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SLAG RECYCLING OF IRRADIATED VANADIUM

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SLAG RECYCLING OF IRRADIATED VANADIUM

**Submitted in Partial Fulfillment of the Requirements for Graduation
with Honors to the Department of Biology and Chemistry
at Carroll College, Helena, Montana**

Patricia Kathleen Gorman

April 7, 1995

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MASTER

This thesis for honors recognition has been approved for the
Department of Biology and Chemistry

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April 7, 1995

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Abstract

SLAG RECYCLING OF IRRADIATED VANADIUM

by Patricia Kathleen Gorman

An experimental inductoslag apparatus to recycle irradiated vanadium was fabricated and tested. An experimental electros slag apparatus was also used to test possible slags. The testing was carried out with slag materials that were fabricated along with impurity bearing vanadium samples. Results obtained include computer simulated thermochemical calculations and experimentally determined removal efficiencies of the transmutation impurities. Analyses of the samples before and after testing were carried out to determine if the slag did indeed remove the transmutation impurities from the irradiated vanadium.

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1.0 INTRODUCTION

Increasing interest in the application of fusion reactors as an alternative nuclear energy source has led to an interest in investigating potential materials to be used as blanket layers in these reactors. The most important criteria for these materials are safety, mechanical properties, performance, and options for disposal and recycling. Many different metals and alloys are under consideration for use in a fusion reactor. Vanadium, one of the chosen metals, meets the first criterion by demonstrating superior safety in environmental characteristics such as low off-site radiation doses from hypothetical accidents (Butterworth, McCarthy, Smolik, & Forty, 1994). Vanadium alloys, i. e. V-5Ti-5Cr, also appear to be excellent candidates for multiple recycling in high vacuum remelting and refining processes such as electroslag and inductoslag remelting.

These vanadium recycling options involve remelting the alloy in one of the processes to remove the radioactive impurities and reclaiming the metal for further use in the fusion reactor. In short, low radiation materials have an important contribution to make towards the development of fusion as a safe and environmentally friendly energy source. Vanadium alloys may provide the key to this contribution, but before it can be used as a fusion material it is imperative to demonstrate a process to recycle the alloy.

Successful recycling of vanadium alloys following 14 MeV neutron irradiation in a fusion reactor depends on a number of factors. Pre-irradiation impurity levels, alloy composition, in service time period, and post-irradiation cooling time are a few variables affecting the success of a recycling process. It is a fair assumption that the recycling method chosen must be able to adapt to changes in the above variables. The most significant change that can be foreseen at this time is a change in the post-irradiation composition. A change in the post-irradiation composition forces a change in the recycling process or requires the recycling process be modified to accommodate the composition change. The recycling process of choice must also meet the following criteria. First, the recycled vanadium product must be easily integrated back into the current vanadium industry production process. Second, the vanadium recycling process must minimize secondary waste streams and minimize the generation of mixed hazardous wastes.

With this in mind, the inductoslag and the electroslag methods have been proposed as possible candidates for this recycling process. The electroslag and inductoslag processes' success are dependent upon using the correct recycling components. One such component, the slag, is used in these processes to "scavenge" for radioactive impurities within a recyclable material such as vanadium. The slag must contain components that are able to bind with the impurities and pull them out of the vanadium and into the slag. This will enable the disposal of just the slag instead of the entire vanadium unit, resulting in less volume to dispose of. However, if the correct formula of slag components is not found, another process will have to be developed in order to recycle the irradiated vanadium.

In order to find the slag with the right chemistry for purifying the vanadium alloy, the information from previous related work and computer simulated thermochemical calculations will be combined and studied. Once a reasonable formula has been predicted to work, the slag will be experimentally tested in both the electroslag and inductoslag processes. The resulting products will then be analyzed to see if the slag did indeed pull the impurities out of the irradiated vanadium. However, for safety reasons the, vanadium used in these experiments will not have the irradiated forms of the impurities.

2.0 BACKGROUND INFORMATION

Recycling fusion reactor materials is thought to be a key to the success of the entire fusion power reactor concept. Fusion reactors are predicted to be in use within the next thirty years, however the only way this will be possible is if the recycling process can be proven cost effective and environmentally friendly. The best way to approach these goals is to find ways to recycle the materials in order to reduce the amount of material placed in a repository. To make this possible, starting material impurities in the recycled alloy will need to be reduced as low as possible. The best approach to all of these considerations will then have to be developed further to modify the processes specifically to fusion reactor use.

2.1 Recycled Starting Material Considerations

Recycling and reducing the amount of radioactive impurities in the recycled starting material in fusion reactors is significant for many reasons. Considering the two broad areas of operation, operational aspects and solid waste management, illustrates the motivation for reducing radioactive impurities, as shown in Figure 2.1 (Butterworth, 1989). This figure illustrates that it is important to employ low radiation materials for the safety of the workers operating and maintaining the reactor as well as for the reduction of radioactive waste.

Butterworth and Dolan addressed the impact of impurities in vanadium recycling from a radiological standpoint (Butterworth & Dolan, 1993 and Butterworth, 1991). These researchers generally accept that the lower impurity levels attained in the starting vanadium dramatically reduces the number of transmutation isotopes produced during irradiation. The removal of select key impurities prior to radiation will also reduce the overall difficulty of vanadium recycling. Another concern about the impurities is the affinity for vanadium to dissolve interstitial elements, i.e., oxygen, carbon, hydrogen, and nitrogen. These elements affect not only initial mechanical properties, but also changes resulting from radiation effects. Although exact levels of these impurities needed to meet the requirements for applications in fusion reactors are not completely known, some data are available. When considering the vanadium alloys using a 5 weight percent titanium and a 5 weight percent chromium composition, the starting materials of these alloys depends on a number of variables including; natural source, process of extraction, and handling. Limits for the various interstitial impurities are not set.

Figure 2.1 - Areas of operation for which low radiation materials may be advantageous (Butterworth, 1989)

2.2 Recycling Considerations

The recycling effort should start as soon as possible following removal from the reactor. This course of action is recommended for two reasons. First the vanadium alloy can be brought back into service following irradiation much faster. Also if certain isotopes can be removed easily early, they will not decay to an isotope that is more difficult to remove from the alloy. The time period is certainly up to debate and is dependent upon a number of factors, including the length of time required to move the vanadium from the reactor to the recycling plant. For this reason, a period of one year seems reasonable for placement into a recycling plant, for this study.

2.3 Recycling Options

After the vanadium has been in storage, researchers propose that the vanadium be placed through a purification operation to remove the rest of the transmutation products. Selecting a candidate purification process is an important step in recycling irradiated materials. The selected possible candidates include the iodide process, the chloride process, pyrovacuum processing, fused salt processes, and slag remelt processes.

The iodide process is a vapor distillation process. It involves mixing the impurity containing metal with iodine and placing it into a quartz vessel. The quartz vessel contains a tungsten wire mounted to the glass-to-metal seal. The air evacuated system heats to 900 to 1000° C and the tungsten wire heats to incandescence by a controlled current. The vanadium di-iodide (VI_2) dissociates in the immediate vicinity of the hot wire, and the metal deposits on it. Then the iodine releases and recirculates back to the molten irradiated metal (Rostoker, 1958). This is one of the few, or perhaps the only, process that could reduce nitrogen levels. Some disadvantages appear to be: 1) the process is a batch method employing only small quantities of material (the largest quantity of vanadium processed is 2 pounds), 2) the reaction forming the VI_2 is slow, and 3) the product formed on the hot filament by decomposition of VI_2 and recirculating iodine is small crystals.

The chlorination process, which also uses vapor distillation for purification, has some advantages and disadvantages in recycling irradiated material. The process can recover other elements, including some in large quantities, e.g., copper, magnesium, etc. The dissociation temperature of the vanadium chlorides is low, less than 500° C (Morgan, Schad, Zakak, 1978). A disadvantage, however, is that an oxychloride, $VOCl_3$, forms and distills along with other vanadium chlorides. Therefore, this process does not effectively remove oxygen.

The purity levels obtained from the fused salt methods, as reported by Singh, were for one electrolysis. Other investigators, using a double-refinement process achieved much purer material. Singh also mentions that the fused salt electrolyses process was particularly useful for vanadium, due to the high volatility of this metal which presents a problem with pyrovacuum processing.

