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Vanadium Recycling for Fusion Reactors

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ABSTRACT

Very stringent purity specifications must be applied to low activation vanadium alloys, in order to meet recycling goals requiring low residual dose rates after 50-100 years. Methods of vanadium production and purification which might meet these limits are described. Following a suitable cooling period after their use, the vanadium alloy components can be melted in a controlled atmosphere to remove volatile radioisotopes. The aim of the melting and decontamination process will be the achievement of dose rates low enough for "hands-on" refabrication of new reactor components from the reclaimed metal. The processes required to permit hands-on recycling appear to be technically feasible, and demonstration experiments are recommended. Background information relevant to the use of vanadium alloys in fusion reactors, including health hazards, resources, and economics, is provided.

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INTRODUCTION

Safety and environmental concerns for fusion reactors include routine emissions, dose rates in working areas, decay heat, fires, mobilization of radioisotopes, offsite doses from accidents, and recycling or disposal of irradiated materials. Here we will be concerned only with the potential for recycling of vanadium alloys. Low-activation vanadium alloys, with selected alloying elements, such as Cr, can have low residual long-term radioactivity, which will permit their recycling, provided that impurity levels are kept very low.

The Rationale for Recycling Vanadium Alloys

At the end of their useful life in a reactor, structural materials, which will have become activated during service, may either be recycled following a suitable period of cooling, or consigned to permanent disposal. The choice between these options will be based on their relative overall costs, taking into account some additional factors, such as the public perception of radioactive waste disposal versus recycling of radioactive materials.

For low level radioactive waste (LLW) to qualify as "Class C" (near-surface disposal) under Rule 10CFR61 in the USA,¹ the calculated dose rate to an "intruder" up to 500 years in the future should be less than 5 mSv/y. However, the specific activity limits (SAL) in 10CFR61 for very long-lived radionuclides are not conservative in today's climate, and conservative SAL could require impurity levels too low to be practically obtainable. In any case, future laws may prohibit near-surface disposal of nuclides which do not decay to benign levels within 100 years. Although current LLW disposal costs at the US Ecology site (Hanford) are 2500 \$/m³, future costs could reach 35,000 \$/m³. Furthermore, the vanadium alloy is quite expensive to replace. Therefore, *recycling* is more desirable than shallow land disposal as a goal for fusion reactor materials.²

The concept of fusion as a long-term, sustainable energy source should be applied to structural materials as well as to the fusion fuel materials. In particular, the ability to recycle structural materials would have clear advantages with respect to the consumption of materials relative to a given energy output and the minimization of radioactive wastes requiring long term isolation. Vanadium-based materials potentially appear to be strong candidates for recycling for the following reasons.

- (1) Vanadium and, to a greater or lesser extent, its neighboring elements in the periodic table, exhibit relatively weak capture reactions with fusion neutrons and give rise to few long-lived activation products.
- (2) The activation products are more volatile than the alloy constituents and so should be readily removable in a high-vacuum remelting operation that would form the first step in any reclamation process. The waste products of such a decontamination process would have a much smaller volume than that of the reclaimed material, thus reducing substantially the volume of waste requiring geological disposal and the attendant costs of this kind of disposal route.

(3) Vanadium is widely distributed in nature. It is, however, expensive (~ 220 \$/kg) in the finished metal form since its concentration at the ore stage, purification, and high temperature forming in a protective atmosphere are costly operations. The intrinsic value of the end-of-service structural material is therefore an important factor favoring its recovery for reuse in future reactors.

(4) In order to satisfy half the current electricity demand of 500 GW_e in the USA, about 250 fusion reactors of capacity 1000 MW_e could be needed. If each reactor contained 400 t of vanadium then at least 100 kt of vanadium could be committed to the fusion system, a substantial fraction of the US 185 kt vanadium reserves. An additional 2400 kt "reserve base" might be recovered at higher cost, and "resources" of 30 Mt are estimated as being available (Appendix A), though possibly difficult to recover. Recycling of vanadium components would therefore significantly extend native sources of vanadium.

(5) With the growing emphasis on recycling programs, the feasibility of recycling fusion reactor structural materials could help fusion power earn public acceptance.

Vanadium Alloys as Structural Materials

Vanadium alloys potentially allow operation at temperatures about 150 °C higher than with steels. They are compatible with lithium up to about 700°C,³ and they have lower residual activity than iron-based alloys.

Advantages of vanadium alloys for fusion reactors include :

- high melting temperature
- low thermal stress factor
- good high-temperature properties (creep, fatigue)
- high ductility
- radiation swelling resistance
- low transmutation rates (He and H)
- low nuclear heating and afterheat
- low long-term activation
- compatibility with liquid metals

Some key issues affecting vanadium alloy use are:

- detrimental pickup of non-metallic elements during normal use, especially with He and H₂O coolants
- oxidation during accidents (including reactions with H, C, N, and O)
- irradiation embrittlement
- upward shift of DBTT and lowering of upper shelf energy with irradiation embrittlement
- swelling^{4,5}
- high tritium permeation rate, with implications for tritium inventory and release.

This report will discuss methods of vanadium production, the radiological requirements for vanadium recycling, vanadium purification, recycling scenarios, and the salient issues which must be resolved.

VANADIUM PRODUCTION

The steps of vanadium alloy production, use, and recycling in fusion reactors are illustrated in Figure 1. Vanadium occurs in iron ores, in crude oils, in lead ores (as vanadinite), and in other ores. There are several processes for production of vanadium metal from ores, dusts, and ashes.^{6,7} The process illustrated in Figure 2 is typical.

First, the vanadium-containing minerals (ore, ash, or dust) are roasted with 10% sodium chloride (or sodium carbonate) at 850°C, producing sodium metavanadate (NaVO₃). After leaching the metavanadate with hot water, sulfuric acid (or hydrochloric acid) is added. The precipitate is dried and baked at 950°C, producing commercially-pure vanadium pentoxide (V₂O₅). Vanadium metal is produced by reduction of the pentoxide using a highly exothermic reaction with aluminum:

Excess aluminum is required, and some aluminum impurity remains in the vanadium metal. Vanadium has also been produced by reduction of oxides or chlorides using C, Ca, Na, Mg, and H₂. The aluminum impurity may be removed by electron beam refining, yielding > 99% pure vanadium metal. The reduction of hardness after refining serves as a simple measure of the vanadium purity.

Figure 1. Vanadium production, use, and recycle.

Figure 2. A typical sequence for production of vanadium metal.

ACTIVATION OF VANADIUM ALLOYS

Current developmental alloys for fusion reactors contain Cr, Ti and Si as alloying additions. The radionuclide inventories of vanadium alloys following irradiation in a fusion power reactor have been predicted using the FISPACT code⁸ and also as part of the ARIES II design study (not yet published). The compositions V-15Cr-5Ti and V-3Ti-1Si can be regarded as models for present purposes. The activities and γ dose rates of *first walls* comprised of these two materials and exposed to a neutron flux of 4.15 MW/m² for 2.5 y are shown in Figures 3-6 as functions of cooling time. Analogous results for materials irradiated in the *blanket zone* for the same first wall flux are shown in Figures 7-10. The specific activity and dose rate contributions for the principal radionuclides are given in Table 1.

* Pure V-15Cr-5Ti in FW of EEF at 4.15MW/m² *

Figure 3. Specific activity of a V-15Cr-5Ti first wall exposed to a neutron flux of 4.15 MW/m² for 2.5 y vs. time after irradiation.

* Pure V-3Ti-1Si in FW of EEF at 4.15MW/m² *

Figure 4. Specific activity of a V-3Ti-1Si first wall exposed to a neutron flux of 4.15 MW/m² for 2.5 y vs. time after irradiation.

Figure 5. Surface gamma dose rate from a V-15Cr-5Ti first wall exposed to a neutron flux of 4.15 MW/m² for 2.5 y vs. time after irradiation.

Figure 6. Surface gamma dose rate of a V-3Ti-1Si first wall exposed to a neutron flux of 4.15 MW/m² for 2.5 y vs. time after irradiation.

Figure 7. Specific activity of V-15Cr-5Ti blanket structure behind first wall exposed to a neutron flux 4.15 MW/m² for 2.5 y vs. time after irradiation.

Figure 8. Specific activity of a V-3Ti-1Si blanket structure behind a first wall exposed to a neutron flux of 4.15 MW/m² for 2.5 y vs. time after irradiation.

Figure 9. Surface gamma dose rate of a V-15Cr-5Ti blanket structure behind a first wall exposed to a neutron flux of 4.15 MW/m² for 2.5 y vs. time after irradiation.

Figure 10. Surface gamma dose rate of a V-3Ti-1Si blanket structure behind a first wall exposed to a neutron flux of 4.15 MW/m² for 2.5 y vs. time after irradiation.

Table 1. Specific activity and dose rate contributions for the principal radionuclides.

