

C.1

REMOVAL OF CALCIUM CONTAINING INCLUSIONS DURING VACUUM ARC  
REMELTING

by

EVA SAMUELSSON

M.Sc., Royal Institute Of Technology, Stockholm, 1981

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF  
THE REQUIREMENTS FOR THE DEGREE OF  
MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES  
Department Of Metallurgical Engineering

We accept this thesis as conforming  
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

November 1983

© Eva Samuelsson, 1983

In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his or her representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Metallurgical Engineering

The University of British Columbia  
2075 Wesbrook Place  
Vancouver, Canada  
V6T 1W5

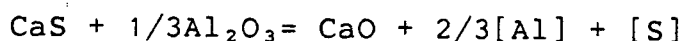
Date: 15 November 1983

### Abstract

The mechanism of removal of calcium containing inclusions in steel during Vacuum Arc Remelting has been investigated.

Laboratory Electron Beam and industrial Vacuum Arc remelting electrodes and ingots were examined. Properties of the steels were determined with the aid of chemical and metallographic methods.

It is proposed that the major mechanism of removal is rejection of calcium aluminates to a free surface. One third of the calcium sulphide is rejected with the calcium aluminates. The remainder reacts with aluminium oxide in the aluminates according to the following reaction:



Subsequently, the calcium oxide is also rejected and the dissolved sulphur reacts with sulphide forming elements during solidification.

The final calcium content of the remelted steels, 5 - 10 ppm, was independent of the calcium content of the electrode.

The results of this study are not in agreement with previous work, which attempts to establish the composition of the calcium aluminates as a function of the steel content of sulphur, aluminium and calcium. Specifically it is found that

the influence of oxygen content has not previously been sufficiently taken into account.

## Table of Contents

Abstract .....	ii
List of Tables .....	v
List of Figures .....	vi
Acknowledgements .....	vii
I. INTRODUCTION .....	1
1.1 Objectives .....	3
1.2 Methods .....	3
II. LITERATURE REVIEW .....	4
2.1 Ladle Treatment Of Steel .....	4
2.1.1 Ladle Injection .....	5
2.1.2 Wire Injection .....	6
2.1.3 Conventional Alloy Addition .....	6
2.2 Remelting Under Vacuum .....	7
2.2.1 Vacuum Arc Remelting .....	8
2.2.2 Electron Beam Remelting .....	10
2.3 Inclusion Shape Control .....	11
2.3.1 Inclusion Modification With Calcium .....	12
2.4 Thermodynamic Properties .....	18
2.4.1 Calcium Metal .....	18
2.4.2 Calcium In Steel .....	18
2.4.3 Calcium Aluminates .....	20
2.4.4 Calcium Sulphide .....	22
2.5 Evaporation Rate .....	22
III. EXPERIMENTAL PROCEDURES .....	24
3.1 Samples .....	24
3.1.1 Industrial Samples .....	24
3.1.2 Laboratory Samples .....	24
3.2 Analysis .....	27
3.2.1 Metallographic Examination .....	27
3.2.2 Bulk Steel Composition .....	28
3.2.3 Inclusion Extraction .....	29
IV. RESULTS AND DISCUSSION .....	30
4.1 Thermodynamic Considerations .....	30
4.2 Electron Beam Remelting .....	34
4.3 Industrial VAR Samples .....	35
4.4 General Observations Related To Calcium Treated Steels .....	40
4.4.1 Calcium Aluminate Composition .....	41
4.4.2 Inclusions In The Liquid Steel .....	42
V. CONCLUSIONS .....	45
BIBLIOGRAPHY .....	47
APPENDIX A - NOTATION .....	51
APPENDIX B - DETERMINATION OF CALCIUM IN STEEL BY ATOMIC ABSORPTION SPECTROPHOTOMETRY .....	52
APPENDIX C - STEEL COMPOSITIONS .....	53
APPENDIX D - UNCERTAINTY OF CHEMICAL ANALYSIS .....	54

List of Tables

1. VAR melting conditions .....	24
2. EB remelting conditions .....	27
3. Description of the hypothetical steel .....	33
4. Summary of analysis. Vx marked samples denotes electrode steels, and VxR marked samples are corresponding remelted ingots. ....	38
5. Results of mass balances .....	39

## List of Figures

1. Schematic outline of the VAR process <sup>8</sup> . . . . .	8
2. Crown region of a VAR ingot which collects inclusion material floated to the ingot periphery <sup>8</sup> . . . . .	9
3. Standard free energy of formation of some oxides important in steelmaking. . . . .	13
4. Standard free energy of formation of some sulphides important in steelmaking. . . . .	13
5. Schematic representation of modification of inclusions with Ca-treatment <sup>1</sup> . . . . .	14
6. The pseudo binary calcium oxide - aluminium oxide phase diagram <sup>44</sup> . . . . .	16
7. Composition of calcium aluminates as a function of steel calcium content. ---Hilty and Farrell <sup>21</sup> , ---Haida et.al. <sup>22</sup> . . . . .	16
8. The pseudo binary calcium sulphide - manganese sulphide phase diagram <sup>25</sup> . . . . .	17
9. Diamond pyramid hardness versus temperature for some(Mn,Ca)S solid solutions <sup>25</sup> . . . . .	17
10. Schematic figure showing where samples and electrodes for EB melting were cut from induction furnace ingots. . . . .	26
11. The Electron Beam furnace at UBC. . . . .	26
12. Schematic description of the problems with microprobe analysis. Note that all three inclusions give the same appearance from the surface. . . . .	28
13. Evaluation of the thermodynamic driving force. . . . .	34
14. "Bead" of coalesced inclusions collected from surface of EB-melted ingot. The black patches are CaS and the bulk phase is $C_xA_y$ . . . . .	36
15. X-ray spectrums showing the relative composition of an inclusion in an electrode steel and corresponding inclusion "bead". . . . .	36
16. Coalesced inclusions on an electrode tip. Light microscope and SEM X-ray images. . . . .	37
17. Composition of calcium aluminates as a function of steel calcium content. Experimental results, and results from Hilty & Farrell <sup>21</sup> and Haida <sup>22</sup> . . . . .	41
18. Inclusion in pinsample taken from the liquid steel. Light microscope and SEM X-ray images. . . . .	43

Acknowledgement

I would like to thank Dr Alec Mitchell for his guidance and time spent on many helpful discussions.

The contribution of samples from my colleagues in the industry was essential for the project and is much appreciated.

The assistance of the technical staff at the Metallurgy department, particularly Gus Sidla, Rudy Cardeno, Mary Mager and Laurie Frederick is gratefully acknowledged.

I would also like to thank my fellow graduate students for their friendship and many interesting discussions.

Economic assistance from the Natural Sciences and Research Council of Canada is gratefully acknowledged.

Finally I would like to thank my husband, Fred Bradley, for his encouragement and many helpful suggestions.



## I. INTRODUCTION

The production of quality steels for demanding applications, such as aircraft landing gears, requires tight control of hydrogen content, quantity and composition of non-metallic inclusions, and metallurgical structure in order to ensure mechanical soundness. Two remelting processes, Vacuum Arc Remelting (VAR) and Electro Slag Remelting (ESR), are commonly used to manufacture these steels.

The ESR process is characterized by the remelting of an electrode through a refining slag, generally under atmospheric conditions. An advantage of the process is that the content and nature of the non-metallic inclusions can be controlled, to some extent, through manipulation of the slag-metal reactions. A desirable metallurgical structure can be attained by monitoring the rate of ingot solidification in the water-cooled copper mould. Special precautions must be taken to avoid hydrogen pick-up during refining.

In North America, for historical reasons, regulations state that many of these steels must be produced using the VAR process. In contrast to the ESR process, in the VAR process an electrode is remelted under vacuum conditions without the benefit of a refining slag. The vacuum processing ensures a low hydrogen content. In a similar way to the ESR process, the ingot solidification structure can be controlled, although the remelting rate is not as easily monitored due to problems of arc instability. Due to the lack of slag refining, the electrode

material must be well desulphurized prior to remelting, since vacuum reactions do not result in significant desulphurization.

Many techniques for the desulphurization of steels, prior to casting the VAR electrode, are available. While traditionally desulphurization in the electric arc furnace has been used for this purpose, the recent trend is to ladle desulphurize with calcium or calcium-containing compounds. The advantages associated with ladle treatment are increased furnace production at lower cost and desulphurization to lower levels than are possible in electric arc furnace steelmaking without the dangers of phosphorus reversion or aluminium pick-up.

In addition to desulphurization the calcium treatment provides inclusion shape control for the electrode steel. Although it is commonly accepted that much of the calcium is lost during remelting, calcium treatment is known to be beneficial for the mechanical properties of the product. Almost all of the calcium is bound in the solidified steel as either sulphide or oxide. From the apparent contradiction one could draw the conclusion that deleterious elements are removed with the calcium during remelting. While stoichiometric evaporation of calcium sulphide has been suggested as a possible explanation, other mechanisms could operate, for instance mechanical removal by buoyancy or fluid flow. Finally, from an economic point of view the question arises as to whether the content of calcium in the electrode has a direct influence on the steel quality after remelting. Since calcium treatment is

an expensive process and the presence of calcium requires extensive precautions to prevent reoxidation during electrode casting, it is advantageous to define precisely how much calcium, and in what form, is required in the electrode.

### 1.1 Objectives

The major objectives of this study are to determine the removal mechanism of calcium during Vacuum Arc Remelting, and to study the influence of the electrode calcium content on the final ingot composition, particularly as it relates to the composition of calcium-containing inclusions.

### 1.2 Methods

Industrial VAR samples and laboratory Electron Beam remelted samples have been investigated. Properties of the steels have been determined with the aid of chemical and metallographic methods.

The thermodynamic driving force for potential chemical reactions was determined to interpret the experimental evidence.

## II. LITERATURE REVIEW

### 2.1 Ladle Treatment Of Steel

The increased demand for high quality steels, the introduction of the Ultra High Power electric furnaces and the BOF processes used in conjunction with continuous casting make secondary steelmaking more attractive for the steelmaking companies. As a result, a large number of secondary steelmaking procedures have been developed during the last twenty years. Here, only those processes which are used for calcium treatment will be discussed.