Pyrovacuum arc melting can sometimes be effective in reducing the levels of oxygen, nitrogen, and hydrogen in metals. In fact, this method is currently the method of choice in forming the vanadium titanium chromium alloy. Preferential vaporization of some species, such as some oxides, will occur when the concentrations of the gaseous species are low, i.e., a good vacuum is maintained. Singh points out that the ability for refinement depends upon the ratio of the impurity concentrations in the gas phase evaporation mixture compared to that in the molten metal. Although vanadium can achieve some deoxidization, it has an oxygen ratio in the gas phase to that in the melt of about six. This ratio, which is lower than those for Nb, Ta, and Hf, means that a greater relative amount of vanadium metal would evaporate to achieve a given reduction in oxygen concentrations. In fact, Singh points out that with an R value of ten, 10% of the metal would be lost while reducing the oxygen level by one-half. "Getters" may be used to aid in absorbing impurities. Practically, however, the vapor pressure of the impurity should be greater than 10^{-3} torr at the working temperature and it should exceed the vapor pressure of the metal by more than a factor of ten.

Butterworth also proposed several methods of remelting vanadium. These include non-consumable electrode arc melting, plasma arc melting, electroslag melting, and inductoslag melting. The first two methods utilize a vacuum environment. However, a substantial loss of vanadium would result due to volatilization as identified by the previous work described for pyrovacuum treatments. The latter two methods, however, have the potential of reducing the loss of vanadium while removing impurities due to the protection imparted by the slag covering the molten material.

Until recently, pyrovacuum arc melting (VAR) was the most widely used. Yet, during the past ten years, use of the electroslag remelting process (ESR) has become more common. Just recently, the inductoslag remelting process (ISR) has become a point of interest. Most of the work in inductoslag research has been carried out on steel based alloys. Some work has been done on metals with similar chemistry to vanadium. These metals include titanium and zirconium. However, as far as it is known there are no documented cases of using vanadium in the electroslag and inductoslag processes.

2.4 Definition of Slag

Both the inductoslag and electroslag remelting processes use a recycling component called a slag. The slag is a compound specifically designed for the chosen irradiated metal and its impurities. It is placed in a copper crucible along with the irradiated metal before both processes begin. Therefore, as the metal and slag mix during melting, the slag attaches to the impurities and "pulls" them out of the metal.

2.5 Optimum Physical Properties of Slags

The slag used in both the inductoslag and electroslag remelting processes must have a composition specific to the metal being recycled. Observations of various slags have provided convincing evidence that physicochemical properties of the slags are of prime importance in establishing successful remelting processes. Knowledge of the thermodynamic properties of molten slags is also of importance. Optimum properties of an ideal slag include: (1) the liquid temperature of the slag should be slightly lower than of the metal to be melted, (2) the density of the slag must be less than that of the metal at its melting point, (3) the electrical conductivity of the slag should be as low as possible for economical operation, (4) the heat of fusion of the slag should be low enough for easy melting, (5) low thermal conductivity should provide an insulating cap on the ingot, (6) the viscosity should be sufficiently low to promote effective stirring for gas removal at the slag-gas interface, yet high enough for maximum metal droplet exposure for maximum refining, (7) the slag should possess a low vapor pressure at the high temperature obtained during the remelting process, (8) the slag should possess as high a surface tension as possible, (9) the slag should possess a relatively large solidification range for optimizing ingot surfaces, (10) the slag should be stable at high temperatures and be compatible with the metal to be melted at such high temperatures, (11) the primary slag phase should possess a melting point lower than that of the metal to permit solid slag skin to form between the ingot and mold during melting. The skin is responsible for smooth, workable ingot surfaces (Nafziger, 1976).

2.6 Slag Systems

Most of the investigations dealing with slags have been in search of finding a slag satisfying as many of the items in the aforementioned list. It has been suggested that halides are the most suitable anionic materials for inductoslag and electros slag. Borides, carbides, and nitrides are not used because they melt at temperatures too high for practical use or decompose at temperatures greater than 1000 C (Nafziger, Lincoln, & Riazance, 1976). Alkali and transition metal halides as well as most chlorides, bromides, and iodides are unusable because they have too high of vapor pressures for the remelt processes. They are also unstable at the temperatures and pressures of interest. Therefore, the materials are limited to alkaline-earth metals and lanthanon (rare earth plus Yttrium) fluorides.

3.0 METHODS AND MATERIALS

The success of the inductoslag and electroslag processes lies within the correct composition of the slag. To find the correct composition, many factors need to be explored. Studying previous slag work performed on titanium is important because its chemistry is very similar to vanadium. Titanium slag work may lead to important clues as far as to what works with the vanadium. Computer equilibrium calculations may also help in determining a suitable slag. By studying the graphs produced by the program calculations, a potential slag can be selected for experimentation and unsuitable slag compositions can be eliminated.

3.1 Impurities

The first step in finding the correct slag for recycling vanadium was to determine what radioactive impurities would be present in the vanadium after use in the reactor. In order to predict the impurities a computer code was used called REAC*3 (Mann, 1990). This code predicts how a metal reacts to 14 MeV irradiation with respect to transmutations formed. The predicted impurities in the vanadium are shown in Table 3.1. The impurities used in this study were chosen by the amount present after irradiation and by availability for experimentation. The most critical impurities that will be present in the vanadium alloy are thought to be argon, calcium, manganese, and scandium. Therefore, these impurities will be placed in the vanadium alloy for the remelt experiments. However, yttrium will be used instead of the scandium because of its scarcity. Scandium has been used in the thermochemical computer calculations because it reacts chemically similar to yttrium.

3.2 Slag Investigation

An investigation of possible slags was carried out through research on what has been done on similar metals, such as titanium. The reason, as mentioned before, is that vanadium's chemistry is very closely related to titanium's. The first step to identify potential slags was to analyze available literature data for important physical properties of some candidate fluoride slag compounds as well as representative reactive metals (Table 3.2). Note that LaF_3 , CaF_2 , and SrF_2 , have melting points that are closest to the melting point of vanadium. The closer the slag melting point is to the vanadium melting point,

Table 3.1. Contact dose rate (R/hr) calculated with REAC*3

At Shutdown		1 year		10 years	
Element	R/hr/cm ³	Element	R/hr/cm ³	Element	R/hr/cm ³
v	1.52E+02	sc	7.25E-02	nb	1.27E-07
sc	2.70E+01	co	6.76E-04	ag	7.38E-08
ti	6.69E+00	mn	4.13E-04	al	4.36E-08
cr	2.77E-01	cr	2.80E-05	mo	2.81E-08
al	1.26E-01	ag	3.57E-06	co	8.86E-10
na	7.24E-02	y	6.54E-07	hf	3.49E-12
n	3.22E-02	nb	2.84E-07	pt	4.70E-14
ca	2.03E-02	fe	1.66E-07	ni	1.20E-14
mg	1.27E-02	zr	7.05E-08	ir	5.00E-15
mn	7.55E-03	al	4.36E-08	v	4.00E-15
co	5.81E-03	mo	2.86E-08	pb	7.21E-16
mo	1.16E-03	rh	3.66E-09	lu	5.28E-22
tc	4.45E-04	hf	3.05E-10	mn	3.20E-38
ni	2.00E-04	ca	6.14E-11	pd	0.00E+00
p	1.88E-04	v	2.87E-11	fe	0.00E+00
nb	8.31E-05	lu	8.84E-12	h	0.00E+00
fe	6.12E-05	hg	2.56E-12	c	0.00E+00
c	5.22E-05	ru	1.72E-12	p	0.00E+00
cu	4.07E-05	tl	1.98E-13	si	0.00E+00
ag	1.88E-05	pt	1.86E-13	be	0.00E+00
y	1.01E-05	ir	1.03E-13	zr	0.00E+00
zr	6.32E-06	pd	2.40E-14	os	0.00E+00
b	5.33E-06	ni	1.20E-14	bi	0.00E+00
pb	5.07E-06	pb	7.21E-16	ti	0.00E+00
si	2.86E-06	os	5.45E-17	cr	0.00E+00
pd	5.42E-07	s	0.00E+00	y	0.00E+00
k	2.25E-07	be	0.00E+00	cd	0.00E+00
hf	1.95E-07	p	0.00E+00	zn	0.00E+00
s	1.48E-07	si	0.00E+00	cl	0.00E+00
rh	2.71E-08	h	0.00E+00	s	0.00E+00
tl	4.12E-09	c	0.00E+00	o	0.00E+00
o	3.20E-09	cl	0.00E+00	n	0.00E+00
ru	1.23E-09	zn	0.00E+00	au	0.00E+00
pt	6.01E-10	cd	0.00E+00	cu	0.00E+00
hg	5.99E-10	ti	0.00E+00	tl	0.00E+00
lu	8.30E-11	f	0.00E+00	hg	0.00E+00
au	6.19E-11	bi	0.00E+00	b	0.00E+00
yb	4.53E-12	au	0.00E+00	ru	0.00E+00
ir	3.38E-12	na	0.00E+00	ca	0.00E+00
os	6.12E-17	li	0.00E+00	ta	0.00E+00
be	0.00E+00	k	0.00E+00	mg	0.00E+00
h	0.00E+00	he	0.00E+00	na	0.00E+00
zn	0.00E+00	yb	0.00E+00	li	0.00E+00
cl	0.00E+00	mg	0.00E+00	k	0.00E+00
ta	0.00E+00	b	0.00E+00	f	0.00E+00
cd	0.00E+00	tc	0.00E+00	sc	0.00E+00
bi	0.00E+00	o	0.00E+00	yb	0.00E+00
f	0.00E+00	cu	0.00E+00	he	0.00E+00
sr	0.00E+00	sr	0.00E+00	sr	0.00E+00
total	1.86E+02	total	7.37E-02	total	2.73E-07