Alloy and Zone	Post Irradiation Time 10 Yr				Post Irradiation Time 50 Yr				Post Irradiation Time 100 Yr			
	Nuclide	Activity Bq/kg	Nuclide	DoseRate Sv.h ⁻¹	Nuclide	Activity Bq/kg	Nuclide	DoseRate Sv.h ⁻¹	Nuclide	Activity Bq/kg	Nuclide	DoseRate Sv.h ⁻¹
V-15Cr-5Ti FW	³ H	1.60E11	⁴² K	9.74E-4	³ H	1.69E10	⁴² K	4.20E-4	³ H	1.02E9	⁴² K	1.47E-4
	⁴³ V	8.10E9	⁵⁴ Mn	5.38E-4	⁴² Ar	4.70E6	⁴⁴ Sc	4.36E-7	⁴² Ar	1.64E6	⁴⁴ Sc	2.09E-7
	⁴² K	1.09E7	⁴⁴ Sc	7.85E-7	⁴² K	4.70E6	⁴⁴ Ti	1.01E-11	⁴² K	1.64E6	⁵⁰ V	5.30E-12
	⁴² Ar	1.09E7	⁶⁰ Co	6.63E-10	³⁹ Ar	2.23E5	⁵⁰ V	5.30E-12	³⁰ Ar	1.96E5	⁴⁴ Ti	4.86E-12
	⁵⁵ Fe	3.76E6	⁴⁶ Sc	2.49E-10	⁴⁴ Sc	8.25E2	⁶⁰ Co	3.43E-12	⁴⁴ Sc	3.96E2	⁴⁰ K	1.09E-13
	⁵⁴ Mn	2.45E6	⁴⁴ Ti	1.82E-11	⁴⁴ Ti	8.25E2	⁴⁰ K	1.09E-13	⁴⁴ Ti	3.96E2	³⁶ Cl	4.59E-18
	⁴⁵ Ca	6.81E5	⁵⁰ V	5.30E-12	⁴¹ Ca	2.43E2			⁴¹ Ca	2.43E2		
	³⁹ Ar	2.47E5	⁴⁰ K	1.09E-13	⁵⁵ Fe	1.30E2			⁵³ Mn	1.21E1		
	⁴⁴ Sc	1.48E3	³⁶ Cl	4.59E-18	⁵³ Mn	1.21E1			⁵⁰ V	1.58E-2		
	⁴⁴ Ti	1.48E3			⁵⁰ V	1.58E-2			⁴⁰ K	2.26E-3		
	rest	-1.64E4		0.00E0		1.02E3		2.91E-11		6.40E1		1.46E-11
	total	1.68E11		1.51E-3		1.69E10		4.21E-4		1.02E9		1.47E-4
V-15Cr-5Ti Blanket	³ H	1.08E10	⁴² K	5.30E-6	³ H	1.14E9	⁴² K	2.29E-6	³ H	6.86E7	⁴² K	8.00E-7
	⁴⁹ V	3.20E8	⁵⁴ Mn	3.18E-6	⁴² Ar	2.56E4	⁵⁰ V	1.49E-12	⁴² Ar	8.94E3	⁵⁰ V	1.49E-12
	⁴² K	5.92E4	⁴⁴ Sc	3.83E-9	⁴² K	2.56E4	⁴⁴ Ti	4.94E-14	⁴² K	8.94E3	⁴⁴ Ti	2.37E-14
	⁴² Ar	5.92E4	⁴⁶ Sc	1.79E-11	³⁰ Ar	1.63E3	⁴⁰ K	4.08E-17	³⁹ Ar	1.43E3	⁴⁰ K	4.08E-17
	⁴⁵ Ca	5.00E4	⁵⁰ V	1.49E-12	⁴⁴ Ti	4.03E0			⁴⁴ Ti	1.93E0		
	⁵⁴ Mn	1.45E4	⁴⁴ Ti	8.89E-14	⁴¹ Ca	4.84E-1			⁴¹ Ca	4.84E-1		
	⁵⁵ Fe	2.91E3	⁴⁰ K	4.08E-17	⁵⁵ Fe	1.01E-1			⁵³ Mn	5.49E-3		
	³⁹ Ar	1.81E3			⁵³ Mn	5.49E-3			⁵⁰ V	4.45E-3		
	⁴⁴ Sc	7.25E0			⁵⁰ V	4.45E-3			⁴⁰ K	8.48E-7		
	⁴⁴ Ti	7.25E0			⁴⁰ K	8.48E-7			³⁶ Cl	4.10E-7		
	rest	0.00E0		-9.09E-13		-1.28E2		0.00E0		-		-
	total	1.11E10		8.48E-6		1.14E9		2.29E-6		6.86E7		8.00E-7

Alloy and Zone	Post Irradiation Time 10 Yr				Post Irradiation Time 50 Yr				Post Irradiation Time 100 Yr			
	Nuclide	Activity Bq/kg	Nuclide	DoseRate Sv.h ⁻¹	Nuclide	Activity Bq/kg	Nuclide	DoseRate Sv.h ⁻¹	Nuclide	Activity Bq/kg	Nuclide	DoseRate Sv.h ⁻¹
V-3Ti-1Si FW	³ H	1.87E11	⁴² K	5.85E-4	³ H	1.98E10	⁴² K	2.53E-4	³ H	1.19E9	⁴² K	8.84E-5
	⁴⁹ V	6.68E9	²⁶ Al	8.80E-6	⁴² Ar	2.83E6	²⁶ Al	8.80E-6	⁴² Ar	9.89E5	²⁶ Al	8.80E-6
	⁴² Ar	6.55E6	²² Na	8.70E-7	⁴² K	2.83E6	⁴⁴ Sc	2.62E-7	⁴² K	9.89E5	⁴⁴ Sc	1.26E-7
	⁴² K	6.55E6	⁴⁴ Sc	4.71E-7	³⁹ Ar	1.34E5	²² Na	2.06E-11	³⁹ Ar	1.18E5	⁵⁰ V	6.82E-12
	⁴⁵ Ca	4.11E5	⁵⁴ Mn	9.13E-9	²⁶ Al	1.16E4	⁵⁰ V	6.32E-12	²⁶ Al	1.16E4	⁴⁴ Ti	2.93E-12
	³⁹ Ar	1.48E5	⁴⁶ Sc	1.50E-10	⁴⁴ Sc	4.95E2	⁴⁴ Ti	6.11E-12	⁴⁴ Sc	2.38E2	⁴⁰ K	6.53E-14
	²⁶ Al	1.16E4	⁴⁴ Ti	1.10E-11	⁴⁴ Ti	4.95E2	⁴⁰ K	6.53E-14	⁴⁴ Ti	2.38E2		
	²² Na	1.54E3	⁵⁰ V	6.32E-12	⁴¹ Ca	1.45E2			⁴¹ Ca	1.46E2		
	⁴⁴ Sc	8.91E2	⁴⁰ K	6.53E-14	³² Si	8.94E1			³² Si	7.31E1		
	⁴⁴ Ti	8.91E2			³² P	8.94E1			³² P	7.31E1		
	rest	0.00E0		0.00E0		4.10E3		2.91E-11		-1.28E2		7.28E-12
	total	1.94E11		5.95E-4		1.98E10		2.62E-4		1.19E9		9.73E-5
V-3Ti-1Si Blanket	³ H	1.27E10	⁴² K	3.17E-6	³ H	1.34E9	⁴² K	1.37E-6	³ H	8.05E7	⁴² K	4.79E-7
	⁴⁹ V	1.68E8	²⁶ Al	4.27E-8	⁴² Ar	1.53E4	²⁶ Al	4.27E-8	⁴² Ar	5.36E3	²⁶ Al	4.27E-8
	⁴² Ar	3.55E4	²² Na	1.88E-9	⁴² K	1.53E4	⁵⁰ V	1.78E-12	⁴² K	5.36E3	⁵⁰ V	1.78E-12
	⁴² K	3.55E4	⁴⁶ Sc	1.08E-11	³⁹ Ar	9.78E2	⁴⁴ Ti	2.98E-14	³⁹ Ar	8.60E2	⁴⁴ Ti	1.43E-14
	⁴⁵ Ca	3.00E4	⁵⁰ V	1.78E-12	²⁶ Al	5.65E1	⁴⁰ K	2.44E-17	²⁶ Al	5.65E1	⁴⁰ K	2.44E-17
	³⁹ Ar	1.08E3	⁴⁴ Ti	5.37E-14	⁴⁴ Ti	2.42E0			⁴⁴ Ti	1.16E0		
	²⁶ Al	5.65E1	⁴⁰ K	2.44E-17	³² Si	4.11E-1			³² Si	3.36E-1		
	⁴⁴ Ti	4.35E0			³² P	4.11E-1			³² P	3.36E-1		
	²² Na	3.32E0			⁴¹ Ca	2.91E-1			⁴¹ Ca	2.90E-1		
	³² Si	4.83E-1			⁵⁰ V	5.33E-3			⁵⁰ V	5.33E-3		
	rest	1.02E3		4.55E-13		0.00E0		1.14E-13		0.00E0		5.68E-14
	total	1.28E10		3.22E-6		1.34E9		1.41E-6		8.05E7		5.22E-7

From Figures 5 and 6 and Table 1 it can be seen that at times longer than 10-20 years the surface gamma dose rate of the pure alloys is dominated by ^{42}K , which is generated by decay of ^{42}Ar with a 32.9 year half-life. The half-life of ^{42}K is only 12.36 hours, so removal of its precursor ^{42}Ar by remelting the vanadium alloy would eliminate this activity in a few days. Thus, starting with *pure* alloys, the removal of ^{42}Ar would reduce the long-term dose rate of the irradiated metal by many orders of magnitude.

Besides the intended alloying elements, the vanadium alloys will contain unavoidable impurities. These impurities may be present in the material prior to its irradiation or they may be picked up during service, by interaction with the plasma, coolant, breeder or other material. It is impossible at this stage to identify the tramp elements that will be dominant or to quantify their probable concentrations, though some general considerations serve to indicate elements likely to be critical to the recycling concept. Table 2 shows the permissible concentrations of elements present for the entire irradiation period, with the condition that their activation products contribute not more than 10% to the dose rate for the pure alloy. At 50-100 years the strictest limit is 5 ppb for Co, followed by 30-60 ppb for Ag, Sm, Eu, Tb, Dy, and Ho. Cobalt leads to the production of ^{60}Co , a 1.33-MeV gamma emitter with a 5.27 year half life. In terms of the vanadium alloy dose rate at less than fifty years, cobalt is by far the most critical impurity.

Although there are no limits on light element impurities from a radiological standpoint, their concentrations must be limited to avoid degradation of the alloy mechanical properties. Initial purification can bring the light elements to acceptable levels, but they may be reintroduced during fabrication and service, if care is not taken to exclude them. For example, vanadium would react with oxygen present in the coolant stream.

Table 2. Permissible concentrations of impurity elements present in V-15Cr-5Ti. These numbers are calculated on the basis of either 10% of the dose of the pure alloy or the 10 μ Sv/h limit, whichever is the higher. (A similar table for V-3Ti-1Si is available from the authors.)