The two major purposes of calcium treatment of steels are desulphurization and inclusion shape control. The desulphurization is due to the high affinity of calcium for sulphur. The resulting inclusions are light and float easily to the slag. In addition, the calcium treatment increases the sulphur capacity of the slag. The second consequence of calcium treatment, inclusion shape control, will be discussed in section 2.3.

The physical properties of calcium, low density and high vapour pressure at steelmaking temperatures, prevent the use of simple addition methods of pure calcium to steel. Therefore, more elaborate techniques such as powder injection and wire injection have been developed. Another alternative is to add calcium in the form of an alloy.

The low solubility of calcium in steel may also cause problems. With the more sophisticated addition techniques it is possible to reach contents high enough for satisfactory desulphurization and inclusion shape control. However, care must be taken not to reoxidize the steel during teeming to such an extent that the inclusion shape control diminishes.

#### 2.1.1 Ladle Injection

Holappa<sup>1</sup> has summarized the published work concerning ladle injection metallurgy.

Ladle injection, which is the newest ladle process, was developed mainly as a rapid desulphurization method. The process also provides a means to introduce calcium in the steel, with subsequent deoxidation and inclusion shape control.

The equipment for injection consist of powder dispensers connected to a lance that can be immersed into the steel. During injection, the powder is fluidized in the dispenser by a carrier gas, usually argon. The powder - gas mixture is then injected deeply into the steel. Thus, one of the main advantages with ladle injection is that light alloy additions are given sufficient time to melt and react with the steel. The second principal feature of ladle injection is the vigorous stirring that the injection causes. The stirring has the advantage of creating a large contact area between steel and slag, but it also causes problems with reoxidation reactions with the ladle lining. Therefore ladles used for injection

treatment are lined with highly stable refractories such as dolomite, magnesite and high alumina. For calcium treatment, the most commonly used powders are calcium silicide ( $\sim 30\%$  Ca), calcium carbide ( $\sim 80\%$   $\text{CaC}_2$ ) and different slag mixtures consisting of  $\text{CaO}$ ,  $\text{CaF}_2$  and  $\text{Al}_2\text{O}_3$ .

#### 2.1.2 Wire Injection

An alternative to the powder injection technique is wire "injection" of calcium into the ladle<sup>2, 3, 4</sup>. By protecting the calcium wire with a steel layer, the calcium can be prevented from reacting prematurely with air or slag. The wire is fed at high speed (80-300 m/min) into the steel. Less than 1.5 m ferrostatic head is required to suppress the boiling of calcium at steelmaking temperatures. Since the steelclad wire will melt in 1 - 3 seconds, the system permits liquid calcium to react with the steel before evaporation of remaining calcium occurs. Economically, powder injection demands a higher initial investment whereas the cost per added unit calcium is higher for wire "injection".

#### 2.1.3 Conventional Alloy Addition

Calcium has considerably higher solubility in silicon and nickel than in iron. This fact allows the production of high calcium alloys which are later used for adding calcium to steel. As the activity of calcium is lowered in these alloys, the reactions with steel become less violent, and a higher recovery is obtained. A serious disadvantage of this kind of treatment

is the introduction of additional elements, which may not always be desirable. Therefore, some companies even add "logs" of metallic calcium covered by steel. The problem with this technique is the violent reaction that occurs when larger amounts of calcium come in contact with the steel.

## 2.2 Remelting Under Vacuum

At present, two processes are available for remelting under vacuum. These are Vacuum Arc Remelting (VAR) and Electron Beam (EB) melting. If the EB furnace is constructed for remelting, then the VAR and EB melting processes are very similar. In both processes some chemical impurities are removed by the exposure of the molten metal to vacuum and the continuous solidification ensures a controlled solidification structure. The fundamental difference is the heat sources, either an electron beam or a vacuum arc. In addition the pressure in the EB process is generally lower, and the melting speed independent of the power input. Krone,<sup>5</sup> Kazakov<sup>6</sup> and Wahlster<sup>7</sup> have compared the EB and VAR processes. The conclusion of their comparison is that due to the slower melting speed the EB melted materials will lose more alloying elements and impurities than the VAR melted materials. The EB and VAR processes will now be discussed in more detail.

### 2.2.1 Vacuum Arc Remelting

The Vacuum Arc Remelting (VAR) process is schematically outlined in Figure 1<sup>8</sup>. The equipment consists of a water-cooled copper crucible, an enclosure connected to a vacuum pumping system, a DC power supply, machinery to move the electrode and process control instrumentation. A more detailed description of the VAR process is given by Mitchell<sup>8</sup>. During remelting an electric arc between ingot and electrode supplies the heat for melting. Molten drops from the electrode tip successively fall into the liquid pool, and heat removal for solidification occurs through the solidified ingot and crucible. Thus, removal of impurities by evaporation is possible from two surfaces, the electrode tip and the molten pool. In addition, solid or liquid

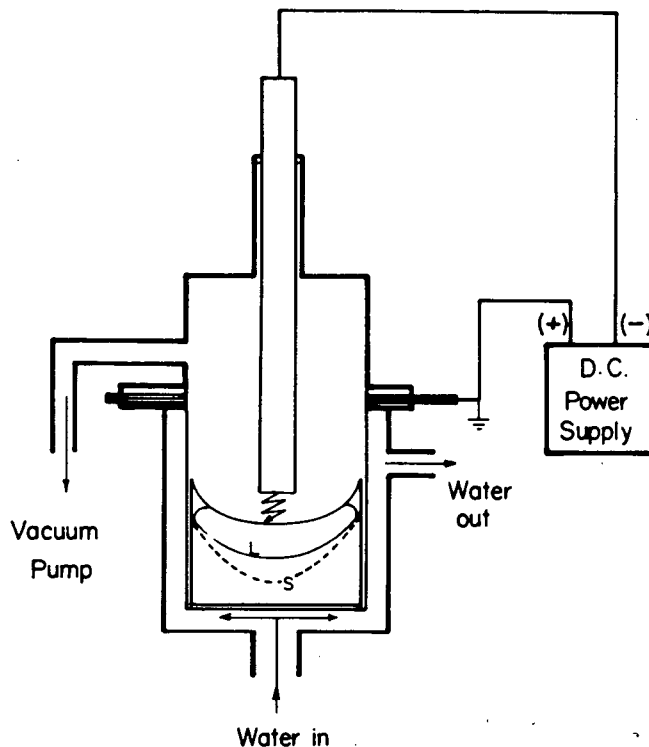


Figure 1 - Schematic outline of the VAR process<sup>8</sup>.



impurities can be removed by the fluid flow and/or buoyancy from the molten pool to the surface of the ingot.

Krone et.al.<sup>5</sup>, Povolotskii et.al.<sup>9</sup>, and Mitchell<sup>8</sup> have discussed the removal of non-metallic inclusions from steel during Vacuum Arc Remelting. It has been suggested<sup>8, 9</sup> that the non-metallic inclusions on the pool surface are mechanically removed, by either floating to the edge of the pool or being splattered on the "crown" of the ingot. Figure 2 shows the top edge of a VAR ingot containing non-metallic inclusions. Povolotskii<sup>9</sup> also found that unstable inclusions such as  $\text{SiO}_2$  are reduced by carbon but that corundum is not affected.

The pressure at the molten surfaces could be as much as

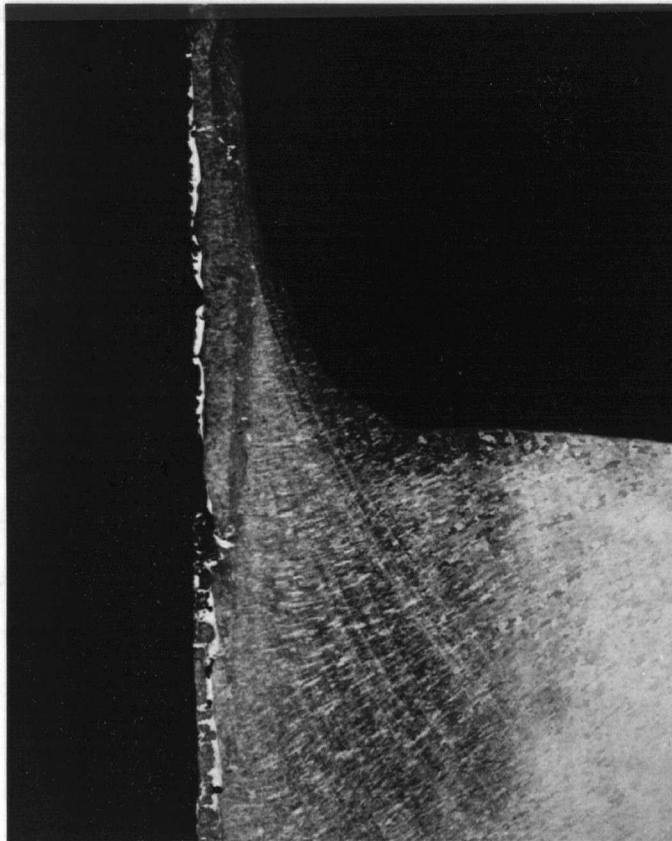


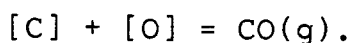
Figure 2 - Crown region of a VAR ingot which collects inclusion material floated to the ingot periphery<sup>8</sup>.

three orders of magnitude higher than that measured at the head of the pumping system<sup>5</sup>. This is reasonable, since the vapour pressure of iron alone is an order of magnitude higher at 1600°C than the "operating pressure" of  $1 \times 10^{-3} - 5 \times 10^{-3}$  torr. It is also known that Mn, which at remelting temperature is present in solution, not as sulphide, does evaporate to a large extent.

### 2.2.2 Electron Beam Remelting

As mentioned, the principal difference between VAR and EB remelting is the heat source. The EB process has been described by Schiller<sup>10</sup>. Apart from the heat source, the other major difference between the two processes is the melting chamber pressure, which is around  $10^{-2}$  torr for an industrial EB furnace. The lower chamber pressure is maintained to assure stable operation of the gun, which requires a pressure of  $10^{-4}$  torr or lower.

The removal of alloying elements and impurities has been discussed by Krone<sup>5</sup> and Doenecke<sup>11</sup>. Doenecke<sup>11</sup> suggests that manganese and sulphur are removed by evaporation, and oxygen according to the reaction



However, he does not, by either calculations or experimental results, prove the mechanisms of removal of either oxygen or sulphur.

