanadium content of the particulate of 0.003% (4). The amount of steel scarfed in 1972 was close to 2.8 million tons (23) and resulted in vanadium emissions estimated at less than 0.01 ton.

Vanadium emissions from the production of primary iron and steel in Canada in 1972 totalled 9.7 tons and are summarized in Table 6.

- 2.3.3 Nonintegrated Steel Mills*. Steel produced in electric furnaces at nonintegrated steel mills amounted to about 2 million tons in 1972. With an uncontrolled particulate emission factor of 11 lb/ton of steel produced (24) and a vanadium content of the particulate emissions of about 0.003% (4) the uncontrolled vanadium emissions are estimated at 0.33 ton. The overall control for these furnaces in Canada in 1972 was about 50% (12), bringing emissions from this source to about 0.17 ton.
- 2.3.4 Iron Foundries. Approximately 1 million tons of cast iron were produced by iron foundries in Canada in 1972. The vanadium present in emissions from iron foundries comes mainly from the original iron ore and from the vanadium used as an alloying element to counteract graphitization. The uncontrolled vanadium emission factor for cast iron production is 0.2 lb/1000 tons of charge (22) and the overall control level is estimated at 25% (12). Based on this information, and on the fact that it takes about 3 tons of charge material to produce 1 ton of cast iron, vanadium emissions from iron foundries in 1972 are estimated at 0.23 ton.

2.4 Emissions from Primary Nonferrous Metals Smelting

2.4.1 Primary Aluminum. The production of aluminum is a two-step process. First, bauxite ore is ground, purified and calcined to produce alumina. Then the alumina is electrically smelted to produce aluminum.

Vanadium emissions from aluminum smelting were investigated because vanadium is found in bauxite and was recovered in 1972 from the sodium fluorovanadate fraction of the ore plant liquor of the Aluminum Company of Canada's smelter at Arvida, Quebec. Vanadium is also found in the petroleum coke used in the manufacture of smelting electrodes.

*Not including nonintegrated primary producers, such as Quebec Iron and Titanium in Quebec and Cominco in British Columbia, which are covered in section 2.3.2.

VANADIUM EMISSIONS FROM PRIMARY IRON AND STEEL PRODUCTION, 1972

TABLE 6

	Iron			Steel	·			
		Blast	Electric	Open hearth	Basic oxygen	Electric		
	Sintering	furnace	furnace	furnace	furnace	furnace*	Scarling	
	Production (23)(tons)	(tons)		Production (23)(tons)	(tons)			
	1 292 491	8 686 078	692 200	4 621 378	6 434 904	72 715	2 777 405	
Province	Emissions (tons)							Total
Nova Scotia	ı	4.52	1	3.41	-	<0.01	<0.01	7.93
Quebec	1	ı	0.18	ı	i	ı	ı	0.18
Ontario	0.25	0.94	ı	0.08	0.27	<0.01	<0.01	1.54
British Columbia	0.02		0.02	1	0.01	ı	<0.01	0.05
TOTAL	0.27	5.46	0.20	3.49	0.28	<0.01	<0.01	9.70

*Only electric arc furnaces at primary iron and steel producers.

In Canada's only alumina-producing plant, at Arvida, a small amount of vanadium enters the alumina while the majority remains with the impurities and eventually finds its way to the sedimentation basin. None is emitted to the air from the alumina-production step (12).

In the smelting of alumina, using carbon electrodes, an unknown but small quantity of vanadium may be released from both the alumina and the electrodes. However, due to the relatively low reaction temperature, the vanadium that might be released remains in the aluminum metal and in the slag (12).

Carbon electrodes (anodes) are produced at three of the aluminum smelters in Canada. Petroleum coke is first calcined, then crushed and dried during the process. Vanadium emissions resulting from the manufacture of carbon electrodes at primary aluminum smelters in Canada in 1972 are estimated at 0.61 ton (Table 7). This result is based on the vanadium content of petroleum coke (Table 16), on the quantity of petroleum coke calcined, and on the associated process particulate emissions (23).