<u>Element</u>	<u>1-10 year</u>	<u>10-25 years</u>	<u>25-50 years</u>	<u>50-100 years</u>	<u>≥ 100 years</u>
H	no limit	no limit	no limit	no limit	no limit
He	no limit	no limit	no limit	no limit	no limit
Li	no limit	no limit	no limit	no limit	no limit
Be	no limit	no limit	no limit	no limit	no limit
B	no limit	no limit	no limit	no limit	no limit
C	no limit	no limit	no limit	no limit	no limit
N	no limit	no limit	no limit	no limit	no limit
O	no limit	no limit	no limit	no limit	no limit
F	no limit	no limit	no limit	no limit	no limit
Ne	5.9E-03	5.9E-03	1.6E-01	no limit	no limit
Na	5.7E-08	5.7E-08	1.6E-06	7.2E-04	no limit
Mg	2.2E-05	2.2E-05	6.1E-04	2.8E-01	4.4E-01
Al	6.6E-05	6.6E-05	2.6E-04	9.1E-05	3.8E-06
Si	1.2E-02	1.2E-02	5.7E-02	2.0E-02	8.4E-04
P	no limit	no limit	4.4E-01	1.7E-01	9.0E-03
S	3.7E-02	1.9E-02	1.2E-02	4.6E-03	2.7E-04
Cl	1.6E-02	8.0E-03	4.7E-03	1.7E-03	7.2E-05
Ar	3.8E-04	2.0E-04	1.2E-04	5.0E-05	3.1E-06
K	7.7E-04	4.0E-04	2.5E-04	1.0E-04	6.1E-06
Ca	1.8E-03	1.2E-03	1.0E-03	7.3E-04	8.5E-05
Sc	5.0E-05	1.6E-03	1.6E-03	1.6E-03	1.6E-03
Ti	5.1E-03	5.0E-03	5.0E-03	5.0E-03	5.0E-03
V	no limit	no limit	no limit	no limit	no limit
Cr	1.6E-02	4.7E-02	no limit	no limit	no limit
Mn	4.1E-07	1.2E-06	1.1E-01	no limit	no limit
Fe	5.9E-06	5.9E-06	2.7E-05	4.3E-04	1.1E-01
Co	8.7E-11	8.3E-11	3.1E-10	5.0E-09	1.2E-06
Ni	1.8E-08	1.7E-08	6.5E-08	1.0E-06	2.6E-04
Cu	3.0E-08	2.9E-08	1.1E-07	1.7E-06	4.3E-04
Zn	4.4E-06	6.5E-06	2.8E-05	4.4E-04	1.1E-01
Ga	6.2E-03	5.7E-02	no limit	no limit	no limit
Ge	8.1E-02	no limit	no limit	no limit	no limit
As	8.8E-04	no limit	no limit	no limit	no limit
Se	1.4E-03	1.8E-01	2.8E-01	8.0E-01	1.5E-01
Br	1.6E-03	1.3E-03	1.8E-03	1.5E-03	6.4E-05
Kr	3.9E-06	3.2E-06	5.1E-06	1.5E-05	1.3E-04
Rb	9.8E-05	8.0E-05	1.3E-04	3.9E-04	3.4E-03
Sr	7.3E-04	5.9E-04	9.6E-04	2.8E-03	2.3E-02
Y	5.3E-05	1.9E-02	2.2E-02	2.7E-02	3.3E-02
Zr	1.3E-03	9.1E-04	9.2E-04	8.4E-04	1.1E-04
Nb	1.7E-06	8.3E-07	4.9E-07	1.7E-07	7.2E-09
Mo	2.0E-04	9.8E-05	5.8E-05	2.1 E-05	8.9E-07

<u>Element</u>	<u>1-10 year</u>	<u>10-25 years</u>	<u>25-50 years</u>	<u>50-100 years</u>	<u>> 100 years</u>
Ru	5.3E-06	5.3E-06	9.6E-05	2.0E-03	8.4E-05
Rh	7.4E-08	7.4E-08	1.4E-06	3.2E-04	3.4E-02
Pd	2.5E-06	2.5E-06	4.3E-06	1.6E-06	8.7E-08
Ag	3.0E-07	1.5E-07	9.4E-08	3.6E-08	1.9E-09
Cd	1.5E-04	8.6E-05	5.4E-05	2.1E-05	1.1E-06
In	1.6E-02	1.4E-01	4.8E-01	4.5E-01	2.6E-02
Sn	5.7E-07	5.7E-07	1.3E-05	4.3E-03	1.4E-03
Sb	6.6E-07	6.6E-07	1.5E-05	5.1E-03	no limit
Te	4.1E-05	4.1E-05	9.8E-04	6.2E-02	2.6E-03
I	8.6E-04	8.6E-04	2.0E-02	no limit	no limit
Xe	1.4E-07	1.4E-07	3.4E-06	5.2E-06	5.9E-06
Cs	8.8E-10	8.8E-10	5.9E-08	1.1E-06	5.8E-06
Ba	8.7E-07	7.3E-07	1.2E-06	3.2E-06	1.3E-05
La	1.3E-03	1.3E-03	3.1 E-03	3.3E-03	3.7E-03
Ce	2.7E-03	3.2E-03	5.8E-03	1.5E-02	5.6E-02
Pr	7.9E-02	no limit	no limit	no limit	no limit
Nd	1.5E-07	1.2E-07	2.4E-07	1.1 E-06	2.0E-05
Sm	4.5E-09	3.8E-09	7.5E-09	3.3E-08	5.9E-07
Eu	6.0E-09	5.0E-09	1.0E-08	4.4E-08	2.7E-07
Gd	2.9E-06	1.8E-06	1.3E-06	5.5E-07	4.0E-08
Tb	4.4E-07	2.3E-07	1.5E-07	6.1E-08	4.1E-09
Dy	4.1E-07	2.0E-07	1.2E-07	4.5E-08	2.0E-09
Ho	4.4E-07	2.2E-07	1.3E-07	4.8E-08	2.2E-09
Er	1.9E-05	9.6E-06	5.8E-06	2.1E-06	9.5E-08
Tm	3.4E-03	2.9E-03	2.1E-03	7.6E-04	3.5E-05
Yb	9.2E-06	9.2E-06	8.1E-05	3.2E-04	3.5E-04
Lu	1.0E-06	1.0E-06	5.8E-06	1.1E-05	1.1E-05
Hf	1.2E-05	8.9E-06	9.1E-06	9.5E-06	1.0E-05
Ta	1.0E-04	1.6E-02	1.6E-02	1.6E-02	4.3E-03
W	2.5E-03	1.3E-03	8.4E-04	3.4E-04	2.2E-05
Re	3.2E-04	1.6E-04	1.0E-04	4.3E-05	2.8E-06
Os	1.9E-05	1.0E-05	6.7E-06	2.8E-06	1.9E-07
Ir	7.4E-06	4.5E-06	3.6E-06	2.2E-06	3.6E-07
Pt	3.3E-05	2.0E-05	1.7E-05	1.2E-05	3.7E-06
Au	1.0E-01	no limit	4.4E-01	2.6E-01	3.0E-02
Hg	no limit	no limit	no limit	no limit	3.2E-02
Tl	no limit	no limit	no limit	no limit	2.2E-01
Pb	1.1 E-02	6.8E-03	6.3E-03	5.2E-03	1.4E-03
Bi	2.5E-07	1.6E-07	1.5E-07	1.3E-07	4.7E-08

From the standpoint of recycling, the influence of radiologically-troublesome impurities is twofold. Firstly, they may significantly raise the dose rate relative to the pure alloy and hence increase the cooling time needed to attain a dose rate level at which the material can readily be transported and remotely recycled, in both cases without the need for excessive shielding. Secondly, particular long-lived radionuclides derived from certain impurities may prove difficult or impossible to remove during reprocessing and may thus give rise to a remanant dose rate high enough to restrict the degree of freedom in handling and fabricating new components from the recovered material. This point will be discussed more fully after considering the radiological criteria for recycling.

Radiological Criteria for Recycling

There appear to be no regulatory guidelines relating to the activity or dose rate levels of radioactive materials presented for recycle. To reduce storage costs, recycling (where this is the preferred option) will be performed as early as possible, subject to the attainment of manageable dose rates and taking account of any benefits from an extension of the cooling period. Although considerably higher levels may be tolerable, it has been suggested that, for constructional materials the surface γ dose rate should not greatly exceed 10 mSv/h in order to allow recycling in a dedicated facility with full radiological protection but without excessively heavy, and therefore expensive, shielding.⁹ At substantially lower dose rates, around 10 μ Sv/h "hands-on" reprocessing could be considered, with only minimal radiological precautions. Few near-plasma reactor materials are likely to reach such a low dose rate level in an acceptable cooling time, however, and even hypothetically-pure V-15Cr-5Ti and V-3Ti-1Si alloys would not attain this limit before about 300 y. After reprocessing, it is assumed that the reclaimed material will be utilized in making components for further reactors. For re-use within the fusion materials cycle there are no statutory limitations on the allowable activity and dose rate of recycled materials, though there are obvious advantages in being able to handle materials without excessively strict precautions. With this objective, a dose rate upper limit of around 10 μ Sv/h would again apply, this time to the recycled material. The re-use of materials exhibiting higher dose rates would not be excluded, though semi-remote or remote handling techniques would be needed, with some reduction in operational feasibility and with increased cost.

Application of Criteria to Vanadium Alloys

As already noted, the dose rates of the model alloys remain at levels that would preclude "hands-on" recycling, even in the absence of impurities. Figures 5 and 6 show that, for first wall materials, the remote recycling limit of 10 mSv/h is attained after about 10 y for V-15Cr-5Ti and 4 y for V-3Ti-1Si, ignoring the effects of impurities. The profound effect of radiologically-potent tramp elements is, however, illustrated by Table 3, which shows the dose rate contribution from 1 ppm by mass of the elements Co, Nb, Ag and Mo in the alloys, at various cooling times. The numbers in parenthesis give the corresponding permissible concentrations for the individual elements, present alone, if the dose rate contributions are not to exceed 10 μ Sv/h.

Table 3. Dose rate contributions in Sv/h from 1 ppm by mass of some typical impurity elements. Quantities in round brackets represent concentrations permitted by the 10 mSv/h limit and those in square brackets correspond to the 10 μ Sv/h limit.