The removal mechanism of non-metallic inclusions from steel during EB melting has not been discussed in any detail in the literature. However, EB-melting has been used for non-metallic inclusion assessment of superalloys<sup>12, 13</sup>. This technique is based on the fact that the light inclusions float to the surface of the ingot where they can later be collected. Sutton<sup>13</sup> claims that the alumina inclusions can be recovered down to the last 1 - 2 ppm using this method.

### 2.3 Inclusion Shape Control

The morphology and composition of indigenous inclusions, as well as their influence on mechanical properties, has been described by several authors<sup>14-16</sup>. The inclusion picture of a steel is directly related to the deoxidation practice. High grade steels are fully killed, usually with aluminium. Unfortunately, the aluminium oxide forms hard, angular inclusions which frequently gather in clusters. These alumina clusters can be deleterious for the mechanical properties of the steel. In addition, aluminium deoxidation promotes the formation of manganese sulphide type II. As a result of the adverse influence of alumina clusters and type II MnS alternative deoxidation practices have been developed. These practices utilize calcium, the rare earth metals, zirconium or titanium. However, in all cases initial ladle deoxidation is usually performed with aluminium. This practice increases the yield of the expensive elements which are used for inclusion modification. Here, only inclusion modification with calcium

will be discussed.

### 2.3.1 Inclusion Modification With Calcium

Calcium is among the strongest oxide and sulphide formers of the elements as can be seen in Figures 3 and 4. Therefore, it will modify existing oxides and it also prevents the formation of MnS type II. The change in inclusion morphology and composition between an untreated and a calcium treated steel is schematically illustrated in Figure 5.

Different explanations have been given for the mechanism of formation of the three types of MnS in steel<sup>14, 17-19</sup>. MnS type I inclusions are found in rimmed or semikilled steels and are of a spherical shape. It is reasonably well agreed that it forms by a monotectic reaction in the interdendritic region during solidification. Type II MnS inclusions are rodlike and found in colonies as "fences" or "fans" in killed steels. When the metal is worked the type II inclusions form almost continuous sheets of MnS which are particularly deleterious for the mechanical properties. Traditionally, type II was assumed formed by an eutectic reaction, but later investigations indicate that it forms by a cooperative monotectic reaction. MnS type III inclusions are angular and the formation is promoted by alloy elements such as C, Cr, Ca and excess Al. It has been suggested that the alloy elements change the phase diagram, the result being that MnS is precipitated as a solid proeutectoid phase. In that case the inclusions would float out of the melt like other light inclusions. Since this phenomenon

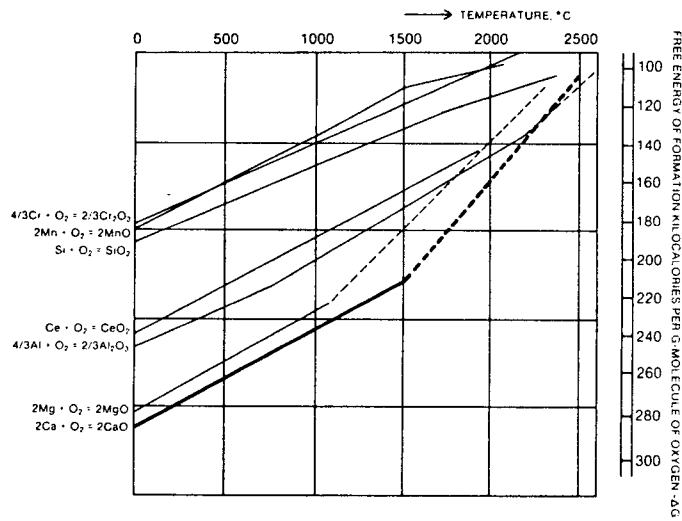


Figure 3 - Standard free energy of formation of some oxides important in steelmaking.

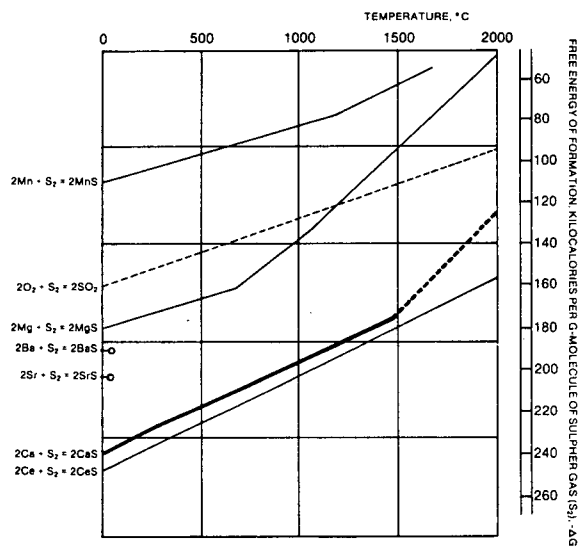


Figure 4 - Standard free energy of formation of some sulphides important in steelmaking.

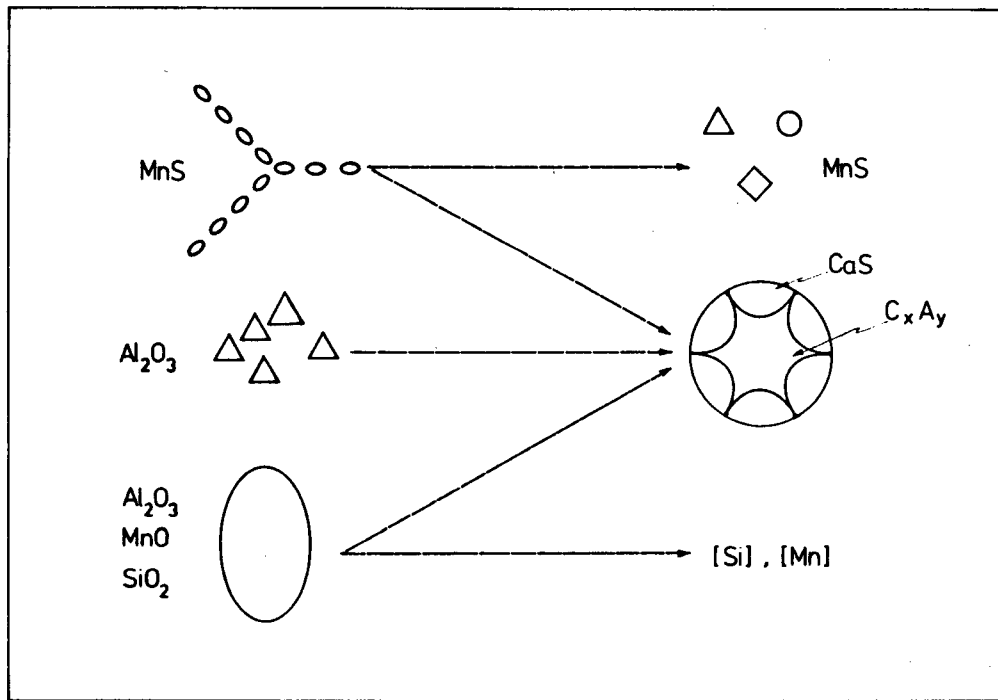


Figure 5 - Schematic representation of modification of inclusions with Ca-treatment<sup>1</sup>

has not been observed the mechanism of formation is probably different.

Salter and Pickering<sup>20</sup> and Hilty and Farell<sup>21</sup> have investigated the transformation of indigenous inclusions after addition of calcium to the steel. Calcium in solution reacts with alumina present to form calcium aluminates, the composition of these being dependent on several elements in the steel. As seen in Figure 6, the calcium aluminates formed will be liquid at steelmaking temperatures if the calcium oxide content of the oxide phase is between 36 and 68 weight %. However, even lower total CaO content can produce round hard inclusions, since the content of aluminium frequently decreases toward the periphery of the inclusion<sup>20</sup>. Hilty and Farell<sup>21</sup> and Haida et.al.<sup>22</sup> have

suggested that the composition of aluminates is related to the steel composition according to Figure 7. The aluminate composition would then be dependent on only sulphur and calcium content at constant aluminium content. However, since the content of oxygen also changes in the same direction as sulphur in these investigations, it is probable that the relationship is more complex. Faulring and Ramalingam<sup>23</sup> have proposed an inclusion precipitation diagram as an aid in determining which aluminates will form. Unfortunately, due to the lack of thermodynamic data for calcium in steel solutions the diagram is given in terms of Henrian activities. In addition, their applied thermodynamic data for the calcium aluminate system appears to be erroneous<sup>24</sup>.

Calcium sulphide is usually found as a peripheral rim around calcium aluminates with calcium content equal to or higher than  $Ca_2$ . As can be seen in Figure 8 the CaS has a solid solubility of MnS of about 10 mole %, and MnS has a solid solubility of about 14 mole % CaS. Any "high content MnS" found in calcium treated steels are of type III, and the deleterious type II is entirely eliminated. In addition to the more advantageous shape, the sulphides for calcium-treated steels are also harder than those in untreated steels, as seen in Figure 9<sup>25</sup>. However, the transformation of sulphides may not be only advantageous. It has been suggested that calcium sulphides are detrimental to the corrosion resistance of steel<sup>26, 27</sup>.