- **2.4.2 Primary Copper and Nickel.** Stack test results at one of Canada's leading copper and nickel smelters indicate that vanadium is emitted at rates varying from 0 0.22 lb/hr (25). Based on the total particulate emissions from this source, an average vanadium content in the particulates of 56.5 ppm is obtained. This latter concentration was utilized to estimate vanadium emissions at each primary copper and nickel smelter. Vanadium emissions from this source totalled 3.99 tons in 1972, (Table 8).
- 2.4.3 Primary Lead and Zinc. The vanadium content of the ores used and of the particulate emissions from primary lead and zinc smelters is unknown. Although they are expected to differ from those estimated for primary copper and nickel smelters, the same figures have been used. Based on this assumption, vanadium emissions from primary lead and zinc smelters in Canada in 1972 are estimated at 0.16 ton, (Table 9).

2.5 Emissions from Coal Use

To estimate the vanadium emissions resulting from the use of coal, either from combustion, cleaning, or metallurgical coke production, it is first necessary to know the vanadium concentration of coal and of coal ash as well as the quantity of each type of coal used in Canada. The vanadium content of coal and coal ash used in Canada, as determined from an extensive literature search, is summarized in Table 10.

Consumption per province of each type of coal (34) and the vanadium content of the resulting ash (Table 10) were used to estimate provincial averages for the vanadium concentrations of coal ash. This method was used for all sectors except power generation, where more complete information was available on the source of the coal used (35,36). Results are listed in Table 11.

2.5.1 Coal Combustion. Estimates of vanadium emissions from various industrial sectors resulting from the combustion of coal were based on coal consumption by these sectors (34-36), on the resulting particulate emissions (23) and on the vanadium content of these emissions (Table 11). Total vanadium emissions from the combustion of coal in Canada in 1972 are estimated at 29.54 tons (Table 12).

Vanadium emissions VANADIUM EMISSIONS FROM THE CALCINING OF PETROLEUM COKE AT PRIMARY ALUMINUM SMELTERS, 1972 (tons) 0.60 0.01 0.61 of petroleum coke* Vanadium content (mdd) 35 670 emissions (23) Particulate 891 265 1156 (tons) Petroleum coke calcined (23) 342 700 101 755 444 455 (tons) British Columbia TABLE 7 Province Quebec TOTAL

*From Table 16

TABLE 8 VANADIUM EMISSIONS FROM PRIMARY COPPER AND NICKEL SMELTING, 1972

Province	Particulate emissions (23) (tons)	Vanadium content (ppm)	Vanadium emissions (tons)
Quebec	14 550	56.5	0.82
Ontario	30 640	56.5	1.73
Manitoba	25 430	56.5	1 . 44
	·		
TOTAL	70 620	56.5	3.99

TABLE 9 VANADIUM EMISSIONS FROM PRIMARY LEAD AND ZINC SMELTING, 1972

Province	Particulate emissions (23) (tons)	Vanadium content (ppm)	Vanadium emissions (tons)
New Brunswick	180	56.5	0.01
Quebec	160	56.5	0.01
Ontario	100	56.5	0.01
Manitoba*	-	-	-
British Columbia	2 350	56.5	0.13
		· · · · · · · · · · · · · · · · · · ·	
TOTAL	2 790	56.5	0.16

^{*}Included in section 2.4.2

TABLE 10	VANADIUM (CONTENT OF C	OAL AND CO	AL ASH (1	5, 26-33)
		Vanadium	in coal		Vanadium in ash
Coal type		(ppm)			(ppm)
Domestic					
Bituminous		14			120
Sub-bituminous		8.8			125
Lignite		8.8			125
Foreign					
Bituminous		21			250
Anthracite		125			1100
TABLE 11	PROVINCIAL	AVERAGES FO	R VANADIUM	CONTENT	OF COAL ASH
		Average* vanad	dium content	(ppm)	
		Power	Ot	her	All
Province		generation	so	urces	sources