Element (main radionuclide)	Cooling time (y)			
	10	25	50	100
Co (⁶⁰ Co)	1.2 (8.6 ppb) [8.6 ppt]	1.6E-1 (68 ppb) [68 ppt]	6.0E-3 (1.7 ppm) [1.7 ppb]	8.4E-6 (1200 ppm) [1.2 ppm]
Nb (⁹⁴ Nb)	9.1E-5 (110 ppm) [110 ppb]	9.1E-5 (110 ppm) [110 ppb]	9.1E-5 (110 ppm) [110 ppb]	9.1E-5 (110 ppm) [110 ppb]
Ag (^{108m} Ag)	8.5E-4 (12 ppm) [12 ppb]	8.3E-4 (12 ppm) [12 ppb]	7.9E-4 (13 ppm) [13 ppb]	7.3E-4 (14 ppm) [14 ppb]
Mo (⁹⁴ Nb, ⁹¹ Nb)	1.0E-6 (9700 ppm) [9.7 ppm]	1.0E-6 (9800 ppm) [9.8 ppm]	1.0E-6 (9900 ppm) [9.9 ppm]	1.0E-6 (10000 ppm) [10 ppm]

Examination of Table 3 reveals several important features. Firstly, of the impurities considered, cobalt dominates the dose rate at medium cooling times, up to about 60 y, through the relatively short-lived isotope ^{60}Co . The remaining elements, which produce long-lived radionuclides, give rise to dose rate contributions that are essentially constant with cooling time and are thus relatively more important at long cooling times, beyond 50 y. It should also be noted that the nuclides responsible for the dose rates are radioisotopes of the impurity element itself (Co, Nb and Ag) or, in the case of Mo, the neighboring element Nb. All of these elements are relatively involatile and would not be removed to any significant extent in a simple vacuum melting or refining process. If this were the case, then their activities would be carried through to the product and the quantities shown within square brackets in Table 3 would represent the maximum permitted concentrations in the starting material if their contribution to the dose rate of the recycled product were not to exceed $10\ \mu\text{Sv/h}$. These concentrations may be compared with those achieved in specially-purified vanadium alloy constituents ¹⁰, to determine their significance, as illustrated by the Table 4.

Table 4. Typical impurity concentrations and corresponding contact dose rates after various cooling times.

Element	Measured Concentration (ppm)	Contact dose rate contribution at cooling time (Sv/h)			
		10y	25y	50y	100y
Co	<0.03*	<3.5E-2	<4.9E-3	<1.8E-4	<2.5E-7
Nb	0.1	9.1E-6	9.1E-6	9.1E-6	9.1E-6
Ag	<0.01	<8.5E-6	<8.3E-6	<7.9E-6	<7.3E-6
Mo	2	2.1E-6	2.0E-6	2.0E-6	2.0E-6

* < denotes below detection limit; this concentration will be conservatively assumed.

With these concentrations and the assumption that the activation products from all these impurities would remain in the melt during reprocessing, it is evident that about 75 y of cooling would be needed for attainment of a "hands-on" dose rate in the recycled product and that this cooling time is governed by the cobalt content. Given sufficient cooling time for decay of ^{60}Co , the residual dose rate would then be largely determined by ^{94}Nb from niobium and possibly $^{108\text{m}}\text{Ag}$ from silver, with an expected value around 10 $\mu\text{Sv/h}$.

The above discussion applies to first wall material irradiated to a fluence of about 12 MW/m^2 and it is helpful at this point to examine what gains might be made by blending the highly-activated first wall material with less highly-activated material from the blanket.

Comparison Of First Wall And Blanket Activation

In the absence of specific predictions for the activation of individual elements within the blanket zone, a simple comparison is performed here for the principal elements on the basis of published activation data for the EEF reference reactor.¹¹ The values in Table 5 apply to activation of 1 kg of the pure elements, including any tritium generated, at a cooling time of 100 y.

Table 5. Activities and dose rates due to activation of 1 kg of various pure elements in the EEF reactor spectrum.¹²

	Co	Nb	Ag	Mo	Ti	V	Cr
Activity in first wall (Bq/kg)	3.22E10	1.29E12	1.44E12	7.37E11	7.20E7	1.08E4	3.04E3
Activity in blanket (Bq/kg)	3.27E9	2.25E11	1.05E12	6.65E10	3.87E5	4.14E0	1.03E0
Dose rate in first wall (Sv/h)	13.3	95.6	457	0.797	3.28E-3	5.34E-7	1.47E-7
Dose rate in blanket (Sv/h)	2.31	27.3	333	0.0716	178E-5	2.08E-10	4.98E-11
First wall activity/blanket activity	9.85	5.73	1.37	11.1	186	2610	7806
First wall dose rate/blanket dose rate	5.76	3.5	1.37	11.1	184	2570	2952

It may be noted that the neutron flux values for the EEF first wall and blanket are 1.80×10^{15} and $3.47 \times 10^{14} \text{ n cm}^{-2}\text{s}^{-1}$, respectively, which are in the ratio 5.19:1. Extremely wide variations in scaling behavior are apparent from the above table. The intended constituents V, Cr and Ti exhibit much reduced 100 y residual activities and dose rates between first wall and blanket, while the critical impurity elements show a much smaller reduction. Silver in particular is only slightly less activated in the blanket, by a factor of 1.37 for both activity and dose rate, while the activity and dose rate of niobium scale roughly linearly with the flux, as does the dose rate of cobalt. For molybdenum both the activity and dose rate decrease by an order of magnitude from the first wall to the blanket. There is thus little relaxation of the purity specification for Ag in the blanket but some advantage in the cases of Co, Nb and Mo. More detailed calculations are needed to quantify these gains more precisely, taking into account a finer gradation of cooling times and the scaling of activation parameters with variations in wall loading and irradiation time. It should also be noted that some potential impurities not considered here, e.g., europium, exhibit substantially *higher* activation in the blanket and shield regions than in the first wall. The rare-earth elements are, however, not found to be present in significant concentrations in vanadium alloy constituents.⁹

Effect Of Blending First Wall And Blanket Waste

Assuming the mass of blanket structural material for reprocessing is much greater than that of the first wall and that both materials have identical starting compositions, blending of these two waste streams in the melting process would lead to a product in which the contributions made by the impurities to the overall dose rate would be approximately as follows:

Silver: $< 7.3/1.37 = 5.3 \text{ } \mu\text{Sv/h}$

Niobium: $9.1/3.50 = 2.6 \text{ } \mu\text{Sv/h}$

Molybdenum: $2.0/11.1 = 0.2 \text{ } \mu\text{Sv/h}$

The factor 5 reduction in ^{60}Co concentration achievable by mixing first wall and blanket material would permit a contraction by about 12 y in the cooling time needed to obtain a given dose rate, assuming the latter is governed by decay of ^{60}Co . Thus the dose rate contribution for ^{60}Co would be reduced below $10 \text{ } \mu\text{Sv/h}$ at a cooling time of about 60 y.

After 60 y cooling the only significant radionuclides derived from the pure V-15Cr-5Ti constituents are (neglecting any tritium)

	^{39}Ar	^{42}Ar	^{42}K
Activity, Bq/kg	4.71E5	5.21E6	5.21E6
Dose rate, Sv/h	bremsstrahlung	0	4.65E-4

The activity would place this material just below the upper limit of 12 GBq/t for Low Level Waste (UK classification system). The above radionuclides could be essentially completely removed in a high-vacuum remelting operation. Any residual ^{42}K would decay with the relatively short half-life of

12 h, leaving only the activity from the involatile activation products of the impurities, which would generate a γ dose rate of below 10 $\mu\text{Sv/h}$ with the current assumptions for composition. In the case of V-3Ti-1Si alloy the nuclide ^{26}Al gives rise to an additional γ dose rate contribution of around 10 $\mu\text{Sv/h}$ for first wall conditions and this value persists indefinitely. For activation in the blanket the contribution from ^{26}Al appears to be reduced by a factor of about 200, hence the mixing of first wall and blanket material will diminish the component from ^{26}Al to an insignificant proportion, even if this radionuclide is retained during remelting.

Extension To Successive Usage Cycles

Further activation analyses are needed to determine the compositional evolution of first wall and blanket materials over several successive cycles of irradiation, cooling, and reprocessing, so as to identify the dominant radionuclides and the cooling times needed to reach the γ dose rate levels required for remote recycling and hands-on fabrication. These calculations will need to take into account not only the potential tramp elements but also the presence of residual intrinsic transmutation products, which may act as precursors for radionuclide generation in the next irradiation.

Requirements For "Hands-On" Recycling After 10 Years

For a first wall comprised of *pure* V-Cr-Ti alloy, the dominant isotopes with half-lives > 0.2 y are

^{46}Sc (83.8 d)

^{54}Mn (312 d)

^{42}Ar (32.9 y) $\rightarrow$ ^{42}K (12.36 h).

These isotopes can be produced by multiple pathways involving (n,α) , $(n,2n)$, (n,p) , and $(n,n\alpha)$ reactions and beta decay. The dominant source of ^{46}Sc and ^{42}Ar is the titanium component of the alloy, and the dominant source of ^{54}Mn is the chromium. Impurities will generate many additional radioisotopes. Because of various processes that limit its structural life (such as swelling, embrittlement, and creep), the wall must be replaced periodically (perhaps every 2-3 years). There are several sources of undesirable radioisotopes and impurities in the irradiated metal:

- impurities remaining after the original purification
- impurities introduced during fabrication, use, and removal from the reactor.
- transmutation products produced by neutron and secondary charged-particle interactions.
- impurities transported by the coolant from other components, such as pumps, valves, and heat exchangers. Vanadium acts as a getter for non-metallic elements.

Thorough purification of the constituent elements in vanadium alloys will be needed to remove troublesome impurities such as Nb, Ag, Mo, and Co. To meet the "hands-on" recycling criterion after **10 years cooling**, very stringent limits are needed on many impurities, as illustrated in Table 6. (This Table is based on a $25\ \mu\text{Sv/h}$ limit, instead of the $10\ \mu\text{Sv/h}$ limit suggested above.) Cooling times > 10 years would permit less stringent impurity limits (Tables 2 and 3).