the more compatible and successful the system will be. The slag melting point must not exceed that of vanadium.

Table 3.2 - Selected properties of materials for remelting ¹

Material	mp, °C	bp, °C
MgF ₂	1,246	2,227 (5)
CaF ₂	1,423	~2,500 (4)
SrF ₂	1,462	2,477 (5)
BaF ₂	1,346	2,200 (5)
YF ₃	1,149	2,227 (1)
LaF ₃	1,487	2,327 (1)
Titanium	1,675 (4)	3,285 (2)
Zirconium	1,815 (3)	4,400 (2)
Vanadium	1,910 (3)	~3,350 (2)

¹ Numbers in parentheses refer to references below

1. Gibson, Miller, Kennedy, and Renstorff, 1959
2. Kubaschewski, Evans, and Alcock, 1968
3. Maurakh, 1964
4. Weast, 1966
5. Wicks and Block, 1963

An optimal property of a slag is that the slag be less dense than the vanadium at melting temperatures. Table 3.3 shows that all of the possible slags have a density lower than vanadium when in liquid form. This is important so that the slag will float to the top during the remelting process, making it easier to remove it after the remelt run.

Further, YF₃ systems can only be used if the YF₃ content remains less than 40 wt. %. YF₃ systems are preferred over the LaF₃ systems because of better electroconductivity. Overall, CaF₂ systems are still the most preferred slag system. Nevertheless, researchers concluded that no single slag composition is ideal from the standpoint of all the considered parameters (Nafziger, Beall, Ausmus, & Dunham, 1976)

Table 3.3 - Densities of molten fluorides at or slightly above melting points
of reactive metals

Metal	Titanium	Zirconium	Vanadium
Temperature.....°C	1,675	1,835	1,930-1,940
Density (g-cm ⁻³) of-			
Metal	4.11	6.06	5.734
CaF ₂	2.417	2.358	2.319
SrF ₂	3.33	3.23	3.126
BaF ₂	3.824	<3.75	<3.75
MgF ₂	2.213	2.133	<2.125
LaF ₃	4.462	4.357	4.29

(Kirshenbaum, Cahill, & Stokes, 1960 and Maurakh, 1964)

Since CaF₂ is the most preferred slag by most researchers, it has had the most experimentation conducted on it. Therefore, most of the information available is about the slag CaF₂. During research with CaF₂, many agents have been experimentally added to remove problem inclusions and impurities. Small amounts of reducing agents were added to CaF₂ slags to remove oxygen from the molten metal during the remelting process. Relatively volatile constituents were also added to assess the selective removal of gaseous impurities. Taking all of this into consideration, the following slags have been used with titanium.

1. CaF₂, reagent, acid-grade, native fluorspar
2. Additions to CaF₂:
 - 1,3,5 wt. % C
 - 2,5 wt. % Y
 - 5 wt. % K₂TiF₆
 - 5, 7.5, 10, 20, 23, 30, 58, wt. % CaCl₂
 - 18.5 wt % SrF₂
 - 4, 12 wt. % MgF₂
 - 4 wt. % MgF₂ - 50 wt % LaF₃
 - 1 wt % C - 9 wt % MgF₂
 - 20, 52, 75, wt. % LaF₃
3. MgF₂
4. Addition to MgF₂: 20 wt. % LaF₃
5. LaF₃
6. BaF₂

(Nafziger, Beall, Ausmus, & Dunham, 1976)

Extensive testing has shown that approximately one-half of the tested slag compositions mentioned previously give satisfactory operating conditions and results (Nafziger, et. al., 1976). Degassing was observed in the slags using MgF_2 . This is due to the less stable nature of this compound at operating temperatures. LaF_3 tends to become trapped in the metal because of its density. The best operating conditions obtained were with either the acid or reagent grade CaF_2 slag (Nafziger, et. al., 1976). It is also important to point out that the top CaF_2 slag can be reused without affecting impurity concentrations. This is imperative from the economical standpoint of the inductoslag and electroslog processes. Unfortunately, side wall, slag is not able to be reused because of contamination (Nafziger, et. al., 1976).

3.3 Chosen Slags

The slags considered for the vanadium remelt processes included CaF_2 , MgF_2 , LaF_3 , SrF_2 , and BaF_2 . However, MgF_2 was eliminated because degassing exists in this slag due to its unstable nature at temperatures needed to run the remelt process. LaF_3 was also eliminated because of its tendency to be trapped in the recycled metal. Therefore, CaF_2 , SrF_2 , and BaF_2 , are the candidate fluoride slags needing thermochemical calculations.

Other slags were also selected for thermochemical calculations because of their potential removal capabilities. They include: $\text{CaF}_2\text{-CaO}$, Al_2O_3 , SiO_2 , and SnO_2 . Unfortunately, oxygen slags react violently with vanadium so these slags could not be used in experimentation. Inclusions of O_2 may also be a problem in the recycled vanadium. It is very likely that the O_2 would alter the physical properties of the metal enough so that the vanadium would be useless for further reactor use.

3.4 HSC Chemistry

After possible candidate slags were selected from titanium studies, the slags were placed into a computer equilibrium program with the vanadium alloy used in the experiment. The alloy that is used in fusion reactors is vanadium with five weight percent chromium and five weight percent titanium. Therefore, this alloy was placed in the calculations and in the experiments. As stated before, the impurities that will be present in the alloy for experimentation are argon, calcium, manganese, and yttrium.

Since the electroslag and inductoslag processes have not been carried out on vanadium, the best slag will need to be determined through the previous information on titanium slags, computer calculations and experimentation. The computer calculations will be used to determine the equilibrium compositions of each system containing the metal and slag. After a possible slag has been estimated, testing will be done using the slag in the remelt process of irradiated vanadium.

The computer program used to estimate the equilibrium compositions of the metal and slag systems is Outokumpu HSC Chemistry. The program utilizes an extensive thermochemical database which contains enthalpy (H), entropy (S), and heat capacity (C) data for more than 7600 chemical compounds. HSC Chemistry carries out chemical experiments in the memory of the computer using the SOLGASMIX code. If given raw materials, amounts, and conditions of a chemical process, the program will give the amounts of the product as a result.

The SOLGASMIX provided with the HSC package is a modified version of the original code from the University of Umea, Sweden. The modification allows the use of grams as input and in that case the result is given both in molar fractions and moles as well in weight percentages and grams. The input file has, therefore, $1+N$ additional rows where N is the number of system components (Roine, 1994).