	Average" vanadiui	m content (ppm)	
Province	Power generation	Other sources	All
Newfoundland	_	_	133
Prince Edward Island	-	-	120
Nova Scotia	120	143	-
New Brunswick	-	-	120
Quebec	_	-	591
Ontario	250	258	-
Manitoba	125	127	
Saskatchewan	125	125	_
Alberta	125	122	-
British Columbia	-	-	120

^{*}Weighted average

- **2.5.2 Coal Cleaning.** For a more combustible product, coal is sometimes cleaned to remove some of the unburnable portions. This practice was used in three provinces in 1972. Based on the assumption that the vanadium concentration in the particulate emissions is the same as that of the original coal, the vanadium emissions from coal cleaning are estimated at 0.05 ton for Canada in 1972. Results are given in Table 13.
- 2.5.3 Metallurgical Coke Production. Vanadium emissions from the production of metallurgical coke are based on the particulate emissions from coking plants (37) and on the vanadium content of the coke produced. These concentrations were derived from the vanadium content of coal (Table 10); it takes about 1.4 tons of coal to produce 1 ton of coke. It was assumed that all vanadium present in coal is also found in coke.

It was also assumed that the coking coal used in Ontario originated in the United States while British Columbia's was domestic bituminous (16). Because coke produced in Quebec and Saskatchewan accounts for only 6% of the total coke produced in Canada (23) it was also assumed that all of Quebec's coal was United States bituminous and all of Saskatchewan's was domestic (lignite). For Nova Scotia, it had already been established that 17% of the coal used was United States bituminous and that the remaining 83% was domestic bituminous (38).

Based on the above assumptions, the total variadium emissions resulting from the production of metallurgical coke in Canada in 1972 are estimated at 0.18 ton (Table 14).

2.6 Emissions from Petroleum Use

When crude oil is refined, virtually all the vanadium content is concentrated in the heavy ends, that is, heavy fuel oil, asphalt, and petroleum coke. Table 15 gives an estimate of the vanadium content of petroleum derivatives, found in Canada, for crude oil received by refineries from either South America (Columbia, Trinidad, Venezuela), the Middle East (Iran, Iraq, Kuwait, Libya, Saudi Arabia), Western Canada or 'other' sources. The vanadium content for the sources classified as 'other' is not determined but has been estimated at about 50 ppm. This assumption should not create a large error because "other sources" account for less than 7% of the total crude consumption in Canada. For the other major crude oil sources vanadium content was found through an extensive literature search.

Table 16 gives the average vanadium content of heavy petroleum products, on a provincial basis. This was determined from information in Table 15 and from the quantities of crude received by refineries in each province from each world source (49). This method assumes that the distribution by world source of crude received by refineries in a province determines the distribution (and therefore the vanadium content) of refined petroleum products consumed in that province in 1972.

2.6.1 Heavy Fuel Oil Combustion. It is estimated that 90% of the vanadium originally present in heavy fuel is emitted as airborne particulates upon combustion (50). The remainder is deposited on the boiler tubes and causes severe corrosion (51). Table 17 gives vanadium emissions, on a provincial

TABLE 12 VANADIUM EMISSIONS FROM COAL COMBUSTION, 1972 (TONS)

	Sector			
Province	Retail	Power generation	Other industrial	Total
Newfoundland	<0.01	_	0.01	0.01
Prince Edward Island	<0.01	-	0.03	0.03
Nova Scotia	0.15	1.38	0.11	1.64
New Brunswick	0.01	1.01	0.06	1.08
Quebec	0.02	-	3.50	3.52
Ontario	0.25	1.72	3.38	5.35
Manitoba	0.05	1.29	0.40	1.74
Saskatchewan	0.02	5.35	0.19	5.56
Alberta	0.34	10.05	0.07	10.46
British Columbia	0.02	-	0.13	0.15
Yukon/N.W.T.	-	-	-	-
				