Table 6. Concentration limits (ppm) for potential impurity elements to meet a surface dose-rate criterion of 25 $\mu\text{Sv/h}$ after 10 years cooling.

[Blanket = 4 Years Irradiation at 5 MW/m²; Shield = 32 Years Irradiation].⁹

<u>Element</u>	<u>First Wall</u>	<u>Blanket</u>	<u>Shield</u>	<u>Dominant Nuclide (half-life)</u>	
Ag	0.003	0.0075	0.60	^{108m} Ag	(418 y)
Al	108	9,000	450,000	²⁶ Al	(0.72M y)
Ca	1200	60,000	no limit	⁴² K from ⁴² Ar	(32.9 y)
Cd	0.08	10	28,000	^{108m} Ag	(418 y)
Co	0.0002	0.00013	0.016	⁶⁰ Co	(5.27 y)
Cu	0.0004	0.011	5.3	⁶⁰ Co	(5.27 y)
Eu	0.00045	0.00045	0.088	¹⁵² Eu	(13.3 y)
Fe	1.6	5.8	no limit	⁶⁰ Co	(5.27 y)
Hf	0.17	0.26	26	^{178m} Hf	(31 y)
Ho	0.19	0.095	7	^{166m} Ho	(1.2 ky)
Mn	0.085	2.9	110,000	⁵⁴ Mn	(312 d)
Mo	2.8	100	7500	⁹⁴ Nb	(20 ky)
Na	0.035	1.4	3100	²² Na	(2.6y)
Nb	0.15	0.43	6.5	⁹⁴ Nb	(20 ky)
Ni	0.00044	0.012	3	⁶⁰ Co	(5.27 y)
Ta	9,300	no limit	no limit	^{178m} Hf	(31 y)
Tb	0.0017	0.05	3.6	¹⁵⁸ Tb	(150y)
W	33	1580	220,000	^{178m} Hf	(31 y)

These concentration limits are for materials averaged over the first wall, breeding zone, and reflector. The dose rate from ⁴²K (from Ti in the alloy) would be much higher than the limit. In order to facilitate recycling, its precursor ⁴²Ar must be removed. Otherwise, cooling times of about 100 years would be required. At 10 years after irradiation, impurities such as Co, Ni, and Cu will make significant contributions. If their activation products are not removed during reprocessing, then longer cooling times would be needed to allow their decay.

For recycling after cooling times of 10 years without decontamination, the concentrations of elements Co, Cu, Eu and Ni must be restricted to < 1 ppb. This emphasizes the need to consider longer cooling times, such as 50 years. Typical vanadium samples have excessive Ag, Mo, Co, and Nb, but generally acceptable concentrations of rare earth elements. Thus, the vanadium, chromium, and other metals of the alloy must be purified very thoroughly before fabrication into fusion reactor components.

Prospects for Recycling

Activation predictions show that the radiologically-significant radionuclides (neglecting tritium) generated from pure V-15Cr-5Ti are ^{39}Ar , ^{42}Ar , ^{42}K , ^{45}Ca , ^{44}Sc , ^{49}V , ^{54}Mn and ^{55}Fe . Two additional radionuclides, ^{22}Na and ^{26}Al , are introduced with V-3Ti-1Si. In the case of the V-15Cr-5Ti alloy the only long-lived nuclides, ^{39}Ar and ^{42}Ar , are generated from the Ti component, while in V-3Ti-1Si the long-lived isotope ^{26}Al is produced from silicon. When utilized as first wall materials, the dose rate from ^{42}K generated by decay of ^{42}Ar would preclude hands-on recycling (dose rate $\sim 10\text{ }\mu\text{Sv/h}$) at an acceptably short cooling time. In both cases, however, the contact dose rate level of 10 mSv/h , at which remote recycling would be feasible, is reached within 10y. As already discussed elsewhere ¹³, a high-vacuum remelting and decontamination process using, for example, electron beam melting and refining, could be employed to segregate most of the radioactive species by volatilization and to produce a reusable material with a residual contact dose rate not exceeding about $10\text{ }\mu\text{Sv/h}$.

Certain radiologically-potent impurities may dramatically alter the behavior of the otherwise pure materials. Firstly, trace quantities of elements such as Co, Ni and Cu, which give rise to production of ^{60}Co , can greatly delay the storage time at which the remote recycling dose rate level is reached. Secondly, these and other elements such as Ag, Nb and Mo which lead to long-lived radionuclides that are not easily removed during remelting, can prevent the attainment of a post-decontamination dose rate that would allow hands-on fabrication of new components.

The description of the effects of potential impurities given here is largely based on the results of a collaborative project involving Culham Laboratory and Johnson Matthey Ltd. The objective of this work was to identify commercially applicable purification routes for the production of vanadium, chromium and titanium metals having a purity specification consistent with the 100 y "hands-on" dose rate limit. At the time this project was started the hands-on limit was taken as $25\text{ }\mu\text{Sv/h}$ after 100 years cooling and it was later revised to $10\text{ }\mu\text{Sv/h}$ in line with the downward revision of dose limits recommended by the ICRP in 1990. The impurity concentrations assumed here were obtained by careful chemical analysis of actual metals prepared by Johnson Matthey and are in accordance with the $25\text{ }\mu\text{Sv/h}$ hands-on criterion. It can thus be claimed that these specifications are applicable to materials available today, albeit in experimental quantities. Although even stricter specifications may be attainable in the future for the starting materials, it remains to be demonstrated that this degree of purity can be maintained throughout subsequent metal-forming operations and during the life of the component in the reactor.

Even with the assumed high-purity materials it appears necessary to mix first wall and blanket materials to ensure that the post-processing dose rate, after about 60 y cooling, falls below $10\text{ }\mu\text{Sv/h}$. On the other hand, no allowance is made for possible removal of non-volatile species during remelting, for example by electroslag refining.

VANADIUM PURIFICATION

Industry has developed sophisticated processes for purifying nickel-based superalloys such as the Nimonic series (80Ni-20Cr) and Hastelloy series (60Ni-15Cr-15Mo), and impurity levels of about 44 elements are routinely analyzed.¹⁴

Because all vanadium compounds are toxic (Appendix A), vanadium vapor must be contained during melting. UO_2 crucibles have been used for vacuum heating of vanadium. Cerium sulfide crucibles are best for melting without increasing the hardness of the vanadium, but the vanadium abstracts some sulfur from the crucible. Graphite crucibles are unsatisfactory. Arc melting and electron-beam melting can be used to avoid sulfur. Levitation melting has been accomplished using induction coils in a vacuum. Cerium is used as a scavenger during melting to remove O, C, N, and S. Vanadium oxidizes rapidly at high temperatures, and protective electroplates adhere poorly to it.⁷

Vanadium compounds can be purified by aqueous processing using both anionic and cationic resin exchangers. Such processing removes Tb, Eu, Ho, Dy, Al, Ni, Cd, Cu by factors ≥ 1000 , and Ag, Nb, Hf, Mo, and W by factors ≥ 100 . Vanadium metal can be purified by electron beam melting. Estimates based on relative volatility factors indicate that this refining lowers concentrations of Cd, Eu, Ag, Ho, Al, Cu, Bi, and Dy by factors ≥ 1000 , but it slightly enriches Ta, W, Hf, Mo, and Nb (due to partial loss of vanadium by vaporization).⁹

Fractional distillation processes for purification of vanadium tetrachloride (VCl_4) and vanadium oxytrichloride (VOCl_3) will be described here. The following description of the VCl_4 process is due to R. L. Miller.¹⁵ The vanadium metal would be chlorinated in a reaction vessel that is resistant to attack by chlorine gas, with the reaction

as illustrated in Figure 11. Excess chlorine is used to prevent the production of vanadium trichloride (VCl_3). The presence of oxygen is undesirable in this process, since it forms vanadium oxytrichloride (VOCl_3), which requires additional processing to form the tetrachloride. Vanadium tetrachloride has low melting and boiling point, as shown in Table 7. Vanadium tetrachloride gradually decomposes with the release of gaseous chlorine:

This instability can be a problem for long-term storage and transport of VCl_4 . The separation factors of vanadium from various impurities attainable by this process have not yet been quantified.

Figure 11. Production of vanadium tetrachloride.

Table 7. Properties of some vanadium and titanium compounds.^{16,17}

	VCl ₄	TiCl ₄	V ₂ O ₅	VOCl ₃	V
melting temperature, °C	-26	-24	670	-79	1919
boiling temperature, °C	152	136.4	1750	127	3400
density at 20°C, kg/m ³	1820	1702	3357	1830	6100
color	brown	colorless	yellow-red	yellow	gray

Figure 12. Fractional distillation of vanadium tetrachloride.

The vanadium tetrachloride can be distilled to obtain a relatively high purity compound, as illustrated in Figure 12. (A comprehensive survey of impurity chloride boiling points is needed to verify which impurities, if any, might remain with the VCl_4 during this process.) Thirty stills processing 3 kg/h (or three stills each processing 30 kg/h) could produce 2 tonnes/day. The purified vanadium tetrachloride can be reacted with carbon dioxide to produce vanadium trichloride, which can be reacted with pure magnesium in a conventional Kroll process

The magnesium chloride can be removed by distillation or by water leaching. The resulting pure vanadium metal can then be alloyed with chromium and other elements for fabrication into fusion reactor components.