3.4.1 Physical Background of H, S, C, and G

Thermochemical calculations are based on enthalpy H, entropy S, heat capacity C_p , or Gibbs energy G values for chemical species. The thermochemical enthalpy, entropy, and Gibbs energy functions for chemical reactions are calculated as a difference between the products and reactants, using Equations (1) - (4). The commonly needed equilibrium constant K, can be calculated using Equation (6) (Roine, 1994).

$$\text{Chemical reaction: } aA + bB + \dots = cC + dD + \dots \quad (1)$$

$$\begin{aligned} \text{Enthalpy of reaction: } \Delta H_r &= \sum v_i H_i(\text{Products}) - \sum v_i H_i(\text{Reactants}) \quad (2) \\ &= (c^*H_C + d^*H_D + \dots) - (a^*H_A + b^*H_B + \dots) \end{aligned}$$

$$\begin{aligned} \text{Entropy of reaction: } \Delta S_r &= \sum v_i S_i(\text{Products}) - \sum v_i S_i(\text{Reactants}) \quad (3) \\ &= (c^*S_C + d^*S_D + \dots) - (a^*S_A + b^*S_B + \dots) \end{aligned}$$

$$\begin{aligned} \text{Gibbs energy of reaction: } \Delta G_r &= \sum v_i G_i(\text{Products}) - \sum v_i G_i(\text{Reactants}) \quad (4) \\ &= (c^*G_C + d^*G_D + \dots) - (a^*G_A + b^*G_B + \dots) \end{aligned}$$

$$\text{Equilibrium Constant: } K = \frac{[C]^c * [D]^d * \dots}{[A]^a * [B]^b * \dots} \quad (5)$$

$$\ln K = \Delta G_r / (-RT) \quad (6)$$

Where the following abbreviations have been used:

[A] = activity or partial pressure of species A, B, C, etc.

a = stoichiometric coefficient of a species A in reaction

v = stoichiometric coefficient of a species in reaction (a, b, c ...)

R = gas constant = 1.987 cal/(K·mol) = 8.314 J/(K·mol)

T = Temperature in K (Roine, 1994)

3.5 CaF₂ equilibrium calculations

The CaF₂ equilibrium calculations were the first to be studied because this was the favored slag in the titanium studies. Because the Outokumpu HSC Chemistry for Windows program can only handle five input elements per calculation, a test matrix was created in order to substitute all possible combinations into the program. This matrix will allow the study of how each possible combination of elements reacts together, which in turn will allow for the whole picture to be pieced together.

Table 3.4 - Test matrix for the CaF₂ slag

	V	Ca	Y	Mn	Ti	Cr	CaF ₂
1.	X	X	X	X			X
2.		X	X	X	X		X
3.		X	X	X		X	X
4.	X	X	X			X	X
5.	X	X	X		X		X
6.		X	X	X			X
	V	Ca	Sc	Mn	Ti	Cr	CaF ₂
7.	X	X	X	X			X
8.		X	X	X	X		X
9.		X	X	X		X	X
10.	X	X	X			X	X
11.	X	X	X		X		X
12.		X	X	X			X

*X - indicates inclusion in the numbered calculations

The above matrix (Table 3.4) shows the calculations carried out on the CaF₂ slag with the vanadium alloy and its impurities. Five hundred grams of the vanadium alloy and its impurities was the weight input into the computer program. The impurities within each of the calculations made up for one weight percent each out of the 500 grams. The slag composition input into the calculation was 1/10 molar ratio to the vanadium. The equilibrium calculation ran at the temperatures between 1000 K and 2673 K. The temperature of interest is around 2175 K because that is the melting point for vanadium. For example, the calculations for the vanadium/CaF₂ system are shown below in Table 3.5. The moles calculated for each element in the system was input into the HSC program to observe how the elements would interact with each other at the temperature of interest. Of most interest, was the possible compounds that form. An estimate of the removal efficiency can then be made and compared to experimental results.

Vanadium =	500 grams				
Slag =	97 wt %	+ Impurities	(1 wt % Y,	1 wt % Ca,	1 wt % Mn)
	1/10	molar ratio to			
		the vanadium			
Temperature=	500 - 1900 °C				
Moles of species:					
	V	485 g	(50.95 g/mol) =	9.5210 moles	
	Ca	5 g	(40.09 g/mol) =	1.077 moles	
	Y	5 g	(88.91 g/mol) =	0.0562 moles	
	Mn	5 g	(54.94 g/mol) =	0.0910 moles	
	F	(18.99 g/mol)	*2 =	1.9042 moles	
	CaF ₂	(40.09 g/mol)	+ (18.99 g/mol)	78.077 g/mol	with a 1/10 ratio to V
			*2 =	0.9521 moles	

Table 3.5 - Input for trial one for CaF₂

3.6 BaF₂ Equilibrium Calculations

The second calculations are carried out on the barium di-fluoride slag. A matrix for this slag was also comprised in order to substitute all possible combinations into the HSC program. This matrix is similar the CaF₂ matrix except for the omission of the scandium. The testing matrix for the BaF₂ slag is in Table 3.6

Table 3.6 - Test matrix for the BaF₂ slag

	V	Ca	Y	Mn	Ti	Cr	Ba	F
1.	X	X	X				X	X
2.		X	X	X			X	X
3.			X	X	X		X	X
4.				X	X	X	X	X
5.	X		X	X			X	X
6.	X	X		X			X	X
7.		X	X		X		X	X
8.		X		X	X		X	X
9.		X	X			X	X	X
10.		X		X		X	X	X
11.			X	X		X	X	X
12.	X		X			X	X	X

*X - indicates inclusion in the numbered calculation

As with the CaF_2 slag, the BaF_2 system input included 500 grams of the vanadium alloy and its impurities and a slag composition of a 1/10 molar ratio to the vanadium. The impurities consisted of 1 w/o each and the titanium and the chromium consisted of 5 w/o. These calculations were also run at the temperatures between 1000 K and 2673 K. The pressure input into the calculations equaled 1 atm. The calculated moles of each element were the actual numbers put into the calculations.

3.7 SrF_2 equilibrium calculations

The last slag to be studied in this set was SrF_2 . The matrix for testing this slag is identical to the previous BaF_2 matrix except the Sr is substituted in for the Ba. As before, five hundred grams of the vanadium alloy with its impurities is the amount used for preliminary calculations. The slag composition of 1/10 molar ratio to the vanadium is also added. The calculations were run at the temperatures between 1000 K and 2673 K and a pressure of 1 atm. As with CaF_2 and BaF_2 , the calculated molar amounts of each element in the system is input into the computer calculations.

3.8 Inductoslag Remelting

Inductoslag remelting is characterized as a radiofrequency induction melting process. The chosen metal melts in a copper crucible with one or more longitudinal slits that prevent attenuation of the field of the surrounding work coil. A thin coat of solid slag forms on the walls of the crucible during the melting process to electrically insulate the molten metal from the copper crucible. This coat of solid slag prevents the molten metal from shorting segments of the crucible (Clites, Beall, Nafziger, 1976). A layer of molten slag tops the molten metal within the crucible. This is the slag that will "draw" the transmutation impurities out of the metal. The advantage of using this technique is the capability of being able to melt loose material. Another advantage of this process is that fabrication of a consumable electrode is not needed and the process is carried out under atmospheric pressure.

3.8.1 Inductoslag Apparatus

The entire schematic of the inductoslag remelt apparatus is shown in Figure 3.2 and in Illustration 3.1. The inductoslag apparatus uses a copper crucible with one or more longitudinal slits. These slits prevent attenuation of the field of the surrounding work coil. The chosen metal and its slag are then placed into the copper crucible to melt. The schematics of the copper crucible used in the experiment are in the following diagrams, Figures 3.2 - 3.3 and in Illustrations 3.2 and 3.3. During a run, water flows through the water cooling lines in order to prevent excessive heating of the crucible. Location of the water cooling lines is shown in detail in Figures 3.3 - 3.5. Water is also run through the work coil to prevent over heating. The copper work coil is shown in Illustration 3.3.

3.8.2 Inductoslag Procedure

Melting of the metal in the crucible is set up by placing a starting stub and an initial charge of metal and flux in the crucible. It is important to center the initial charge of metal in the work coil, as shown in figure 3.2. At the beginning of the run, the starting stub is placed against the lip at the bottom of the crucible (Clites, et. al., 1976). The starting stub and the piston it sits on are shown in Illustrations 3.4 and 3.5. Melting is initiated by applying power to the work coil until the initial charge of the metal and slag has melted. Power is limited at the start of melting to insure melting of some slag before melting the metal (Clites, et. al., 1976). This causes a layer of flux to form against the wall as mentioned before. As soon as a portion of the slag has melted the power is increased, shown in Figure 3.1. The stub is slowly pulled out of the bottom of the crucible as the molten metal solidifies on top of it. As the molten metal mixes with the slag and solidifies, the irradiated impurities are taken up by a specific slag for the metal being tested.