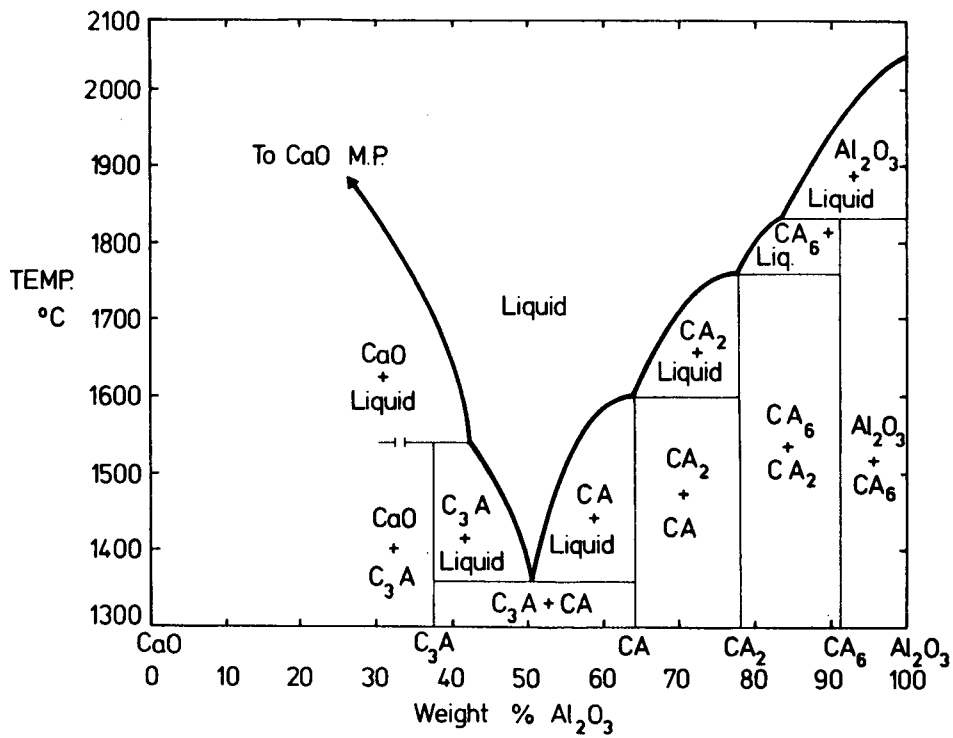


Figure 6 - The pseudo binary calcium oxide - aluminium oxide phase diagram<sup>44</sup>.

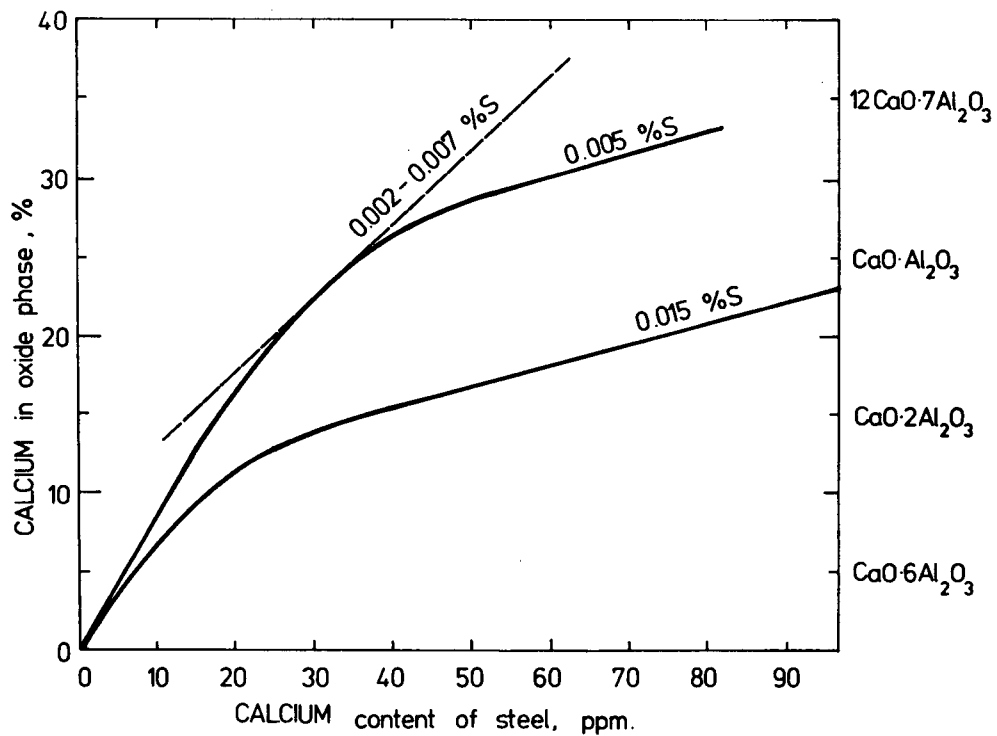


Figure 7 - Composition of calcium aluminates as a function of steel calcium content. —Hilty and Farrell<sup>21</sup>, ---Haida et.al.<sup>22</sup>.



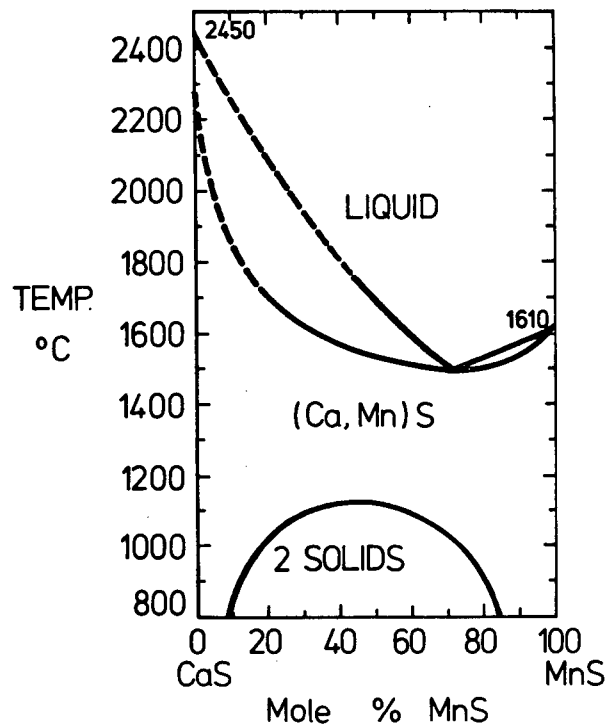


Figure 8 - The pseudo binary calcium sulphide - manganese sulphide phase diagram<sup>25</sup>.

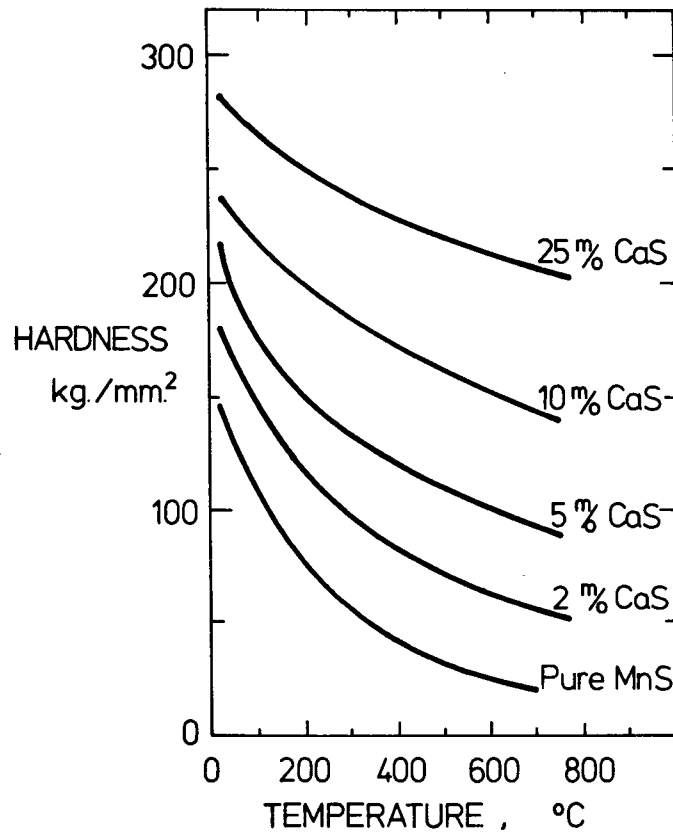


Figure 9 - Diamond pyramid hardness versus temperature for some (Mn,Ca)S solid solutions<sup>25</sup>.

## 2.4 Thermodynamic Properties

### 2.4.1 Calcium Metal

The thermodynamic data for pure calcium are well established and have been compiled by Kubashewski<sup>28</sup> and in the JANAF tables<sup>29</sup>. Vapour pressure data have been evaluated by Schurmann<sup>30</sup> at a later date. Calcium has a melting point of 839°C and a boiling point of 1494°C<sup>29</sup>. The vapour pressure is given by the following equation between 1200 and 1700°C<sup>30</sup>:

$$\ln p^0 = 10.48 - \frac{18482}{T} \quad (p \text{ in atm, } T \text{ in K}) \quad \dots (2.1)$$

### 2.4.2 Calcium In Steel

Numerous attempts have been made to establish the thermodynamic properties of calcium in iron solutions<sup>31-37</sup>. In addition, several compilations or comparisons of data exist<sup>38-41</sup>.

The reactions of interest are:



These reactions can be obtained by combining the following reactions:



The equilibrium constants for reactions 2.4 to 2.7 are reasonably well-known<sup>28, 29, 39</sup>. Sponseller<sup>31</sup> measured the solubility of calcium in liquid steel in equilibrium with liquid pure calcium. Based on this maximum solubility of 0.032 weight %, an equilibrium constant for reaction 2.8 can be calculated. The data of Sponseller also yield a Raultian activity coefficient,  $\gamma_{\text{Ca}}$ , of 2270 for calcium in pure iron solution. However, Sponseller<sup>31</sup> did not consider the oxygen and sulphur in the "pure" iron solution. Thus, part of the calcium "soluble" in iron was probably bound as sulphide or oxide. This would mean that the actual solubility of calcium in iron is lower than the value given by Sponseller. However, as other data are lacking it will be applied to calculate the equilibrium constant for reactions 2.2 and 2.3. At 1600°C this yields:

$$K_{2,2} = 5.3 \times 10^{-11} \quad \dots (2.9)$$

$$K_{2,3} = 1.6 \times 10^{-9} \quad \dots (2.10)$$

Corresponding interaction coefficients have been suggested for the calcium oxygen interaction assuming that the self-interaction coefficient for calcium is zero,  $e_0^{\text{Ca}} = -535$  and

$$e_{\text{Ca}}^0 = -1330.$$

A different approach has been taken by several other workers<sup>33-37</sup>. They assume that all non-metallic inclusions have been removed from a steel melt in contact with CaO or CaS after a certain time. Thus, the chemically analysed content of calcium in the quenched steel is assumed equal to that in solution. This approach yields "an apparent equilibrium constant",  $K_{2,2}^*$  or  $K_{2,3}^*$ , which is coordinated with interaction parameters. One such set of values is given by Gustafsson<sup>34</sup>.

$$K_{2,2}^* = 4.5 \times 10^{-8}; \quad e_{\text{O}}^{\text{Ca}} = -150 \quad \dots (2.11)$$

$$K_{2,3}^* = 3.2 \times 10^{-7}; \quad e_{\text{S}}^{\text{Ca}} = -110 \quad \dots (2.12)$$

#### 2.4.3 Calcium Aluminates

Due to the importance of the calcia alumina system in cement technology, geology and metallurgy, several authors have discussed its thermodynamic properties<sup>42-51</sup>. In spite of this fact, the thermodynamic data for the system are still not well established. For instance, recent literature values<sup>29, 52</sup> for the seemingly simple property of melting temperature of CaO, vary between 2580°C and 2950°C. Thus, all thermodynamic calculations connected to the melting point could introduce errors.