TOTAL	0.86	20.80	7.88	29.54

basis, resulting from heavy oil combustion in various sectors. These estimates are based on the quantities of fuel oil consumed (35, 36, 52), on the vanadium content of this fuel (Table 16), on the assumption that no emission control equipment exists and on the above estimate that 90% of the vanadium present will be emitted. Vanadium emissions from the combustion of heavy fuel oil are therefore estimated at 1940 tons in Canada in 1972.

2.6.2 Petroleum Coke Combustion. Petroleum coke is used in the iron and steel industry, in melting and refining operations, in abrasives manufacture, and in the chemical industry (53). The balance of petroleum coke produced, which is used as a fuel, was tentatively quantified provincially by the national ratio of petroleum coke burned to total disposition (49). The vanadium emissions were derived using the vanadium content of petroleum coke (Table 16), assuming no control and total emission of contained

TABLE 13 VANADIUM EMISSIONS FROM COAL CLEANING, 1972

Province	Particulate emissions (tons) (23)	Vanadium content of coal* (ppm)	Vanadium emissions (tons)
Nova Scotia	389	14	0.01
Alberta	1216	8.8	0.01
British Columbia	1962	14	0.03
TOTAL	3567		0.05

^{*}From Table 10.

TABLE 14 VANADIUM EMISSIONS FROM METALLURGICAL COKE PRODUCTION, 1972

			
	Particulate emissions (37)	Vanadium content of coke	Vanadium emissions
Province	(tons)	(ppm)	(tons)
Ontario	7023	30	0.15
Balance of Canada	1840	12.5–30	0.03
			
TOTAL	8863		0.18

vanadium. Based on these assumptions vanadium emissions resulting from petroleum coke combustion in Canada in 1972 are estimated at 63 tons (Table 18).

2.6.3 Degradation of Road Oils. The potential collection of used lubricating oil in Canada is about80 million gallons annually (54). Assuming that 10% of this total was blended for use as fuel (55), and

TABLE 15 VANADIUM CONTENT OF PETROLEUM DERIVATIVES (1, 4, 6, 8, 10, 16, 18, 26, 29, 30, 39-48)

	World source			
Petroleum type	Western Canada (ppm)	South America (ppm)	Middle East (ppm)	Other (ppm)
Crude oil	10 (Tar sands: 150) bitumen	300	50	50
Heavy oil	10	300	60	50
Petroleum coke	35	1 000	215	175
Asphalt	500	15 000	500	500

that about 8 million gallons were rerefined, then about 64 million gallons were deposited on roads for dust control. It has also been indicated that 70%-75% of the deposited oil leaves the road through dust transportation and runoff (54) and it is estimated that half of this, or about 35% of the total deposited, becomes airborne particulates.

Vanadium emissions, based on the above assumptions and using a waste oil density of 8.5 lb/gal and a vanadium content of 10 ppm (54), are estimated at 0.95 ton from the degradation of road oils in Canada in 1972.

- 2.6.4 Waste Oil Burning. Based on the sales of lubricating oil in Canada in 1972, it has been estimated that 80 million gallons of lubricating oil are produced annually (55). Assuming that 10% of this total is disposed of by burning, and that the vanadium content of this oil is 10 ppm (54), and using a waste oil density of 8.5 lb/gal, it is estimated that total vanadium emissions from this source reached 0.34 ton. No provincial breakdown was made but burning of waste oil is not permitted in the provinces of Manitoba, Saskatchewan, Alberta and British Columbia.
- **2.6.5 Erosion of Asphalt.** About 13 million barrels of asphalt were used in Canada in 1972 in the paving of roadways (52). It is thought that no vanadium will escape to the atmosphere from evaporation or weathering of asphalt (39, 56); however, there are likely to be significant emissions from the erosion of pavement by automobile tires. Emission factors are not available. The amount of vanadium