Figure 3.1 - Relationship between power input, melting rate, and energy needed to melt chopped titanium alloy (Clites, et. al., 1976).

square = Melting rate

circle = Energy needed to melt

Inductoslag Remelt

Figure 3.2 - Schematic of the inductoslag apparatus

Illustration 3.1 - Inductoslag Apparatus

Inductoslag Crucible - side view

Figure 3.3 - Schematic of copper crucible- side view
(dashed lines indicate location of water cooling lines)

Copper Crucible Top View

Figure 3.4 - Schematic of copper crucible - top view

Illustration 3.2 - Copper crucible

Inductoslag Crucible - side view

Figure 3.5 - Schematic of copper crucible - cut out side view

Illustration 3.3 - Copper crucible with work coil

Illustrations 3.4 - 3.5 - Starting stub on piston

3.9 Electroslag Remelting

Electroslag remelting is the current method used to produce the purest available large ingots of both alloy steels and nickel-base alloys. This method produces cleaner material than the vacuum induction melt-vacuum arc remelt (VIM-VAR) process. Both austenitic stainless steels and vanadium bearing alloy steels are produced by this method for critical components such as large forging to be used for rotors, pressure bearing components, etc. This process is used to produce clean, homogeneous, large ingots.

In the electroslag process a cell is made with two poles. One pole is made of a high current source, and a water cooled crucible is the other pole. The connection between the two poles occurs through the slag present in the crucible. The heat produced from the slag melts the tip of the electrode droplet by droplet. The electrode melts progressively into a crucible similar to the one used in the inductoslag process (Fleming, 1975). As each droplet passes through a highly reactive slag, inclusions and impurities are removed. When the electrode's molten metal reaches the bottom of the slag it begins to cool. The cooling metal solidifies at the bottom of the crucible. A very critical part of this process, as in the ISR, is that a thin layer of solid slag coats the inside of the crucible insulating the metal from direct contact with the copper. A basic schematic of the electroslag remelt is shown in Figure 3.6.

3.9.1 Electroslag Apparatus

The electroslag entire electroslag apparatus is shown in Figure 3.7 and in Illustration 3.6. This process also utilizes a work coil wrapped around a copper crucible. A picture of the copper crucible is shown in Illustrations 3.7 and 3.8. A drive motor is used to slowly lower the eletrode into the crucible during a remelt run.

Electroslag Remelt

Figure 3.6 - Schematic of the electroslag remelt process - side view

Electroslag Remelt

Figure 3.7 - Schematic of actual electroslag remelt apparatus

Illustration 3.6 - Electroslog apparatus

Illustration 3.7 - Electrosag copper crucible

Illustration 3.8 - Electrosag copper crucible

3.9.2 Preparing Electrodes

The sample electrodes were fabricated from a mixture of powders (3 wt.% CaO, 3 wt % Mn, 3 wt % YtO, 5 wt % Ti, and 5 wt % Cr) and dendritic vanadium. The dendritic vanadium is not a powder but a large "crystal" of vanadium about the size of small gravel. The powders were mixed in a triaxial mill and then cold pressed into disks. The disks were then loaded into a standard Hot iso-static Press (HIP) for powder metallurgy. The disks were placed in a metal tube stacked one on top of the other. These tubes were then evacuated and backfilled with welding grade argon to 1/4 atm. The tubes were sealed and were placed into the HIP machine with a pressure of 30,000 psi at a temperature of 1200°C for two hours. In this environment, the cans collapse against the material inside and fuse it together. The stainless steel tube is removed to reveal the vanadium alloy with impurities electrode. Five electrodes were prepared for experimentation (shown in Illustration 3.9). On the top of each of the electrodes a threaded stinger was added in order to connect the vanadium electrode to the copper electrode in the electroslog apparatus (see Illustration 3.10). A metal pin was placed at the bottom of the steel stinger to ensure that the process would be stopped before it melted the steel and contaminated the ingot.

3.9.3 Electroslog Procedure

The vanadium electrodes were run through an electroslog remelt furnace in a helium backfill with calcium fluoride as the chemical reaction slag system. The calcium fluoride was obtained from Aldrich Chemical Supply as reagent grade. It was baked in a furnace to agglomerate it from powder form so the water and impurity content is not what is reported by the manufacturer. The electroslog procedure started by placing a vanadium alloy base pad and vanadium dendrites at the bottom of the crucible. A picture of the vanadium dendrites is shown in Illustration 3.11. The slag was added to the crucible after the pad and dendrites were in place. A picture of the CaF₂ slag is shown in Illustration 3.12. The crucible was heated until the slag and metal formed a molten pool. At this time the vanadium electrode was lowered into the crucible. Since CaF₂ is an insulator, the electrode was lowered to touch the vanadium pad to start an arc between the crucible and the electrode in order for the electrode to start melting. The electrode continued to lower into the crucible until it was consumed. The left over portion, called a stub, is shown in Illustration 3.13.

Illustration 3.9 - Fabricated electrodes with stingers

Illustration 3.10 - Electrode attached to apparatus

Illustration 3.11 - Vanadium dendrites

Illustration 3.12 - CaF_2 slag

Illustration 3.13 - Melted electrode stub

3.10 Ingot and slag analysis

To analyze the ingots and slags to determine the chemical composition, a different chemical analysis was performed according to the element being studied. For example, an atomic absorption method was used for analyzing manganese and chromium. This method involved dissolving in sodium peroxide. Yttrium compositions were determined by an inductively coupled plasma method. A volumetric wet chemistry analysis was used to determine titanium and vanadium compositions.

In order to analyze the compositions of each ingot, representative samples were taken from the ingot at the top and the bottom. Figure 3.8 shows the sampling layout for the composition analysis for the ingots after remelt. To obtain these samples the ingots had to be polished to remove the slag covering the surface after the process was complete. Illustration 3.14 show the ingot being polished.

Sampling Layout For Ingot

Figure 3.8 - Sampling layout for ingot

Illustration 3.14 - Polishing the ingot

Procedure Flow Chart

Figure 3.9 - Procedure flow chart

4.0 RESULTS

4.1 Thermochemical Calculations

The results of the HSC Chemistry thermochemical calculations are shown in both graph and table form. The graphs show the predicted amount of species present in the system in log moles versus the temperature in Kelvin. The tables show the initial species in the system in molar amounts and the predicted ratios of the species present in the slag and in the vanadium alloy after a remelt run.

4.1.1 CaF_2 Calculations

As the calculations ran, general trends could be seen for each of the impurity elements in the system. The representative graph for yttrium in Figure 4.1, shows that some yttrium remains in elemental form. Yet, almost as much yttrium settles in the yttrium fluoride compounds. This calculation is promising because nearly half of the yttrium may be removed from the metal alloy into the slag by the fluoride. As with the previous elements, it is important after the experimentation to determine where the yttrium settles, in the alloy or in the slag. The computer calculations predict that 54% of the yttrium will remain in the vanadium alloy as Y and 46% will be present in the slag in the form of YF_3 (calculations shown in Table 4.1).

Figure 4.1 - Representative yttrium graph for CaF_2

As mentioned before, yttrium is used in the place of scandium in the experiments because of cost. Therefore, it is important to insure that the scandium and yttrium react in much the same way within the CaF_2 system. It appears from Figure 4.2 that they do indeed react similarly to each other. There is a slight difference in the molar amount of the fluoride compound species that is present, but this factor should not contribute to any major differences within the experiments.

Figure 4.2 - Representative scandium graph for CaF_2

The representative graph for manganese in Figure 4.3, shows that at the temperature of the remelt process, 2175 K, most of the manganese is in elemental form. A positive aspect about this system is that very little manganese and manganese fluoride gas is emitted. HSC calculations predict that almost 100% of the Mn will remain in the metal. However, minute amounts of manganese fluoride species will form in the slag.

Figure 4.3 - Representative manganese graph for CaF₂

The representative graph for calcium in Figure 4.4 shows that calcium difluoride is the most abundant species in this system. Elemental calcium is also present in a substantial amount. It appears from the graph that calcium has not binded to any of the impurities. However, previous graphs illustrate the fluoride of the CaF_2 slag does bind to some impurities. From this graph it is impossible to deduce whether the fluorine from the slag stays with the original slag calcium or if it actually binds to the calcium impurities in the vanadium alloy. This too will have to be investigated after experiments have been run. It is also important to note that at the testing temperatures very little Ca or CaF_2 gas is emitted. It is predicted that almost 100% of the CaF_2 will remain as slag.