Another purification process uses vanadium oxytrichloride, a yellow liquid that boils at 127°C. It hydrolyses quickly in moist air. It may be produced by a variety of processes, including:

The last of these reactions is used in laboratory preparations, and the first may be more suitable for large-scale processing. The vapor pressure of vanadium oxytrichloride is given by

$$p(\text{atm}) = 10^{(4.92 - 1.968/T)}$$

(valid for $35^\circ\text{C} < T < 120^\circ\text{C}$). According to Clark,¹⁶ "The oxychloride has no action on phosphorus, arsenic, bismuth, or mercury or, indeed, on most metals, but it reacts with caesium at 30, rubidium at 60, potassium at 100 and sodium at 180°C ." This probably means that the reaction rates are appreciable above these temperatures. Some of the sensitive impurity elements (Nb, W, Mo) form similar oxytrichlorides and some impurity elements (Pr, Y, U) form chlorides, but only molybdenum oxytrichloride is volatile. Thus, distillation of VOCl_3 separates V from most of the sensitive elements. The VOCl_3 can then be distilled and hydrolyzed to V_2O_5 , as illustrated in Figure 13. The V_2O_5 is converted into metal using conventional aluminothermic reduction with very pure aluminum, followed by electron beam refining. This process is being developed by the Johnson-Matthey Company and Culham Laboratory.¹⁰

The availability of titanium and chromium with very high purity stems from their use in the aerospace industry, which demands very tight compositional specifications. Pure titanium is also required for sputter ion targets. Vanadium metal, on the other hand, has few applications, so there has been no industrial incentive to strive for higher purities.

With any purification process, the remaining impurity concentrations must be carefully monitored. Glow discharge mass spectrometry (GDMS) is probably the best analytical tool for determining impurity content. It can determine ppb levels in one minute per peak.¹⁸ GDMS has interferences in analysis of Cr and Ti for Nb, so spark source mass spectrometry is used for those determinations. Care is needed during fabrication to avoid introduction of new impurities.

Figure 13. Purification of vanadium by fractional distillation of vanadium oxytrichloride.

VANADIUM ALLOY RECYCLE

The general principles needed to facilitate vanadium alloy recycle are:

- 1. Purification of initial alloy materials.** The steps described in the preceding section can achieve the desired purity levels, using multiple stages, if necessary. However, the cost of such operations on an industrial scale has not been determined. Purity would be less crucial for components in low-fluence regions, such as the shield, and less expensive metals could be considered for use there.
- 2. Remote handling and storage.** Remote handling and storage of reactor components are needed to allow several years' decay, even if recycling were not planned. Care must be taken to avoid the introduction of contaminants onto the surface of the vanadium alloy components during handling.
- 3. Melting.** Remote electron beam or plasma arc melting on a cold hearth in a vacuum (or other suitable melting process) will drive off volatile impurities, which can then be trapped. Many of the high-technology alloy procedures are already accomplished remotely, even for non-radioactive materials, so this automation should not be difficult. Shielding will be required, however, and maintenance of the metallurgical equipment may require robotic equipment. After removal of volatile impurities, the dose rate will be greatly reduced.

For an example case Butterworth calculated (using the FISPACT code) the radioactivity present after 5 cycles of *pure* V-15Cr-5Ti, each cycle having 2.5 years irradiation at 5 MW/m², followed by 10 years cooling, melting, refabrication, and re-irradiation in a fusion reactor. The following isotopes have significant activities, but insignificant dose rates:

³ H	(12.3 y)	weak beta, no gammas
⁴⁵ Ca	(0.45 y)	beta and weak gamma
⁴⁹ V	(0.907 y)	electron capture, no gammas
⁵⁵ Fe	(2.68 y)	electron capture, no gammas.

The dose rate would be dominated by

1500 μSv/h	from ⁴² K (12.36 h, 1.525 MeV gamma), daughter of ⁴² Ar (33 y)
635 μSv/h	from ⁵⁴ Mn (0.86 y, 0.835 MeV gamma) .

Practically all of the tritium and calcium would be released during melting, and the remaining ⁴⁹V and ⁵⁵Fe are relatively benign, because they emit no gammas. (The x-rays they emit could pose a problem if vapors or aerosols of these isotopes were inhaled.) The argon and most of the manganese and potassium would be released during melting, and most of the remaining ⁴²K would decay away in a week. Thus, in the case of a *pure* alloy, the melting process would probably remove all the dominant radioisotopes, except for a small fraction of the ⁵⁴Mn. At its melting point (2173 K) the vapor pressure

of vanadium is 3 Pa, and the vapor pressure of Mn is about 70 kPa, so a large separation factor may in principle be attainable during melting. The degree of removal depends upon the thickness of the vanadium, upon the diffusion coefficient of manganese in vanadium, and upon the time available for release of the manganese. If the manganese dose rate could be reduced by about a factor of 100, then the alloy should already be near "hands-on" recycling levels, unless other nonvolatile long-lived isotopes were present from activation of impurities in the alloy.

Butterworth finds that, after five cycles through the reactor, the dose rates from these transmutation products are not substantially higher than after the first cycle. There would be a gradual build-up of ^{60}Co , but after five cycles it would cause a dose rate of only $0.49 \mu\text{Sv/h}$. Thus, for the pure alloy considered, hands-on recycling would probably be feasible after melting. The waste streams from isotopes released during melting would include about 6.6 mg (^{42}Ar), 15 g (^{45}Ca), 45 g (^{44}Sc), and 2.9 g (^{54}Mn) per tonne of alloy processed.¹⁹ These isotopes could be sold for commercial use, or disposed as waste. With its long-lived precursor (^{42}Ar) and 12-hour half life, ^{42}K may be useful for medical applications. The other isotopes have half lives less than one year, and would decay during storage. Transmutations would gradually increase the concentrations of Cr and Ti, and decrease that of V, so that makeup vanadium stock will need to be added during remelting.

Significant levels of impurities (especially Ag, Nb, Pd, Co, and Ir) in the original vanadium alloy would increase the long-lived activity of the irradiated alloy, so the initial purification (step 1) should ensure that such elements are removed to sufficiently low concentrations (< 1 ppb in some cases). If that can be done, then no further processing of the alloy would be required before the first recycle. The processing required during subsequent recycles would depend upon the detailed amounts of impurities and their transmutation products.

4. Remote purification. If the initial purification were not adequate, or if the alloy became contaminated with impurities or transmutation product elements during fabrication, use, and removal, then three options would be open:

- (a) disposal as waste (wasteful and expensive),
- (b) shielding and remote handling throughout the fabrication (rolling sheets, extruding tubes, machining, welding) and installation processes.

This option is undesirable, because:

- the fabrication and installation would be hazardous and slow
- the remote handling, fabrication, and installation equipment would be complex and expensive
- that equipment itself would probably require remote maintenance.

(c) additional purification of the remelted alloy by the same processes used for purification of initial vanadium metal: aqueous resin chemistry or fractional distillation of halides, followed by electron beam refining, as described above. This processing would require remote handling, shielding, and probably some remote maintenance, but it would remove the hazardous elements and permit hands-on operations for the rest of the cycle.

If an activation product is difficult to separate in a single stage distillation, then a *dilution-distillation* process may be appropriate. For example, if radioactive element X is produced by some nuclear reaction in vanadium alloy, then natural, nonradioactive X could be added to the alloy before

distillation, diluting the radioactive X. This dilution would reduce the concentration of X remaining after distillation. However, the benefits of this process would be reduced if the remaining nonradioactive X in the vanadium generated long-lived radioisotopes from neutron irradiation during subsequent cycles.

5. New alloys. It is desirable to develop new vanadium-based alloys, avoiding elements that generate significant long-lived radioactivity.

The main long-term activation problem with present pure vanadium alloys is due to the titanium constituent. If a new alloy were developed replacing Ti with more radiologically benign elements, it could simplify the recycling process, shorten the necessary cooling time, diminish the required precautions, and reduce the recycling costs.

After exposure to a first wall neutron fluence of 12.5 MW-y/m^2 and 100 years cooling, Butterworth found that the following pure elements would have surface contact dose rates $\leq 25 \text{ } \mu\text{Sv/h}$: Li, Be, V, Cr, Mn, Na, Mg, Ga, Ge, Se, As, Sb. Since only a few percent or less of the alloying elements would be present, some additional elements like P, Fe, Zn, Y, In, Te, Au, and Hg might qualify radiologically. Thus, if the structure contained only these elements, then hands-on recycling could be feasible in less than 100 years without purification of the irradiated vanadium alloy.²⁰ However, many of these elements would fail to qualify for other reasons, such as metallurgical uselessness, safety (due to high short-term radioactivity), toxicity, and cost. Detailed activation data and decay curves for 30 elements are provided by Forty, Forrest, Compton, and Rayner.¹²

Piet et al surveyed all the elements and designated the best elements for recycling to be Grade A, the next best (with a factor of 10 higher long-term activity) to be Grade B, and so on, with the results shown partially in Table 8. Grades are also assigned for safety, relating to short-term radioactivity that might be released during an accident. For example, Mg has good recycle potential, but high short-term activity.

Table 8. Elements with favorable grades for recycling and safety.²¹

Grade A for recycling

H, He, Li, Be, B, C, N, O, F, Ne, Mg, Si, P, S, Cl, Ar, K, Ca, V, Cr, Mn, Ga, Ge, As, Se, Br, Y, Zr, Ru, In, Sb, Te, I, Ta, W, Re, Au, Hg, Tl, Pr.

Grade B for recycling

Na, Ti, Fe, Rb, Sn, Pb.

At least Grade B for recycling and average Grade C for safety:

H, He, Li, Be, B, C, N, O, F, Ne, Si, P, Cl, Ar, K, Ca, Cr, V, Ge, Se, Br, Te, I, Y, Pb.

Thus, elements with high grades for recycling and satisfactory grades for safety are desirable. The Table lists those elements with at least Grade B for recycling and Grade C for safety. Hydrogen and the noble gases would not be feasible alloying elements, and some of the metals tend to evaporate at the melting temperature of vanadium (Li, Ca, K). Although the low-Z elements are practically all

good radiologically, some of them may produce hazardous chemical compounds, such as HF, HCN, and BeO. Low fractions of other alloying elements may also be acceptable. For example, 10% of a Safety Grade D element and 1% of a Safety Grade E element would have safety hazards comparable to that of a pure Safety Grade C element.

The current candidate vanadium alloys, such as V-15Cr-5Ti are only model alloys used for preliminary studies. Further development of multicomponent alloys will be needed to achieve optimum thermal, mechanical, and neutronic properties. Metallic alloying additions more radiologically benign than Cr and V are hard to find. Although Ti is not ideal, its long-lived activation products (such as ^{42}Ar) are easy to remove during reprocessing. Isotopes posing safety hazards (such as Sc) can be allowed to decay before reprocessing is begun. Although it may be difficult to find better alloying elements for vanadium than Cr and Ti, it is still worthwhile to explore the possibilities for vanadium alloys which contain small amounts of other low-activation elements (Table 8).