An effort has been made to determine the most recent available thermodynamic data. The phase diagram for the pseudo-binary  $\text{CaO} - \text{Al}_2\text{O}_3$  system as given in Figure 6 was determined by Nurse et.al.<sup>44</sup>. The phase  $\text{C}_{12}\text{A}_7$  is stable only in the presence of water or halogens<sup>44, 49</sup> and is not included in this diagram. Eliezer et.al.<sup>50</sup> have evaluated literature data and suggested Redlich-Kister<sup>53</sup> coefficients for the enthalpy of mixing for liquid calcium aluminates and for the activity coefficient. The integral enthalpy of mixing for the liquid  $\text{CaO} \cdot \text{AlO}_{1.5}$  system is given by

$$H = X_1 X_2 [-123.16 + 41.79(X_1 - X_2) + 30.80(X_1 - X_2)^2 - 27.06(X_1 - X_2)^3], \quad \dots (2.13)$$

where  $X_1$  (or  $X_2$ ) is either  $X_{\text{CaO}}$  or  $X_{\text{AlO}_{1.5}}$ . The activity coefficient for the same system at 1000K, with liquid pure oxides as standard state is given by

$$\log \gamma_1 = X_2^2 [-5.885 + 1.145(3X_1 - X_2) + .723(X_1 + X_2)(5X_1 - X_2) - .610(X_1 - X_2)^2(7X_1 - X_2) + .493(X_1 - X_2)^3(9X_1 - X_2)] \dots (2.14)$$

This activity coefficient, corrected for temperature and standard state will be used in the calculations involving calcium aluminates together with fusion data from JANAF<sup>29</sup>.

The most recently published experimental data of this system are those of Lourtou et.al.<sup>49</sup>. They determined activities of  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  in order to obtain the free energies

of formation of the inter-oxide compounds, and presented a relatively complete set of data for the system.

#### 2.4.4 Calcium Sulphide

The thermodynamic data for CaS have been taken exclusively from JANAF<sup>29</sup>. Similarly, as with CaO, data related to the melting of CaS may not be reliable due to the high melting point.

#### 2.5 Evaporation Rate

In a good vacuum ( $p < 10^{-3}$  atm) the evaporation rate from the surface of a metal melt is described by the Langmuir equation<sup>54-58</sup>:

$$m = 44.33St\sqrt{M/T} \gamma Xp^0\alpha \quad \dots (2.15)$$

This equation shows that the evaporation rate is independent of total pressure but dependent on evaporation area, time of exposure and temperature.

If almost all calcium is bound as either CaS or  $C_xA_y$ , evaporation of calcium in solution will occur from a very dilute solution. A sample calculation shows that for realistic VAR melting conditions, ( $A = 3700 \text{ cm}^2$ ,  $T = 1600^\circ\text{C}$ ) an amount in excess of 1 ppm calcium would hypothetically evaporate, assuming that the Henrian activity in the steel is 0.1 ppm. Thus, the rate limiting step will not be evaporation of calcium from solution, but rather the reaction of the inclusion compounds

present on the surface giving rise to the calcium in solution.

### III. EXPERIMENTAL PROCEDURES

#### 3.1 Samples

Two types of samples were investigated. Samples from corresponding electrode and VAR ingots were obtained from three different companies. To supply additional data, laboratory samples produced with the aid of the induction and electron beam furnaces at UBC were prepared.

##### 3.1.1 Industrial Samples

The industrially produced steels were of the high-strength low-alloy type. In all cases, the electrode steels were ladle treated with calcium, either by direct addition of "Ferrocium" or by wire addition. The steels were Vacuum Arc Remelted under approximately the conditions given in Table 1.

##### 3.1.2 Laboratory Samples

The laboratory electrodes were prepared in a five kilogram induction furnace. Magnesia crucibles were used to avoid pickup of impurities. The initial charges of "Armco iron" were melted

Table 1 - VAR melting conditions

Electrode diameter:	470 mm	Note: Parabolic distribution.
Ingot diameter:	500 mm	
Melting rate:	300 kg/hr	
Pool temperature:	1500 - 1680°C	
Operating pressure:	$10^{-3}$ - $5 \times 10^{-3}$ torr	



under a shield of argon. When the entire charge was molten, preliminary deoxidation was performed by stirring the melt with graphite rods. Appropriate amounts of the alloy additions, ferromanganese, iron sulphide and aluminium were added. Finally calcium metal was added by plunging pellets wrapped in iron foil into the melt. The melts were then allowed to solidify in the crucible. Unfortunately, melts poured into a mould before solidification did not contain the desirable types of inclusions. This could have been due to excessive reoxidation. In some cases, pin samples of a diameter of 4.2 mm were taken from the bath, in order to study the inclusions in the liquid melt.

The melting procedure produced a cylindrical ingot. Samples for analysis were cut from the middle of the ingot in such a manner as to avoid the areas associated with the outside surface and solidification shrinkage (see Figure 10). One or several electrodes for subsequent Electron Beam remelting were cut along the cylinder.

The electrodes were remelted in a 15 kW laboratory electron beam furnace utilizing a gun manufactured by the Manfred von Ardenne Research Institute<sup>10</sup>. The furnace is shown in Figure 11. The conditions for remelting are given in Table 2. An arrangement of mirrors made it possible to watch the melt in progress.

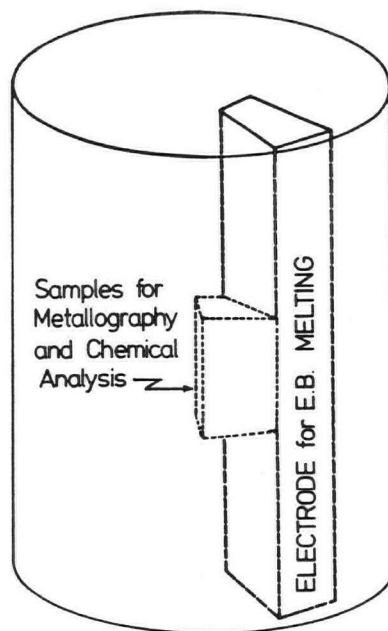


Figure 10 - Schematic figure showing where samples and electrodes for EB melting were cut from induction furnace ingots.

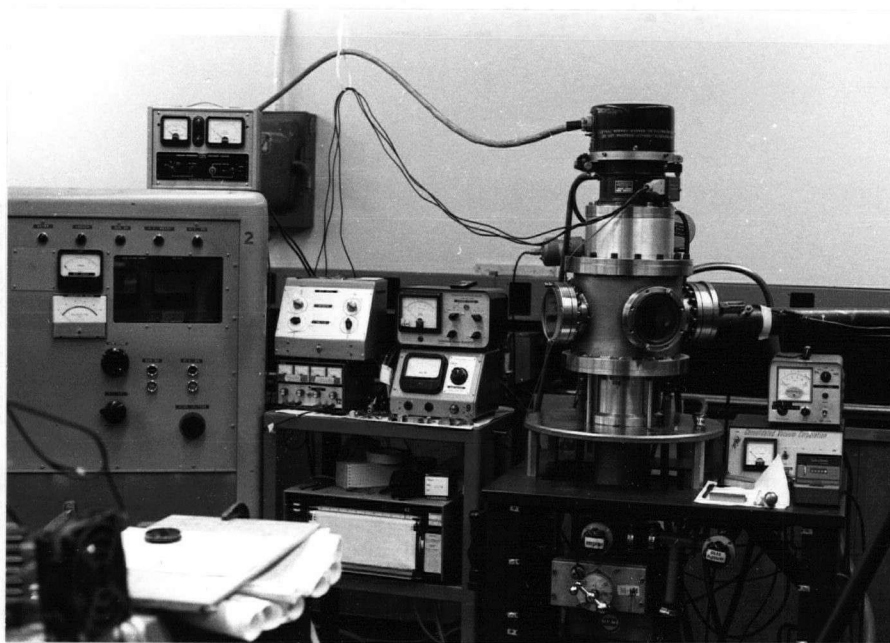


Figure 11 - The Electron Beam furnace at UBC.

Table 2 - EB remelting conditions

Electrode crossection:	2.2 - 4 cm <sup>2</sup>
Melting rate:	0.7 - 1 kg/hr
Melt size:	200 g
Operating pressure:	10 <sup>-4</sup> torr

### 3.2 Analysis

#### 3.2.1 Metallographic Examination

Sections of both electrode and ingot materials were ground and polished. To prevent oxidation of the calcium sulphides, contact with water was avoided during the preparation stage and the samples were stored in a dessicator<sup>15</sup>.