Figure 4.4 - Representative calcium graph for CaF_2

As calculations ran for the vanadium alloy species, general trends for each of the elements in the system could be seen. The representative graph of vanadium for the slag CaF_2 in Figure 4.5, shows that most of the vanadium in this system remains in elemental form. However, some of the fluorine from the slag CaF_2 does bind to the vanadium. If this slag is chosen to be used in the remelt experiments it will be important to determine if the vanadium fluoride compounds are contained within the slag or within the vanadium alloy. For the particular purpose of this experiment, it is necessary that the vanadium fluoride compound settle in the slag and not in the vanadium alloy. The calculations predict that almost 100% of the vanadium will remain as metal. However, $2.5 \times 10^{-5} \%$ of VF_2 , $7.8 \times 10^{-11} \%$ of VF_3 , $8.8 \times 10^{-18} \%$ of VF_4 , and $1.5 \times 10^{-27} \%$ of VF_5 will form in the slag.

Figure 4.5 - Representative vanadium graph for CaF_2

The representative graph for titanium in Figure 4.6, shows that most of the titanium remains in elemental form. Unfortunately, it cannot be determined from the graph whether the titanium stays in the metal alloy or moves to the slag. As far as the elemental titanium is concerned, it does not matter whether it settles in the metal or the slag. However, it is imperative that the titanium fluoride compound does not settle within the vanadium alloy. After experimentation, it will be important to investigate where these compounds settle. It is estimated that almost 100% of the Ti in the system will remain in the alloy, while $1.6 \times 10^{-7} \%$ of TiF_3 , and $2.5 \times 10^{-7} \%$ of TiF_2 will form in the slag.

Figure 4.6 - Representative graph for Titanium for CaF_2

The representative graph for chromium (Figure 4.7) also shows that it remains mostly in elemental form. As with the vanadium and titanium it is important to investigate after experimentation where the chromium fluoride compound settles. Ideally these compounds will settle in the slag. The HSC calculations predict that almost 100% of the Cr will remain as metal. However, minute amounts of chromium fluorides will form in the slag.

Figure 4.7 - Representative graph for Chromium for CaF₂

CaF₂	Initial Amounts (moles) V-5Ti-5Cr + Impurities	Predicted amounts in metal after melt (ratio)	Predicted amounts in slag after melt (ratio)
Y	0.056	0.538 (54%)	YF ₃ 0.462 (46%)
Mn	0.091	~1 (100%)	MnF ₂ 4.2 x 10 ⁻⁹ (<1%)
			MnF ₃ 6.1 x 10 ⁻¹⁹ (<1%)
			MnF ₄ 4.3 x 10 ⁻³⁰ (<1%)
Ca	0.125	~ 1 (100%)	
V	9.128	~ 1 (100%)	VF ₂ 2.5 x 10 ⁻⁷ (<1%)
			VF ₃ 7.8 x 10 ⁻¹³ (<1%)
			VF ₄ 8.8 x 10 ⁻²⁰
			VF ₅ 1.5 x 10 ⁻²⁹
Ti	0.522	~ 1 (100%)	TiF ₂ 2.5 x 10 ⁻⁹
			TiF ₃ 1.6 x 10 ⁻⁹
Cr	0.481	~ 1 (100%)	CrF ₂ 3.6 x 10 ⁻¹⁰
			CrF ₃ 5.7 x 10 ⁻¹⁷
			CrF ₄ 2.6 x 10 ⁻²⁷
CaF₂ - Slag	0.952		~ 1 (100%)

Table 4.1 - Predicted result amounts for the CaF₂ slag system after remelt

4.1.2 BaF₂

General trends in the impurity graphs were also found with BaF₂ slag system. General trends can also be seen between the BaF₂ and CaF₂ graphs. The representative graph for yttrium in Figure 4.8, shows that more than half of the yttrium in the system appears to bind to the fluorine. The rest of the yttrium is present in the elemental form. It is important to analyze the experiments to locate where the yttrium and yttrium fluoride species settle within the system. The computer calculations predicted that 23% of the yttrium will remain in the alloy as Y and 77% of the yttrium will be taken up by the slag (calculations shown in Table 4.2).

Figure 4.8 - Representative yttrium graph for BaF₂

The representative graph for manganese in Figure 4.9, illustrates that most of the manganese remains in elemental form. However, some manganese does bind to the fluorine. It is possible that by doing this the manganese impurity will be pulled out of the alloy into the slag. The graph also illustrates that very little gas is emitted at the remelt testing temperature. It is estimated that almost 100% of the Mn will remain in the alloy in its elemental form, while $6.0 \times 10^{-6} \%$ of MnF_2 , $5.1 \times 10^{-15} \%$ of MnF_3 , and $7.1 \times 10^{-26} \%$ of MnF_4 will form in the slag.

Figure 4.9 - Representative manganese graph for BaF_2

The representative graph for calcium in Figure 4.10, illustrates that the most abundant species in the system is CaF_2 . Since the slag BaF_2 is used, it appears that much of the input fluorine has bound to the Ca present as an impurity in the vanadium. It will need to be determined where the Ca and CaF_2 settle after testing. HSC predicts that 5% of the Ca will remain in the alloy in its elemental form, while 95% of the Ca will be present in the slag as CaF_2 .

Figure 4.10 - Representative Calcium Graph for BaF_2

General trends in the vanadium alloy system can also be seen in the BaF_2 slag system. The representative graph for vanadium in Figure 4.11 shows that most of the vanadium is present in elemental form. Unfortunately some of the vanadium does bind to the fluorine. As long as the vanadium fluoride compounds stay in the slag then this should not be a problem. It appears from the graph that very little gas is emitted from the vanadium at the testing remelt temperatures. It is estimated that almost 100% of the vanadium will remain in the alloy. Nevertheless, minute amounts of vanadium will form in the slag as VF_2 , VF_3 , VF_4 , and VF_5 .

Figure 4.11 - Representative vanadium graph for BaF_2

The representative graph for titanium in Figure 4.12, shows that not only does it remain mostly in elemental form in the CaF_2 slag system but also the BaF_2 system. As mentioned before it does not matter if the fluoride binds to the titanium as long as it does not stay in the vanadium alloy. As with the vanadium, almost 100% of the titanium is predicted to remain in the alloy in its elemental form. However, $5.1 \times 10^{-8} \%$ of TiF_3 , $1.3 \times 10^{-7} \%$ of TiF_2 , and $3.0 \times 10^{-15} \%$ of TiF_4 will form in the slag.

Figure 4.12 - Representative titanium graph for BaF_2

The representative graph for chromium in Figure 4.13, shows that chromium is present in mostly elemental form. Some chromium is bonded to fluorine, however, as in titanium this is not a problem unless these species settle in the alloy. The graph also demonstrates that very little gas is emitted at the remelt testing temperature. The computer calculation estimate that nearly 100% of the Cr will remain in the alloy in its elemental form.

Figure 4.13 - Representative chromium graph for BaF₂

The representative graph for barium in Figure 4.14, illustrates that the most abundant species in this system are BaF_2 and Ba . Very little gas is emitted from the barium species at the remelt testing temperatures. It will need to be determined after actual experimentation where these species settle. Ideally, they will settle in the slag. The amount of BaF_2 predicted to be left as slag is 88%.

Figure 4.14 - Representative barium graph for BaF_2

BaF₂	Initial Amounts (moles) V-5Ti-5Cr + Impurities	Predicted Amounts in metal after melt	Predicted Amounts in slag after melt
Y	0.056	0.229 (23%)	YF ₃ 0.771 (77%)
Mn	0.091	~ 1 (100%)	MnF ₂ 6.0 x 10 ⁻⁸
			MnF ₃ 5.1 x 10 ⁻¹⁷
			MnF ₄ 7.1 x 10 ⁻²⁸
Ca	0.125	0.046 (5%)	CaF ₂ 0.954 (95%)
V	9.619	~ 1 (100%)	VF ₂ 2.7 x 10 ⁻⁹
			VF ₃ 1.1 x 10 ⁻¹⁵
			VF ₄ 1.6 x 10 ⁻²³
			VF ₅ 2.0 x 10 ⁻³⁴
Ti	0.522	~1 (100%)	TiF ₂ 1.3 x 10 ⁻⁹
			TiF ₃ 5.1 x 10 ⁻¹⁰
			TiF ₄ 3.0 x 10 ⁻¹⁷
Cr	0.481	~ 1 (100%)	CrF ₂ 3.1 x 10 ⁻⁶
			CrF ₃ 1.8 x 10 ⁻¹¹
			CrF ₄ 2.6 x 10 ⁻²⁰
BaF₂ - Slag	1.023		0.884 (88%)

Table 4.2 - Predicted result amounts for the BaF₂ system after remelt

4.1.3 SrF_2

General trends seen in the BaF_2 and the CaF_2 slag calculations can also be seen in the SrF_2 slag system. For example, the representative graph for yttrium in Figure 4.15 shows that more than half of the yttrium binds to the fluorine from the slag, possibly removing the yttrium impurity from the vanadium alloy. However, the rest of the yttrium remains in elemental form. The important question is whether these species end up in the alloy or in the slag compound. The predicted amount of Y remaining in the metal is 33%, while 67% of the yttrium will be removed by the slag (calculations shown in Table 4.3).