Recycling Procedures

Various procedures for recycling and disposal may be applicable, depending upon the surface dose rate of the component. Let H_s = alloy surface dose rate (Sv/h), H = dose rate to worker (Sv/h) and D = effective annual dose to a worker (Sv). For estimating the worker dose the following assumptions are made:

1. The worker gets 4 weeks vacation and holidays, and 3 weeks are spent on other activities, such as equipment maintenance, so exposure occurs 45 weeks/y, 40 h/week. (The vacation and holiday periods and h/week vary greatly from one country to another, so this assumption has limited validity.) Then the worker is exposed to the recycled materials for 1800 h/y, and

$$D = 1800 H.$$

2. The average size of the vanadium objects handled by the worker is comparable to a hollow sphere with radius $R = 1$ m. (For thick objects, Compton scattering of gamma rays escaping from the surface would soften the gamma energy spectrum and reduce the worker dose.)

3. The effective distance for exposure is the reciprocal of the root mean inverse square of the worker's distance r from the center of the object during an 8 hour working day:

$$r_{\text{eff}} = \left[\frac{1}{8} \int_0^8 dt / r^2 \right]^{-1/2} \approx 2 \text{ m}.$$

4. It is required to keep the annual worker dose below 10 mSv (1 rem).²²

As a consequence of assumptions 2 and 3, the effective average dose rate experienced by the worker is

$$H = (R/r_{\text{eff}})^2 H_s = (1/4) H_s$$

so

$$D = 450 H_s.$$

If the object radius R were larger than the assumed 1 m, then the $(R/r)^2$ factor would be larger, increasing the effective dose rate, and additional precautions might be needed. We will consider the

procedures to be used in various surface dose rate regimes.

$H_s < 10 \mu\text{Sv/hr}$: Hands-on processing

If $H_s < 10 \mu\text{Sv/h}$, then $D < 4.5 \text{ mSv}$, which is comparable to the average annual dose from background radiation (3.6 mSv in the USA). For this case true "hands on" refabrication techniques may be used, with conventional saws, drill presses, lathes, milling machines, and other equipment. Film badges and dosimeters would be worn. Cutting, grinding, and welding operations should have a forced air flow removing particulates and fumes, to prevent their inhalation by the worker.

$10 < H_s < 100 \mu\text{Sv/hr}$: Modified hands-on processing

In this regime some added precautions should be used to achieve dose rate reduction factors up to 10. Parts not being worked on should be stored in shielded rooms away from the work area. The worker should minimize the time spent close to the alloy. Daily whole body and hand doses will be carefully monitored with dosimeters and film badges, to ensure that safe practices are being followed. When substantially radioactive pieces are being machined, a shadow shield is used between the worker and the alloy, as illustrated in Figure 14. The worker will be exposed to a higher dose rate only while mounting the object on the machine. Small objects should be handled with tongs, and large objects, with an overhead crane, to increase their distance from the worker. These added precautions will effect an order of magnitude reduction of the effective dose rate, so that "modified hands-on" processing may be done. Many fabrication procedures (such as extrusion, rolling, flange machining and welding) will be done on a highly automated basis, even with unirradiated materials, so the machining by a human illustrated in Figure 14 may be an exceptional case, rather than the general procedure, for most components.

Figure 14. Machining a vanadium alloy tube with a partially shielded lathe.

$0.1 < H_s < 1$ mSv/hr: Quasi-remote processing

In this regime dose rate reduction factors up to 100 are required. Radiation scattered off floors, walls, and ceilings may be significant. The worker could work in a shielded cab, as illustrated in Figure 15. Alternatively, fully remote handling equipment could be used, as described below.

$1 \text{ mSv/hr} < H_s < 10 \text{ mSv/hr}$: Remote processing

In this regime hot cells, robots, and fully remote handling equipment would be required. The cost of machining and fabricating components with fully remote equipment is not estimated here. The remote handling equipment has high capital cost, maintenance cost, and operating cost (due to slow throughput). Recycling would be economically attractive when

$$\text{Cost (reprocessing \& recycling)} < \text{Cost (waste disposal)} + \text{Cost (new alloy)}.$$

Figure 15. A worker in a shielded cab.

Materials with dose rates > 10 mSv/hr are routinely handled in hot cells, but are not considered here for two reasons:

- (1) The initial vanadium alloy will consist of very pure metals. After irradiation, most of the radioactive isotopes (^3H , ^{42}Ar , ^{45}Ca , ^{42}K , ^{54}Mn) can be removed by melting the alloy. Therefore, it is likely that the surface dose rate can be below 10 mSv/hr during fabrication.
- (2) Highly radioactive materials would be less desirable for recycling as reactor components. The 10 mSv/hr value is not a clearly-defined limit, but rather a nominal value used for illustrative purposes.

Discussion

The initial purification processes have a high probability of attaining the desired impurity levels to achieve at least "modified hands-on" reprocessing. The main uncertainties are the number of stages needed and the costs. The techniques for remote handling and cooling have been well developed by the fission reactor industry and defense laboratories. The remelting process for radioactive vanadium alloys looks good in principle, but it needs to be tested experimentally on a small scale, to quantify separation factors and to identify problems.

Figure 16. Vanadium recycling doses and potentially useful computer codes.

Some potential dose mechanisms are illustrated in Figure 16. The potential doses to workers and to the public should be estimated at each stage, to fully assess the recycling process.

The main uncertainty is the impurity levels present in the fabricated reactor components. These should be studied parametrically, to determine what dose rates would accrue for postulated impurity levels. Since tiny fractions of impurities would not have much effect on neutron propagation, the neutronics codes can establish the one-dimensional neutron energy spectrum without knowledge of the exact impurity concentrations.

The routine effluents of concern are volatile elements, such as tritium and ^{42}Ar . Tritium permeation rate calculations are well established, and argon is easier to contain, so the routine effluents can be readily controlled by good engineering practices.

The worker dose is difficult to quantify, because of several factors:

- Vanadium alloy impurity levels are unknown.
- The levels of activated impurities in the coolant and purge gases are unknown.
- The worker man-hour exposure requirements per tonne throughput are unknown.
- Self-shielding effects of 3-dimensional objects are difficult to quantify.

Doses during melting and impurity removal from recycled vanadium can probably be kept very low, using remote handling techniques. The main hazard is accidental release of the volatile isotopes released from molten vanadium, especially ^3H , ^{39}Ar , ^{42}Ar , and ^{54}Mn . (If a cooling time of 60 y is used, then the quantity of ^{54}Mn will be negligible.) Containment of these isotopes can be assured by the use of multiple barriers around the melting equipment: a vacuum chamber, a double wall with a purge gas stream, and an airtight building with air cleanup system, as illustrated in Figure 17. Some V, Mn, and other metals would plate out on the chamber walls. Smolik²³ recommends consideration of electroslag refining for removal of volatile isotopes, in order to minimize loss of vanadium. The volume of waste streams, such as contaminated filters, should also be estimated during the plant design.

Once these hazardous isotopes have been removed by melting the alloy, the dose rates should be low enough for fabrication and assembly. The magnitude of the surface dose rate determines whether the processing can be hands-on, modified hands-on, quasi-remote, or fully remote. If initial impurity levels are low, it may be feasible to recycle the vanadium for many cycles with hands-on or modified hands-on fabrication and reassembly. Experimental investigation of the efficacy of transmutation element removal from vanadium alloys is needed.

SUMMARY

Vanadium alloys with carefully selected constituents and very low impurity levels are promising for their recycle potential. Recycling is useful to conserve space in radioactive waste repositories, to win public acceptance for fusion energy, and to prevent vanadium price escalation. After each cycle in the reactor, the dose rate is initially very high (though not as high as from some alternative materials). Cooling for many years removes short-lived radioisotopes. The dose rate of the alloy after decontamination by vacuum refining may be low enough for "hands-on" fabrication. The concentrated radioisotopes removed during vacuum refining of the irradiated alloy could be sold for commercial applications or disposed as small quantities of concentrated waste.

Although preliminary studies have found attractive recycle potential for vanadium alloys, many questions remain to be answered:

1. What vanadium alloy compositions are optimum for achieving low long-lived radioactivity, good thermal and mechanical properties after irradiation, and satisfactory safety characteristics (reasonable short-lived radioactivity and toxicity)? The effects of low-activation additives (Table 8) on vanadium alloy properties should be studied.

Figure 17. Multiple barriers for containment of volatile isotopes during remelting of an irradiated vanadium alloy reactor component.

2. What impurity concentrations can be attained for troublesome elements (such as Nb, Co, Cu, Ag, Eu, and Ni) by known processes (such as aqueous resin exchange, fractional distillation of VOCl_3 or VCl_4 , and electron beam refining) during the initial purification of vanadium?
3. What fractions of the dominant long-lived radioisotopes (such as ^{42}Ar , ^{46}Sc , and ^{54}Mn) can be removed from irradiated vanadium alloys by vacuum melting or other refining methods? A demonstration experiment is needed.
4. What hazardous transmutation products, if any, continue to accumulate during successive cycles of the alloy through the reactor? Are there effective ways of removing them?
5. How many man-hours of contact with the radioactive materials will be required for vanadium alloy recycle, and what will the average worker dose be ($\mu\text{Sv/tonne}$ of alloy recycled)?

6. How much will the remote handling, storage, vacuum refining, refabrication, and reinstallation processes cost per tonne of alloy recycled?

Much experimental research will be required to answer Questions 1-3. Question 4 can be answered by neutronics analysis, based on purity levels and refining efficiencies determined by that experimental research. The worker dose (Question 5) depends upon the answers to Questions 1-4. An approximate cost estimate (Question 6) could be based upon current technology for titanium manufacture and for reprocessing fission reactor fuels, but no cost estimate has been done yet.