PROVINCIAL AVERAGES FOR VANADIUM CONTENT OF HEAVY PETROLEUM FRACTIONS

TABLE 16

	Refinery crude	Refinery crude receipt (49) from:	:wo		Weighted ave	Weighted average vanadium content*	lent*
	Western	South	Middle		Heavy	Petroleum	
Province/Territory	Canada (%)	America (%)	East (%)	Other (%)	lio (mdd)	coke (ppm)	Asphalt (ppm)
Newfoundland	1	34.1	49.0	16.9	140	475	5445
Prince Edward Island	1	34.1	49.0	16.9	140	475	5445
Nova Scotia	1.	34.1	49.0	16.9	140	475	5445
New Brunswick	ı	34 . 1	49.0	16.9	140	475	5445
Quebec	ı	59.3	18.1	22.6	200	029	9100
Ontario	99.1	0.3	ı	9.0	11	36	545
Manitoba	100	I	ł	ſ	10	35	200
Saskatchewan	100	1	į	ſ	10	35	200
Alberta	100	ı	1	ſ	10	35	200
British Columbia	100	ı	ı	I	10	35	200
Yukon/N . W . T .	100	ı	1	l	10	35	200

*From information given in Table 15.

VANADIUM EMISSIONS FROM HEAVY FUEL OIL COMBUSTION, 1972 TABLE 17

	Sector				
Province	Residential	Commerical	Industrial	Power	Total
Newfoundland	99.0	17.32	43.89	10.86	72
Prince Edward Island	0.16	8.21	3.41	15.22	27
Nova Scotia	1.12	146.58	43.86	93.31	284
New Brunswick	0.91	100.84	42.60	85.16	229
Quebec	53.58	464.10	742.33	9.42	1269
Ontario	1.42	19.27	23.17	I	43
Manitoba	ı	0.42	98.0	ı	-
Saskatchewan	1	0.18	0.70	0.11	0
Alberta	ı	0.43	0.50	0.07	-
British Columbia	0.49	2.72	9.36	0.44	13
Yukon/N.W.T.	1	60.0	I	0.12	0
TOTAL	58.34	760 . 16	910.68	214.71	1943

VANADIUM EMISSIONS FROM PETROLEUM COKE COMBUSTION, 1972 TABLE 18

	Quantity of petroleum coke burned (49)	ma	Vanadium content	Vanadium
Province/Territory	Barrels	Tons	(mdd)	(tons)
Newfoundland	ļ I	I	ı	1
Prince Edward Island	6 201	1 302	475	0.62
Nova Scotia	67 259	14 124	475	6.71
New Brunswick	62 489	13 123	475	6.23
Quebec	341 063	71 623	029	47.99
Ontario	51 038	10 718	39	0.42
Manitoba	ı	I	ı	ı
Saskatchewan	12 299	2 583	35	60.0
Alberta	8 734	1 834	35	90.0
British Columbia	157 208	33 014	35	1.16
Yukon/N.W.T.	I	1	ı	1 .
TOTAL	706 291	148 321		63.28

*From Table 16

contained in asphalt used in 1972 is estimated at 6000 tons, although vanadium contained in previous paving could substantially increase this total.

2.7 Emissions from Other Sources

2.7.1 Abrasives Manufacture. Vanadium is present in the petroleum coke used in the manufacture of silicon carbido abrasives. Consumption of petroleum coke for this purpose was 136 225 tons in 1972 (57). Based on the estimated production of abrasives in 1972 (23), the national consumption of petroleum coke was prorated 17% to Quebec and 83% to Ontario (the only provinces producing silicon carbido).