General metallographic examination was done with optical microscopy. Qualitative and semiquantitative analysis of the inclusions in situ was obtained by Scanning Electron Microscopy - EDX analysis. Quantitative inclusion analysis was performed for some of the samples by electron microprobe analysis. The standards for microprobe anaylsis were: Pure Mn, pure Fe, Al<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub> and ZnS. The raw intensities were corrected using a Magic IV program. The phases frequently interfere with each other during microprobe analysis, as the calcium sulphide is present as a peripheral rim around the aluminates. This problem is schematically described in Figure 12. The problem can be overcome if 5 elements (Fe, Mn, Ca, S, and Al) are analysed simultaneously. Unfortunately, the microprobe at UBC can only analyse two elements simultaneously. Therefore, most of the microprobe analysis was done on electrode materials where larger

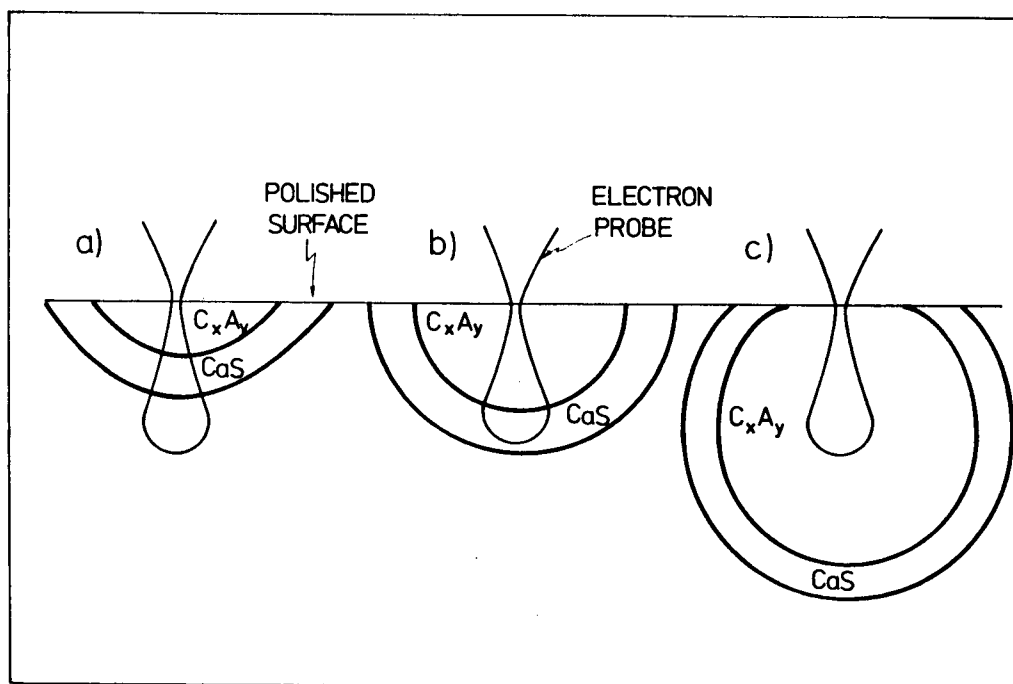


Figure 12 - Schematic description of the problems with microprobe analysis. Note that all three inclusions give the same appearance from the surface.

- a) Ca, Al, S, Fe, (and sometimes Mn) must be analysed simultaneous to determine the C/A ratio.
- b) Ca, Al, S, (and sometimes Mn) must be analysed.
- c) Only in this case can an accurate C/A ratio be obtained by analysing only two elements.

inclusions could be found.

### 3.2.2 Bulk Steel Composition

Bulk analysis of most elements was obtained by spectrographic analysis. The oxygen content was determined by the vacuum fusion method and the sulphur content by the combustion iodometric method according to standard procedures. The calcium contents were determined with atomic absorption spectrophotometry using a modified version of the method described by Hilty and Farrell<sup>21</sup>, as described in Appendix B.

### 3.2.3 Inclusion Extraction

In order to confirm the electron microprobe analysis and to determine the inclusion composition for the materials with inclusions too small for microprobe analysis, chemical inclusion extraction was performed. Methanol bromine extraction under dry conditions was applied according to the technique described by Reyes-Carmona<sup>59</sup>. By subjecting artificial calcium aluminates and calcium sulphide to the extraction, it was determined that a mixture of  $C_3A$  and  $CA$  or pure  $CA$  do not dissolve whereas  $CaS$  does dissolve. Thus, this separation technique made it possible to determine the quantity of calcium bound as oxide and as sulphide assuming that all calcium is bound as either sulphide or oxide in the solid steel.

The collected inclusions were transferred to aqueous solution by the lithium-metaborate method<sup>60</sup> for subsequent atomic absorption analysis. By analysing for  $Ca$  in the inclusions, the average composition of the calcium aluminates could be determined assuming that all oxygen was bound as calcium aluminate in the steel.

An attempt was made to analyse the calcium in solution from the extraction. This calcium represents the calcium bound as sulphide. Unfortunately, this failed probably due to pick up of calcium from the apparatus. Another problem was the contamination of the extracted precipitates by carbides. This prevented weighing of the oxide phase and made x-ray diffraction very difficult.

#### IV. RESULTS AND DISCUSSION

##### 4.1 Thermodynamic Considerations

Calcium could be present in four phases during remelting, liquid metal, solid sulphide, liquid or solid oxide, and gas phase. Consider the equilibrium between dissolved calcium and gas at 1600°C:

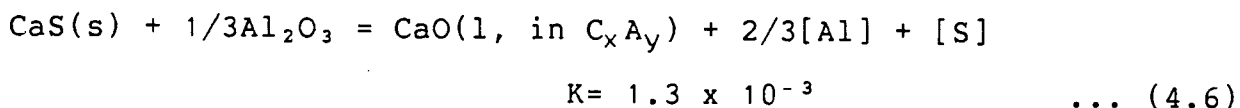
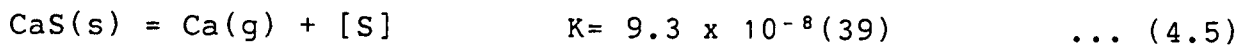
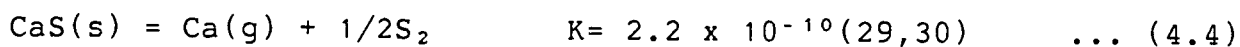
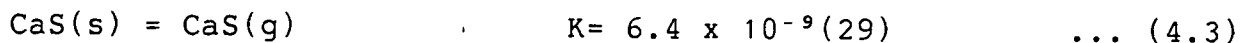


As the total pressure does not exceed  $10^{-3}$  atm during VAR remelting, and the partial pressure of calcium can not be higher, it follows that the activity of calcium in the melt according to reaction 4.1, will be lower than 0.2 ppm. Therefore, calcium in the metal phase will not be considered. However, it is possible that dissolved calcium takes part in the reactions as an intermediate species. The equilibrium constant for reaction 4.1 is probably inaccurate as pointed out in the literature review. The anticipated lower solubility of calcium in steel would yield an even higher  $K_{4.1}$ . Thus, the assumption would be valid also in that case.

---

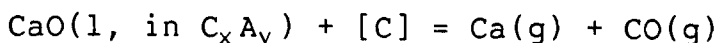
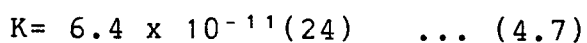
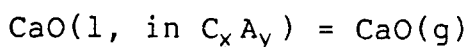
\* The standard state for sulphides and oxides is pure solid compounds. The standard state for elements dissolved in iron solution is Henrian infinitely dilute solution. References are given in parenthesis where new equilibrium data have been applied.

Calcium sulphide could take part in the following reactions during vacuum remelting:



It has been shown<sup>47</sup> that the maximum solubility of sulphur in a  $\text{C}_x\text{A}_y$  melt containing 50 weight % CaO is 1.4 weight %. The average composition of the aluminate inclusions in a steel is likely to be on the alumina rich side. Since these aluminates have a lower solubility of sulphur, even if reaction 4.2 takes place it will not be of quantitative importance. The equilibrium constants show that 4.5 is most likely to occur under standard conditions. However, the probability that reactions 4.5 and 4.6 will occur depends on the activities of the species. These reactions will be discussed later in conjunction with other possible reactions.

Possible reactions that the oxide phase could take part in are:



$$K = 1.5 \times 10^{-5} \quad \dots (4.8)$$



$$K = 2.1 \times 10^{-1} \quad \dots (4.9)$$

Of these reactions, 4.8 and 4.9 appear most likely to occur.

Further investigation of the feasibility of reactions 4.5, 4.6, 4.8 and 4.9 in an industrial steel requires a knowledge of the thermodynamic properties of the elements in steel solution. However, as mentioned in the literature review, the thermodynamic data for calcium in steel solution and its interaction parameters with other elements are not well established. Because of this, a hypothetical steel with only carbon, aluminum and sulphur in the steel solution will be discussed. The Henrian activities of the dissolved elements and the activities of  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  in  $C_xA_y$  for the "example" composition has been determined using the mentioned literature data<sup>28, 29, 39, 49-51, 53</sup>. The hypothetical steel is described in Table 3. The activities in the hypothetical steel yield the following ratios of reaction products over reactants ("=R") for the interesting reactions:

$$R_{4.5} = 2.7 \times 10^{-6} \quad (K_{4.5} = 9.3 \times 10^{-8})$$

$$R_{4.6} = 4.9 \times 10^{-5} \quad (K_{4.6} = 1.3 \times 10^{-3})$$

$$R_{4.8} = 2.5 \times 10^{-5} \quad (K_{4.8} = 1.5 \times 10^{-5})$$

$$R_{4.9} = 4.6 \times 10^{-4} \quad (K_{4.9} = 2.1 \times 10^{-1})$$

As can be seen, there is a thermodynamic driving force for both



Table 3 - Description of the hypothetical steel

	ASSUMED PROPERTY	VALUE USED IN CALCULATIONS	REFERENCES
METAL PHASE: Sulphur Aluminium Carbon	$c_S = .0025 \text{ wt}\%*$ $c_{Al} = .025 \text{ wt}\%*$ $c_C = .30 \text{ wt}\%*$	$h_S = .0027$ $h_{Al} = .027$ $h_C = .33$	39 39 39
INCLUSIONS: CaS(s) $C_xA_y$	$X_{CaS} = 1$ $c_{CaO} = 40 \text{ wt}\%$	$a_{CaS} = 1$ $a_{CaO} = 0.12**$ $a_{Al_2O_3} = 0.21**$	- 29, 49, 50 28, 49, 50
GAS PHASE: Calcium CO	$p_{Ca} = 10^{-3}$ $p_{CO} = 10^{-3}$	$p_{Ca} = 10^{-3}$ $p_{CO} = 10^{-3}$	- -

\* S, Al and C are the only elements assumed present in solution.

\*\*  $a_C = .13, .11$  at  $1550^\circ\text{C}$  and  $1650^\circ\text{C}$  and  $a_A = .23, .19$ .

reactions 4.6 and 4.9 to occur.

The temperature of  $1600^\circ\text{C}$  has been adopted as a reasonable average temperature in the liquid film on the electrode and in the pool during VAR melting. To ensure that a shift in temperature does not change the relationship, reactions 4.5, 4.6, 4.8, and 4.9 were evaluated at  $1550$  and  $1650^\circ\text{C}$ . The results of this evaluation are given in Figure 13. The figure shows that an increase in temperature will increase the driving force of reaction 4.8. However, the driving forces for reactions 4.6 and 4.9 are still higher at all temperatures.