Figure 4.15 - Representative yttrium graph for SrF_2

As with previous manganese graphs, most of the manganese in the SrF_2 slag system (Figure 4.16) exists in the elemental form. Some of the manganese does bind to the fluorine from the slag, hopefully pulling the manganese impurities out of the slag. The estimated amount of Mn remaining in the metal as Mn is almost 100%, with trace amounts of manganese fluorides present in the slag.

Figure 4.16 - Representative manganese graph for SrF_2

The representative graph for calcium in Figure 4.17, shows that the most abundant species in this system are Ca and CaF_2 . Ideally, the Ca is drawn out of the vanadium and binds to the fluorine. It will need to be determined after testing as to whether this occurs or not. It is also evident that very little gas will be emitted at the testing temperature. The predicted amount of Ca that remains in the metal is 28%. Therefore, 72% of the calcium will be removed by the slag.

Figure 4.17 - Representative calcium graph for SrF_2

The representative graph for vanadium (Figure 4.18) in the SrF_2 system is very similar to the previous vanadium graphs. Unfortunately, some of the vanadium does bind to the fluorine in the slag. Yet, as long as the vanadium fluoride species do not settle in the alloy, this should not present a major problem. HSC calculations show that almost 100% of the vanadium will remain in the metal. $5.5 \times 10^{-7} \%$ of VF_2 , $1.4 \times 10^{-13} \%$ of VF_3 , $3.8 \times 10^{-21} \%$ of VF_4 , and $5.5 \times 10^{-32} \%$ of VF_5 will form in the slag.

Figure 4.18 - Representative vanadium graph for SrF_2

As with the vanadium the titanium representative graphs share similarities. In the SrF_2 system (Figure 4.19), the most abundant species is elemental titanium. Some fluorine does bind to the titanium. As long as the titanium fluoride species stay within the slag this is not of major concern. It is predicted that almost 100% of the Ti will remain in the alloy while trace amounts of titanium fluorides will form in the slag.

Figure 4.19 - Representative titanium graph for SrF_2

In the chromium representative graph in Figure 4.20, most of the chromium is present in elemental form. Some of the chromium does bind to the fluorine from the slag. It is important to find out where the chromium fluoride species settle after experiments have been executed. Ideally these species should be in the slag and not the alloy. Computer calculations show that almost 100% of the Cr will remain in the alloy.

Figure 4.20 - Representative chromium graph for SrF_2

The representative strontium graph in Figure 4.21 illustrates that the most abundant species in the SrF_2 system are Sr and SrF_2 . This graph is consistent with the rest of the data because it would appear that the elemental form of strontium is present because the fluorine previously bound to it has bound to the impurities within the vanadium alloy. Calculations predict that 94% of the SrF_2 will remain as slag.

Figure 4.21 - Representative strontium graph for SrF_2

SrF₂	Initial Amounts (moles) V-5Ti-5Cr + Impurities	Predicted Amounts in metal after melt	Predicted Amounts in slag after melt
Y	0.056	0.330 (33%)	YF ₃ 0.670 (67%)
Mn	0.091	~ 1 (100%)	MnF ₂ 1.6 x 10 ⁻⁸
			MnF ₃ 1.0 x 10 ⁻¹⁸
			MnF ₄ 1.2 x 10 ⁻²²
Ca	0.125	0.277 (28%)	CaF ₂ 0.723 (72%)
V	9.620	~ 1 (100%)	VF ₂ 4.5 x 10 ⁻⁹
			VF ₃ 1.4 x 10 ⁻¹⁵
			VF ₄ 3.8 x 10 ⁻²³
			VF ₅ 5.5 x 10 ⁻³⁴
Ti	0.522	~ 1 (100%)	TiF ₂ 3.1 x 10 ⁻⁹
			TiF ₃ 2.2 x 10 ⁻⁹
			TiF ₄ 6.7 x 10 ⁻¹⁶
Cr	0.481	~ 1 (100%)	CrF ₂ 3.9 x 10 ⁻¹⁰
			CrF ₃ 4.9 x 10 ⁻¹⁷
			CrF ₄ 5.4 x 10 ⁻²⁶
SrF₂ - Slag	0.962		0.941 (94%)

Table 4.3 - Predicted result amounts of SrF₂ slag system after remelt

4.2 Inductoslag Remelt

No results were obtained with the Inductoslag remelt process because the power supply could not be coupled to the apparatus. Therefore, the core of the crucible never obtained enough heat to melt the vanadium alloy and slag. However, it was definitely determined that oxygen containing slags cannot be used in this process from the heat that was obtained within the crucible.

4.3 Electroslag Remelt

All experimental remelt runs were performed with a power supply providing approximately 1500 amps and 20 volts.

4.3.1 **Electrode 1**

Initial weights:

Electrode weight = 801.1 g

Electrode + stinger = 1110.0 g

Base pad = 71.5 g

Vanadium dendrites = 28.5 g

CaF₂ slag = 250g

Weights after first melt:

Ingot = 831.1 g

Stub = 399 g

Slag = 217.8 g

Weights after second melt:

Ingot = 582.5 g

Slag = 240.7 g

The electroslag remelt trial with electrode 1 was very successful. The process was carried out with the apparatus backfilled with 1/3 ATM of He. The results from this trial are shown in Table 4.4. The analysis of electrode 1 shows that in the first melt approximately 98% of the Y, 0% of the Mn, 87% of Ca, 0% of Ti, 0% of Cr, and 0% of O₂ were removed. A second remelt resulted in a 99% removal of Y, an 85% removal for

Ca, and again no removal for Ti, Cr, or O₂. Because there is not significantly more removal by performing a second melt, it is concluded that a second remelt is not needed. It is also important to note that because of the electrode fabrication process, equal mixing of each variable is very rarely achieved. Therefore, Cr and Ti appear to be present in more amounts after a melt. This is most likely because the elements are better mixed within the ingot than in the fabricated electrode. Pictures of electrode are shown in Illustrations 4.1 - 4.5.

Electrode 1	Amounts in initial fabricated electrode (moles)	Amounts in top of ingot after melt (moles)	Amounts in bottom of ingot after melt (moles)	Amounts in slag after melt (moles)
First Melt				
Y	0.00481	9.05×10^{-5}	8.22×10^{-5}	0.1335
Mn	0.0128	0.0267	0.0266	5.75×10^{-4}
Ca	0.0230	0.00294	0.00268	
V	15.2			0.00128
Ti	0.209	0.435	0.792	0.0159
Cr	0.287	0.671	0.654	0.00130
O ₂	0.0551	0.0525	0.0551	
Second Melt	(approx.)			
Y	8.64×10^{-5}	1.08×10^{-5}	5.43×10^{-5}	1.57×10^{-4}
Mn	0.0267	0.0183	0.0176	9.38×10^{-4}
Ca	0.00281	0.00246	0.00177	
V				0.0137
Ti	0.615	0.305	0.792	0.0302
Cr	0.663	0.444	0.431	0.00201
O ₂	0.0538	0.0422	0.0551	
Average removal fraction	First melt	Second melt		
Y	0.98	0.99		
Mn	-1.28	-1.32		
Ca	0.87	0.85		
Ti	-2.22	-2.29		
Cr	-1.53	-1.53		
O ₂	-0.03	-0.15		

Table 4.4 - Results from electrode 1

It is also important to note that the negative values shown in the average removal fraction are due to error in the calculating system performing the analysis. However, negative numbers can be interpreted as 0.

When comparing these data to the predicted data, a much better Y and Ca removal ratio is achieved with the actual apparatus than with simulated thermochemical calculations. However, the predictions look to be fairly accurate in the amounts of Ti, V, Cr, O₂, and Mn that remain in the metal and move to the slag.