Because the reaction temperature necessary to produce silicon carbide is above 1827 °C (58) and near the boiling point of vanadium pentoxide (2054 °C), it is assumed that some vanadium is released in this process. It has been estimated that 10% of the vanadium contained in the petroleum coke will be released, resulting in an uncontrolled emission factor of 200 lb vanadium/ton of vanadium content. Uncontrolled emissions of vanadium from the manufacture of abrasives in Canada in 1972 are estimated at 1.99 tons (Table 19).

TABLE 19 VANADIUM EMISSIONS FROM ABRASIVES MANUFACTURE, 1972

Province	Petroleum coke consumption (23) (tons)	Vanadium content* (ppm)	Contained vanadium (tons)	Emission factor (lb/ton)	Vanadium emissions (tons)
Quebec	23 158	670	15.52	200	1 . 55
Ontario	113 067	39	4.41	200	0.44
					
TOTAL	136 225		19.93		1.99

^{*}From Table 16

2.7.2 Cement Manufacture. Vanadium emissions from cement plants are due to the presence of vanadium as an impurity in one of the chemicals used in cement production. In the dry process, used at some cement plants, vanadium emissions have been reported to be below the detection limit of analytical techniques (22); however, vanadium has been detected in the emissions of cement plants using the wet process (22). Based on the above, vanadium emissions from plants operating with the dry process are assumed to be negligible.

The production estimates from wet-process cement plants and the breakdown of resulting vanadium emissions for 1972 (0.56 ton) are listed in Table 20.

- 2.7.3 Waste Incineration. Incineration of waste material containing vanadium is another source of emissions for this trace metal. Limited information provides for an uncontrolled emission factor of 0.001 lb of vanadium/ton of waste burned (22). Based on 2.5 million tons of solid waste burned in Canada in 1972 in municipal, pit and apartment incinerators (23) and assuming that emissions are controlled at a level of about 55%, vanadium emissions from this source are estimated at 0.55 ton.
- 2.7.4 Miscellaneous Sources. Vanadium is used for the production of a yellow stain used in colouring pottery and glass. It has been estimated that only 2 tons of vanadium were used for this purpose in the United States in 1968 (4). On this basis, it was assumed that Canadian consumption in 1972 was minor and that the resulting vanadium emissions were negligible.

In the manufacture of paint and varnish, the chemicals and metals used as colourants and drying agents may contain minor quantities of vanadium compounds. Potential emissions from this source are assumed to be negligible.

Vanadium is also used in colour film processing, and in the production of catalysts, nonferrous alloys, magnetic alloys and pharmaceuticals. Based on 1968 consumption figures for the United States (4), it is estimated that miscellaneous uses of vanadium in Canada in 1972 accounted for 8% of the total consumption, or 30 tons. With an emission factor of 10 lb vanadium/ton of vanadium processed (4), it is estimated that 0.15 ton of vanadium was emitted from miscellaneous sources in Canada in 1972.

TABLE 20 VANADIUM EMISSIONS FROM WET-PROCESS CEMENT PLANTS, 1972

Province	Wet capacity/total capacity (59) (%)	Total production (59) (tons)	Estimated wet production (59) (tons)	Controlled vanadium emissions factor* (22) (1b/ton product)	Vanadium emissions (tons)
Quebec	53.1	3 214 000	1 706 635	1.742 × 10 ⁻⁴	0.15
Ontario	65.5	3 743 000	2 451 665	1.742 × 10 ⁻⁴	0.21
Manitoba	100.0	550 000	550 000	1.742 × 10 ⁻⁴	0.05
Alberta	100.0	938 000	938 000	1.742 x 10 ⁻⁴	0.08
British Columbia	86.1	885 000	761 985	1.742 X 10 ⁻⁴	0.07
TOTAL	68.7	9 330 000	6 408 285	1.742 x 10 ⁻⁴	0.56

*With electrostatic precipitator on kiln and clinker cooler, and baghouse on finishing mill.

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