From this simple thermodynamic discussion it appears that two reactions are most likely to occur during VAR melting. These are:

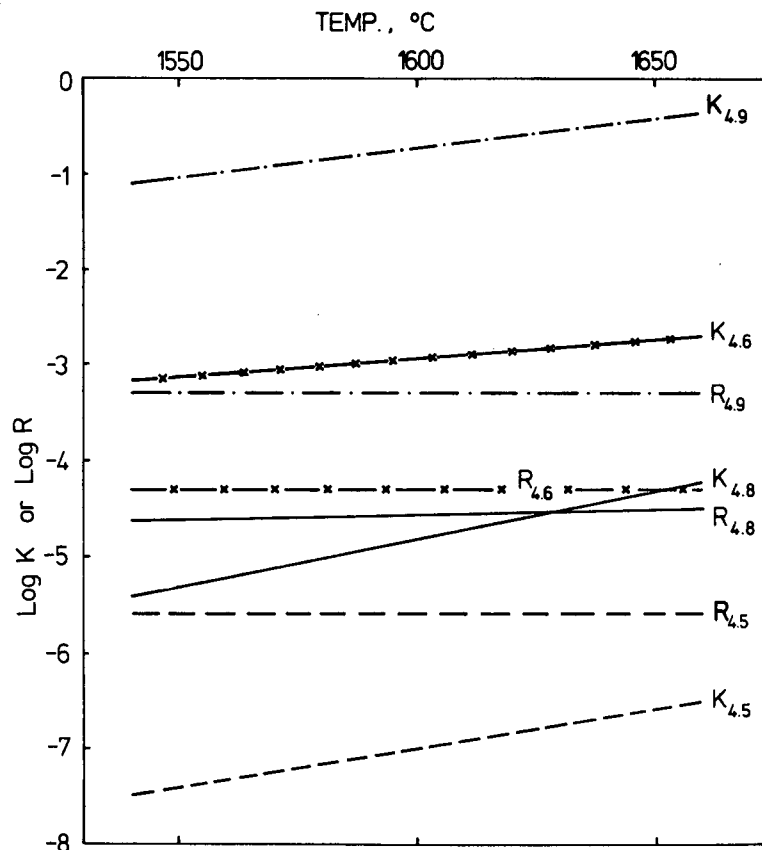
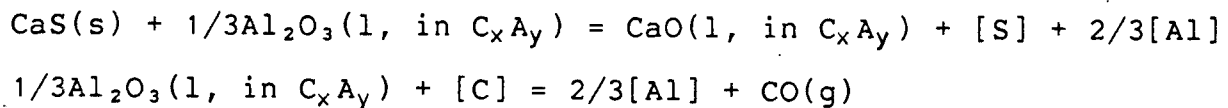


Figure 13 - Evaluation of the thermodynamic driving force.



#### 4.2 Electron Beam Remelting

The electron beam remelting experiments served to show in a qualitative manner the effect of vacuum remelting on calcium containing inclusions.

During remelting, inclusions could be observed both on the electrode tip and on the pool surface. These inclusions started coalescing on the electrode and formed "beads" of inclusions on the pool surface. The beads had a tendency to float to the

edges of the ingot, where they would freeze to the solid shell. Figure 14 shows an inclusion bead which was collected from the surface of a frozen ingot. As the figure shows, both the calcium aluminate and the calcium sulphide inclusions float out together. However, the amount of calcium sulphide in the bead was smaller than expected. Microprobe and SEM-EDX analysis show that the oxide phase in the coalesced beads contains more calcium oxide than the calcium aluminates in the electrode steel, as can be seen in Figure 15. These observations together with the thermodynamic discussion indicate that reactions 4.6 and/or 4.9 possibly take place during remelting. Both reactions give enrichment of calcium oxide in the oxide phase but only 4.6 explains the small amounts of calcium sulphide which remains in the coalesced beads.

Metallographic analysis of sectioned electrodes confirm that the inclusions coalesce during remelting. Figure 16 shows the earlier molten film on an electrode tip containing an example of coalesced inclusions.

#### 4.3 Industrial VAR Samples

The results of the chemical bulk analysis of the industrial electrode and ingot samples are given in Table 4. In this table it is interesting to note that regardless of the electrode content of calcium, the ingot will contain only between 5 and 10 ppm. Another interesting observation is that the loss of sulphur is generally less than 10 ppm.

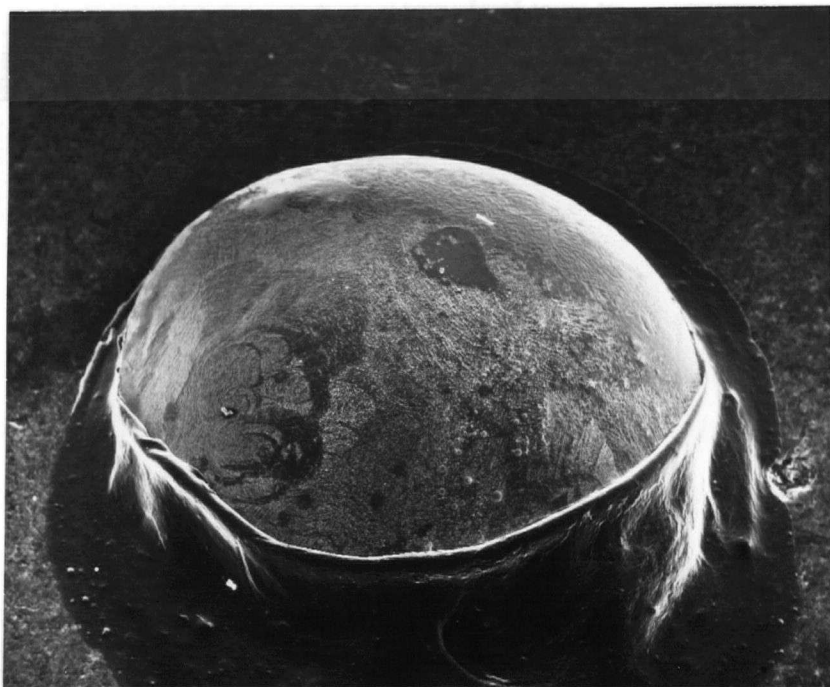


Figure 14 - "Bead" of coalesced inclusions collected from surface of EB-melted ingot. The black patches are CaS and the bulk phase is  $C_xA_y$ . (The bead has been glued to the substrate.) SEM image x28.

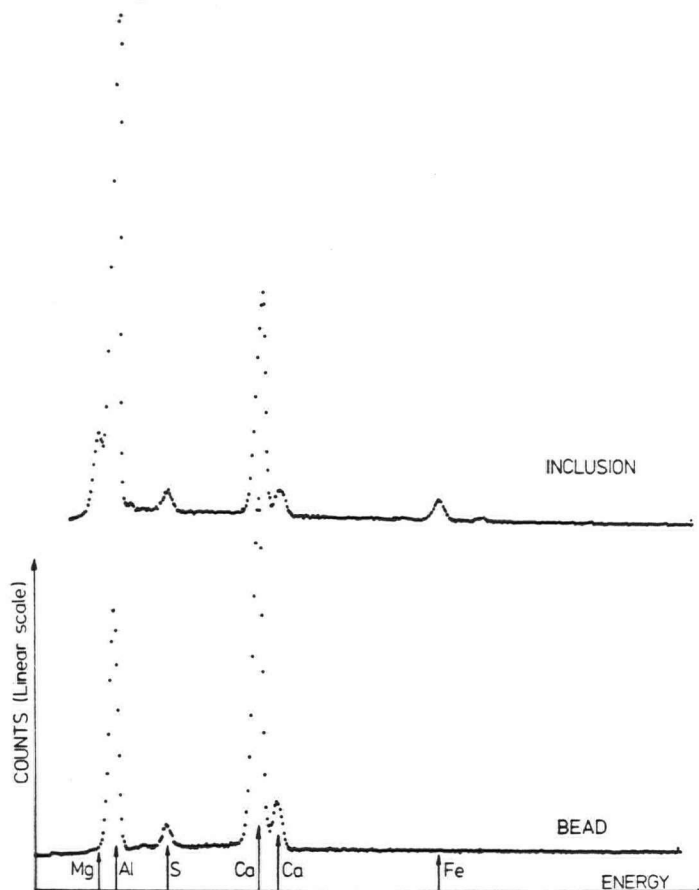
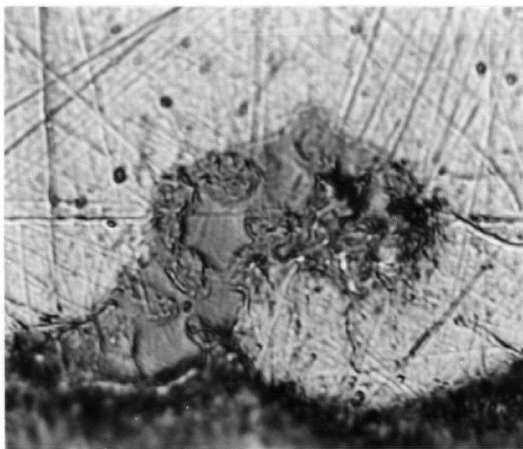


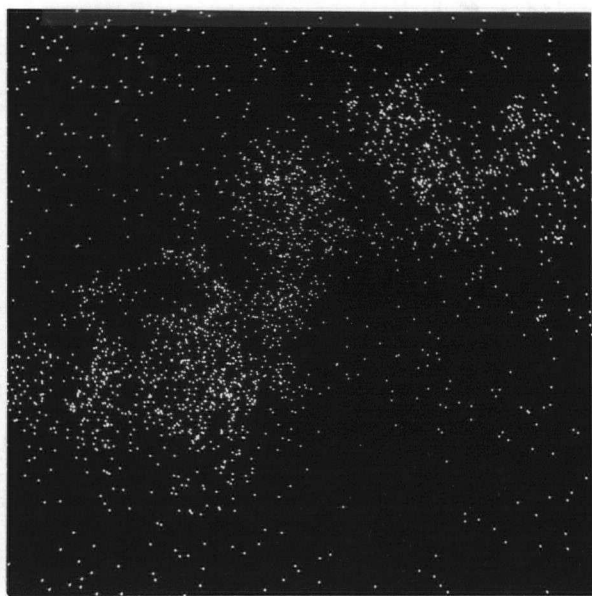
Figure 15 - X-ray spectra showing the relative composition of an inclusion in an electrode steel and corresponding inclusion "bead".