APPENDIX A. BACKGROUND INFORMATION ON VANADIUM

Uses

About 82% of vanadium consumed in the USA in 1983 was used as an alloying element in steel. As a minor constituent (< 0.2%) it strengthens steel by forming hard carbide and nitride precipitates, which promote fine grain size. Vanadium enhances steel's abrasion resistance, toughness, ductility, weldability, and the high temperature strength of various alloys. Vanadium is used to strengthen titanium alloys, such as Ti-6Al-4V. Vanadium compounds are useful as chemical catalysts, such as in the production of sulfuric acid and of synthetic rubber. A variety of vanadium compounds, such as V_3Si and V_3Ga , are superconducting at low temperatures. The Japanese National Research Institute for Metals has wound a V_3Ga coil capable of producing fields up to 17.5 Tesla. The National Bureau of Standards and Westinghouse patented the use of $V_2(Hf,Zr)$ for use in superconducting magnets, because it has the ability to withstand intrinsic mechanical strains generated at fields above 8 Tesla. This alloy may find applications for fusion reactor magnet coils, accelerators, and electrical machinery.

Occurrence

Vanadium is ubiquitous. The average vanadium concentration in the earth's crust is 150 $\mu\text{g/g}$, mostly in the form of insoluble salts. The average vanadium concentration in western US coal is 15 ppm, and that in eastern and interior coals is 30-34 ppm. The emission of vanadium into the atmosphere from coal combustion in the USA in 1969 was about 2100 tons. Vanadium content of petroleum ranges from < 1 ppm (Louisiana, Colorado, New Mexico) to 1400 ppm (Boscan, Venezuela), with most sources having 1-100 ppm. About 12,000-22,000 tons/year of vanadium were released by combustion of residual fuel oils in the US in 1968-70. Vanadium concentration in the air ranges from < 1 ng/m^3 (most states) to 20-60 ng/m^3 (northeastern states), with higher concentrations (> 100 ng/m^3) in a few regions. Vanadium is present in seawater with concentrations of 2-29 $\mu\text{g/litre}$, and the total amount present is about 7.5×10^{12} kg. It is present in fresh water rivers in concentrations of 0.3-20 $\mu\text{g/litre}$, with some concentrations in Wyoming, Montana, and the Dakotas over 100 $\mu\text{g/litre}$. The vanadium concentrations in various plants, animals, and foods are typically 0.1 - 1 $\mu\text{g/g}$.²⁴

Vanadium Resources

Vanadium is usually produced as a by-product of another element, such as iron, uranium, or phosphorus, with smaller quantities recovered from clays, petroleum residues, and spent catalysts. The main sources of vanadium are listed in Table A1. Vanadium occurs as a fraction of a percent in hematite, and hundreds of ppm in other ores. The world "Reserve" of vanadium is 4800 kte. The world "Reserve Base" of vanadium (including economic reserves, marginally economic reserves, and some sub-economic resources) is 18,300 kte.²⁵

Table A1. Sources of vanadium. 25

major sources:

vanadiferous magnetite (Fe_3O_4)	83% of world production
South Africa, USSR, China	
various petroliferous materials	6% of world production

secondary sources:

pig iron plants
elemental phosphorus smelters
petroleum residues, ashes, and spent catalysts

less important sources: (producing V_2O_5 , V_2O_3 , NH_4VO_3)

acid leaching plants with solvent extraction circuits
salt roasting operations

The United States will need hundreds of GWe additional electrical capacity in the next century. Construction of 250 fusion reactors each using 400 te of vanadium over a 50 year period would consume 100 kte, over half of the United States' 185 kte vanadium "reserves".²⁵ Such consumption would provide an incentive to recycle vanadium. The corresponding consumption rate of 1.6 kte/y would be less than the present total consumption rate of vanadium in the USA, but present consumption is mainly ferrovanadium and pentoxide, with almost no ultrapure vanadium produced. About 2400 kte of vanadium in the USA are classified as "reserve base", which would be more expensive. (The total US "resources" of vanadium are estimated to be about 30 Mte, but recovery of the "resources" would be much more expensive.) In spite of the substantial reserves, large supplies of vanadium are not readily available, because its recovery is usually uneconomical, except as a by-product.

Environmental and Health Concerns

Vanadium is often associated geochemically with uranium and thorium, which have radioactive mining and mill tailings. Environmental regulations limit the amount of radon gas that can be released from such tailings to below 20 pCi/m²-s.

Trace amounts of vanadium are essential to physical processes in some animals. The sea squirt, a marine chordate, concentrates vanadium to 4% in its blood. Humans contain about 10-25 mg of vanadium, in intestines, blood serum, bones and teeth, and it appears that vanadium may have some beneficial effects on cholesterol levels, iron metabolism, and prevention of dental caries.²⁴

In higher concentrations vanadium is toxic to animals both as a cation and as an anion. Toxicity increases with valence, and pentavalent vanadium is most toxic. Vanadium irritates mucous tissues of the respiratory tract. Most airborne vanadium contamination occurs from combustion of coal and fuel oil. Breathing dust containing vanadium or vanadium compounds at concentrations of several mg/m³ produces symptoms of cough, sputum, wheezing, eye, nose, and throat irritation. Prolonged exposure results in labored breathing, pneumonia, nausea, diarrhea, loss of appetite and emaciation. In some

cases, it also produces weakness, neurasthenia, and slight anemia. Vanadium can be detected in urine for up to two weeks after exposure. The recommended threshold exposure limit (NIOSH) is 0.05 mg/m³-air for vanadium compounds, and 1 mg/m³-air for metallic vanadium or vanadium carbides.²⁶ For comparison, the recommended exposure limit for beryllium is 2 mg/m³ (chronic) or 25 mg/m³ (acute).²⁷

Properties of Vanadium:

Some properties of vanadium are listed in Table A2. To avoid rapid oxidation of vanadium at high temperatures, the oxygen concentration in the coolant must be kept very low. With helium coolant at high temperatures, oxidation can be a serious problem.

Neilson and colleagues studied the oxidation and volatility of vanadium alloy at various temperatures. In a high neutron flux, transmutation products would include Sc and Ca. Sc was added to V, to observe the rates at which it diffused out and vaporized at high temperatures. No calcium could be added, because it evaporated away during arc melting of the alloy buttons. The oxide forming above 10 Pa (oxygen) was predicted to be V₂O₅ (melting at 670 C), and below 10 Pa it was predicted to be VO₂ (melting at 1545 C). However, it appeared that V₂O₅ did not form below 1000 Pa of O₂. Minor amounts of Cr and Ti were observed in the oxide layer. The volatility of Sc was not detectable below 1200°C. At 1586°C its volatility was 110 ppm/h, and at very high temperatures (~ 2600°C), it was 30,000 ppm/h. Below 1600°C the maximum volatilities of V, Cr and Ti were 2000, 160 and 50 ppm/h, respectively.²⁸

Table A2. Properties of Vanadium Metal.

Melting point = 1890°C

Boiling point = 3350°C

Density = 6100 kg/m³

Atomic weight = 50.942

Vapor pressure: $\log_{10} p(\text{Torr}) = -26,650/T - 0.000112 T + 10.815$

Latent heat of sublimation = 9850 kJ/kg at melting point (119.9 kcal/mole)

**$C_p = 444 + 0.164 T \text{ J/kg-K}$ (298-1900°C)
For V-5Ti-5Cr, $C_p = 391 + 0.227 T(\text{K}) \text{ J/kg-K}$**

Coefficient of linear thermal expansion (200-1000°C) = $8.95 \times 10^{-6}/\text{C}$

Resistivity at 20°C = 24.8 microohm-cm

Superconducting below 5 K

Poissons ratio = 0.36

Youngs modulus = 136 GPa (19.7×10^6 psi)

Exposure limit for vanadium metal in air²⁹ = 1 mg/m³

Exposure limit for V₂O₅ in air = 0.05 mg/m³

Immediate Danger to Life and Health (IDLH) for V₂O₅ in air = 70 mg/m³

Vanadium Production and Demand

The major producers of vanadium are listed in Table A3. US demand for vanadium, which fell from 9.3 kte in 1979 to 3.0 kte in 1983 due to a world decline in steel production, is expected to reach 10-17 kte/y by the year 2000, with a probable value of about 13 kte/y, as shown in Table A4. There is little demand for production of vanadium metal at present. Most vanadium is supplied to the steel industry in the form of ferrovanadium.

Table A3. World annual vanadium pentoxide production capacity, as of December 31, 1990.³⁰ This includes vanadium pentoxide in vanadiferous iron slags and petroleum refinery residues.

<u>Country</u>	<u>Rated Capacity, te/y</u>
Australia	1,500
Canada	770
Chile	2,300
China	8,200
Republic of South Africa	27,200
USSR	9,500
USA	11,000
Venezuela	2,500
Other	550
Total	63,520

Table A4. US vanadium demand in 1983 and forecast for year 2000, kte/y.²⁵

	<u>1983</u>	<u>2000</u>
Construction & industrial machinery	0.35	1.64
Metalworking machinery	0.41	1.27
Building & heavy construction	0.45	2.27
Oil & gas industries	0.09	0.91
Mining, quarrying, lumbering	0.05	0.27
Transportation equipment	1.23	4.64
Chemicals	0.05	0.45
Other	<u>0.37</u>	<u>1.45</u>
totals	3.00	12.9

Economics

As of 1987, the United States imposed import duties on ferrovanadium, vanadium metal, and vanadium chemicals of 4-11% (Most Favored Nations) and 25-40% (other nations), but no duties on vanadium ore, concentrate, or vanadium-bearing slags or residues. In 1984 the USA had 0.49 kte of vanadium (as pentoxide) in its strategic metals stockpile, with goal of increasing the stockpile to 7.9 kte.

From 1963 to 1983 the cost of vanadium pentoxide varied between \$5 and \$10 per pound (1984 dollars). Since V_2O_5 is about 56% vanadium by mass, the effective cost of vanadium metal is twice as high, not including refining and fabrication costs. The 1992 price of V_2O_5 was about 2.3 \$/lb = 5.1 \$/kg. The price of vanadium alloys is about 100 \$/lb, which would increase to about 150 \$/lb (330 \$/kg) for high purity alloys (with a factor of 100 reduction in Nb content).³¹

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