Illustration 4.1 - Electrode 1 ingot after first melt - polished

Illustration 4.2 - Electrode 1 ingot after first melt - cut in half

Illustration 4.3 - Electrode 1 ingot after second melt - slag covered

Illustration 4.4 - Electrode 1 ingot after second melt - polished

Illustration 4.5 - Electrode 1 ingot after second melt - cut in half

4.3.2 Electrode 2

Initial weights:

Electrode + stinger = 875 g

Base pad = 75 g

Vanadium dendrites = 25 g

Slag = 250 g

This electrode was the first to be tested in the Electrosag apparatus. This trial was used to set the parameters for the succeeding remelt runs. The only analysis that was carried out on this electrode was the initial component amounts which can be seen in Table 4.5. Pictures of electrode 2 can be seen in Illustrations 4.6 - 4.7.

	Amounts in initial fabricated <u>electrode 2</u> (moles)	Amounts in initial fabricated <u>electrode 3</u> (moles)	Amounts in initial fabricated <u>electrode 5</u> (moles)
Y	0.00804	4.23×10^{-4}	0.00701
Mn	0.0214	0.0269	0.0208
Ca	0.0363	0.0399	0.0323
V	14.7	14.1	14.7
Ti	0.371	0.9135	0.514
Cr	0.574	0.637	0.452
O₂	0.0500	0.0750	0.0675

Table 4.5 - Results from initial analysis performed on electrodes 2, 3, and 5

Illustration 4.6 - Electrode 2 ingot after first melt and slag cap - unpolished

Illustration 4.7 - Electrode 2 ingot after first melt - polished

4.3.3 Electrode 3

Initial weights:

Electrode + stinger = 1081.3 g

Base pad = 75 g

Vanadium dendrites = 25 g

Slag = 250g

After melt weights:

Ingot = 594.9 g

Slag = 262.1 g

Stub + 4 " of electrode not melted = 544.3 g

Electrode 3 did not have after-remelt analysis performed because the trial was prematurely stopped due to human error. Therefore, it was felt that the results would be skewed due to the lesser amount of electrode reacting with the slag. A picture of electrode 3 can be seen in Illustration 4.8.

Illustration 4.8 - Electrode 3 ingot after first melt and slag cap - unpolished

4.3.4 Electrode 4

Initial weights:

Electrode + stinger = 1090.8 g

Base pad = 70.6 g

Vanadium dendrites = 29.4 g

Slag = 250 g

After first melt weights:

Ingot = 734.9 g

Slag = 274.2 g

Stub = 379.2 g

After second melt weights:

Ingot = 265.8 g

Slag = 206.4 g

A very successful trial was also obtained with electrode 4. This run was also performed under a backfill of 1/3 ATM of He. This electrode's analysis shows that in the first melt, 99% of Y, 0% of Mn, 91% of Ca, 0% of Ti, 0% of Cr, and 26% of O₂ was removed from the vanadium alloy. The second melt results of this electrode also indicate that a second melt is not needed for additional removal of impurities.

An increase in Cr and Ti also shows up in this analysis, however it is not as dramatic as in electrode 1. It is possible that better mixing was achieved when fabricating this electrode, or a sample location with more representative mixing was chosen. Pictures of electrode 4 can be seen in Illustrations 4.9 - 4.11.

Electrode 4	Amounts in initial fabricated electrode (moles)	Amounts in top of ingot after melt (moles)	Amounts in bottom of ingot after melt (moles)	Amounts in slag after melt (moles)
First Melt				
Y	0.00660	9.92×10^{-5}	5.79×10^{-5}	0.0168
Mn	0.217	0.0268	0.0257	6.49×10^{-4}
Ca	0.0345	0.00334	0.00257	
V	14.7			0.00161
Ti	0.414	0.462	0.425	0.00916
Cr	0.442	0.660	0.574	0.00141
O ₂	0.0825	0.0574	0.0574	
Second Melt	(approx.)			
Y	7.86×10^{-5}	1.48×10^{-5}	2.22×10^{-5}	4.20×10^{-5}
Mn	0.0263	0.0258	0.0229	5.55×10^{-4}
Ca	0.00296	0.00286	0.00297	
V				0.00448
Ti	0.444	0.384	0.313	0.0195
Cr	0.617	0.514	0.552	9.77×10^{-4}
O ₂	0.0574	0.0473	0.0370	
Average removal fraction	First melt	Second melt		
Y	0.99	1.00		
Mn	-0.32	-0.36		
Ca	0.91	0.90		
Ti	-0.17	-0.02		
Cr	-0.52	-0.47		
O ₂	0.26	0.38		

Table 4.5 - Results from electrode 4

Illustration 4.9 - Electrode 4 ingot after first melt - includes base pad, polished ingot, slag cap, and electrode stub

Illustration 4.10 - Electrode 4 ingot after second melt - polished

Illustration 4.11 - Electrode 4 ingot after second melt - cut in half

4.3.5 Electrode 5

Initial weights:

Electrode + stinger = 1097 g

Base pad = 71.6 g

Vanadium dendrites = 28.4 g

Slag = 250 g

After melt weights:

Ingot (approx.) = 635.0 g

Slag (approx.) = 412.5 g

Electrode 5's trial was different from the others because it utilized a vacuum over the slag of ~ 40 microns, instead of backfilling with 1/3 ATM of He. This procedure was not successful because the slag and vanadium alloy splattered and deposited up onto the crucible walls (~ 4" above the metal level). The splattering was due to an unstable arc between the electrode (+) charge and the crucible (-) charge. Therefore, after melt analysis was not carried out on this electrode. Pictures of electrode 5 can be seen in Illustrations 4.12-4.13.

2-2-22-49

V-5Ti-5Cr Alloy
Electroslag Remelted in Vacuum
CaF₂ Slag - 1500 amps - 20 Volts

Illustration 4.12 - Electrode 5 ingot after first melt - unpolished

Illustration 4.13 - Electrode 5 ingot after first melt - polished

4.4 Predicted versus actual removal

When comparing predicted values versus actual experimentation values, there was far better removal achieved in the experimentation than what the computer calculations predicted. The slag was predicted to remove 46% of the yttrium, yet in reality 98-99% of the yttrium was removed from the vanadium alloy. Calcium also had a much better removal ratio from the predicted 0% to the actual, 87-91%. However, the predicted values for vanadium, titanium, chromium, and manganese were fairly accurate. These calculations are shown in Table 4.6.

	Predicted removal (approx)	Removal from <u>Electrode 1</u> (approx.)	Removal <u>Electrode 4</u> (approx.)
Y	46%	98%	99%
Mn	0%	0%	0%
Ca	0%	87%	91%
V	0%	0%	0%
Ti	0%	0%	0%
Cr	0%	0%	0%
O₂	not predicted	0%	26%

Table 4.6 - Predicted versus experimental removal

5.0 DISCUSSION AND CONCLUSION

Overall, there was much better removal of the impurities from the vanadium alloy by the calcium fluoride slag in the actual electroslag remelt experiments than predicted by the HSC Chemistry thermochemical calculations. The discrepancies in the predicted removal could have been due to a couple of factors. First, the calculations were carried out under a closed system in equilibrium. Second, the calculations did not take into consideration all of the kinetics involved in the system.

When comparing actual experimental data to the predicted data, a much better removal of yttrium and calcium ratio was achieved with the electroslag apparatus than with the thermochemical calculations. However, the predictions were fairly accurate for the amounts of titanium, chromium, vanadium, and oxygen. The manganese was also predicted to remain in the vanadium alloy which it did in the experiment. It is possible that nothing will be able to remove the manganese from the vanadium alloy because the vanadium and manganese form a mixture called a binary alloy at the operating temperatures of both the testing systems. The binary alloy phase diagram showing this formation is shown in Figure 5.1. Through the electroslag experimentation process, it was also determined that a second remelt was not necessary for the optimum removal of the removable impurities, calcium and yttrium.

The calcium fluoride slag was fairly successful in the electroslag remelt process. However, before a definite decision is made as to which slag composition is best for the vanadium alloy with its included impurities further testing will need to be performed with other slags such as strontium fluoride and barium fluoride. All of these slags will also need to be tested using the inductoslag remelt process in order to determine which process has the higher amount of removal.

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Binary Alloy Phase Diagrams

Figure 5.1 - Binary alloy phase diagram for vanadium and manganese

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