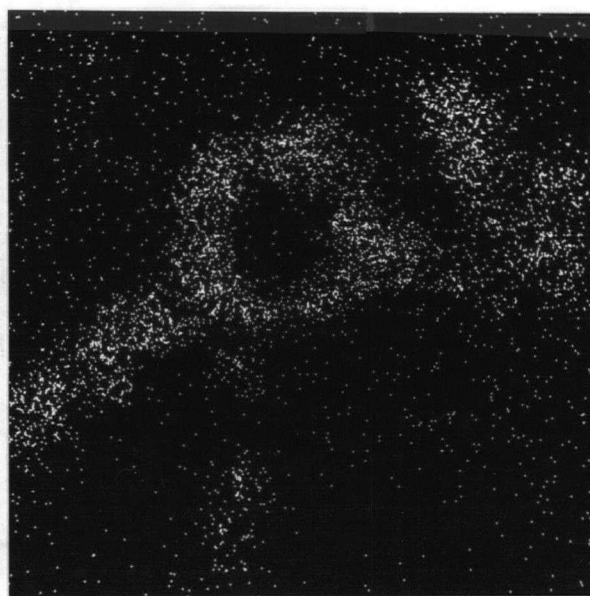
10  $\mu\text{m}$



Ca



Al



S

Figure 16 - Coalesced inclusions on an electrode tip.  
Light microscope and SEM X-ray images.

Table 4 - Summary of analysis. Vx marked samples denotes electrode steels, and VxR marked samples are corresponding remelted ingots.

Steel	Total content in steel (wt%)				Content in aluminate (wt%)		Ca/Al
	Ca	Al	O	S	Ca	Al	
V1	.0029	.030	.0066	.0050	.0014	.013	.16
V1R	.0006	.017	.0022	.0015	.0003	.0024	.08
V2	.0063	.030	.0068	.006	.0025	.008	.26
V2R	.0005	.024	.0014	.0052	.0002	.0042	.10
V3	.0060	.026	.0060	.0070	.0018	.011	.20
V3R	.0007	.022	.0021	.0060	.0004	.010	.13
V4	.0062	.053	.0069	.0037	.0035	.027	.38
V4R	.0006	.034	.0014	.0031	.0005	.0064	.25
V5	.0030	.023	.0054	.0015	.0015	-	.18
V5R	.0008	.021	.0016	.0012	.0001	-	.05
V6	.0020	.024	.0032	.0023	.0011	.0035	.26
V6R	.0002	.024	.0025	.0021	.0003	.011	.02

\*Based on Ca/O balance for the aluminates.

Table 5 shows the loss of the elements of interest during VAR melting. The predicted loss of aluminium, oxygen and sulphur was calculated assuming that all calcium is bound as either oxide or sulphide in the electrode and that the sole removal mechanism of inclusions is rejection to a free surface. The prediction was further based on the loss of calcium in the oxide phase, the known composition of the calcium aluminates and the distribution of calcium between sulphide and oxide in the electrode and the ingot. As can be seen, the predicted loss of oxygen agrees well with the actual oxygen loss. On the other hand, the analysed loss of aluminium is erratic as compared to the predicted aluminium loss. This is probably due to

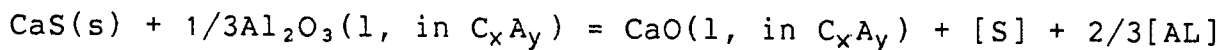
Table 5 - Results of mass balances

Steels	Atom% lost during remelting				Predicted loss*		
	Ca	Al	O	S	Al	O	S
V1: In incl.	.0016	.022			.010	.017	.0017
Total	.0033	.027	.013	.0062			
V2: In incl.	.0032	.007			.012	.022	.0049
Total	.0081	.012	.019	.0019			
V3: In incl.	.0021	.002			.010	.018	.0053
Total	.0074	.008	.014	.0020			
V4: In incl.	.0034	.043			.009	.017	.0039
Total	.0073	.040	.019	.0011			
V5: In incl.	.0020	-			.011	.018	.0011
Total	.0031	.002	.013	.0003			
V6: In incl.	.0011	-			.004	.007	.0006
Total	.0025	.0	.002	.0003			

\*Assumption: The inclusions float out. The mass balance is based on calcium loss.

interference from aluminium nitrides. Firstly, the aluminium nitrides would follow a similar removal pattern during remelting as the oxides, and secondly the aluminium nitrides are resistant to bromine-methanol dissolution<sup>61</sup>. However, it appears that rejection to a free surface is the major mechanism of removal of calcium aluminates.

The predicted loss of sulphur is, except in one case, three times higher than the actual loss. Evidently, some other mechanism takes part in the removal of calcium from sulphide while the sulphur remains in the steel. Consideration of the thermodynamic calculations and the EB experiments suggests that the likely additional removal mechanism is that of reaction 4.6:



This agrees well with the fact that calcium is removed while sulphur remains in the steel.

To summarize, the calcium aluminates are removed by rejection to a free surface. One third of the calcium sulphide is also removed by rejection. The remainder reacts according to equilibrium 4.6 to form calcium oxide and dissolved sulphur. Subsequently, the formed oxide will be removed with the original oxide phase by rejection, and the sulphur will form manganese sulphide, iron-sulphide or chromium sulphide during solidification depending on the steel composition.

Reaction 4.9 could contribute to the increase of CaO in the oxide phase during remelting. However, it does not account for the loss of calcium while sulphur remains in the steel. This fact, in addition to literature data<sup>9</sup>, suggests that reaction 4.9 is inhibited or slowed down, while reaction 4.6 occurs more readily.

#### 4.4 General Observations Related To Calcium Treated Steels

During the course of this work some observations were made which are not directly connected to vacuum remelting but to calcium in steel in general. These observations will now be discussed.



#### 4.4.1 Calcium Aluminate Composition

As discussed in the literature review, (section 2.3.1.) it has been suggested that the calcium aluminate composition is dependent on calcium and sulphur content at constant aluminium content according to Figure 7. However, in this work it was found that the electrode steels, with an oxygen content of 60 - 70 ppm, but only 50 ppm sulphur, yield the graph given in Figure 17. Considering that the steels of Hilty and Farell contain 50 ppm sulphur and 30 ppm oxygen and for the other graph 150 ppm sulphur and 43 ppm oxygen it appears that the oxygen content influences the composition of the aluminates more than

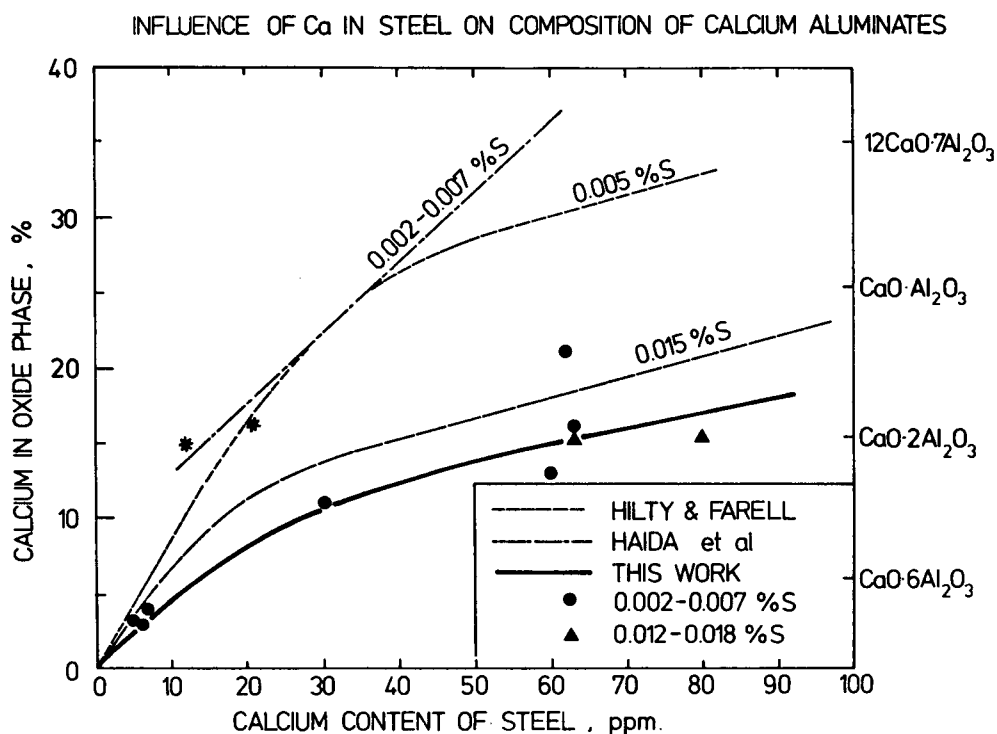


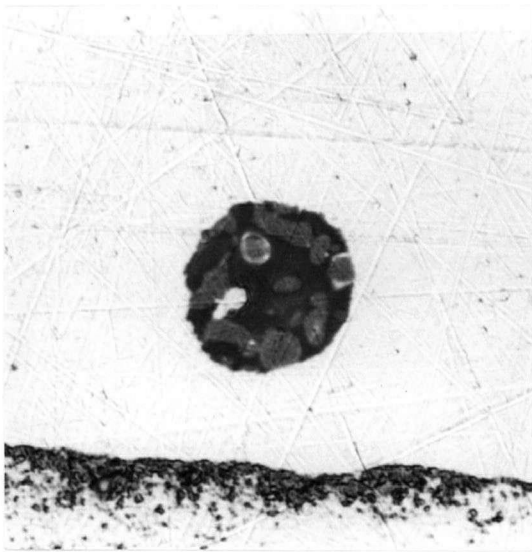
Figure 17 - Composition of calcium aluminates as a function of steel calcium content. Experimental results, and results from Hilty & Farell<sup>21</sup> and Haida<sup>22</sup>  
 \*marked steels have lower oxygen contents than the other steels

the sulphur content. Probably the resulting aluminate composition will be dependent not only on sulphur and calcium content but also on aluminium and oxygen content. This relatively complex subject can only be resolved after further investigation.

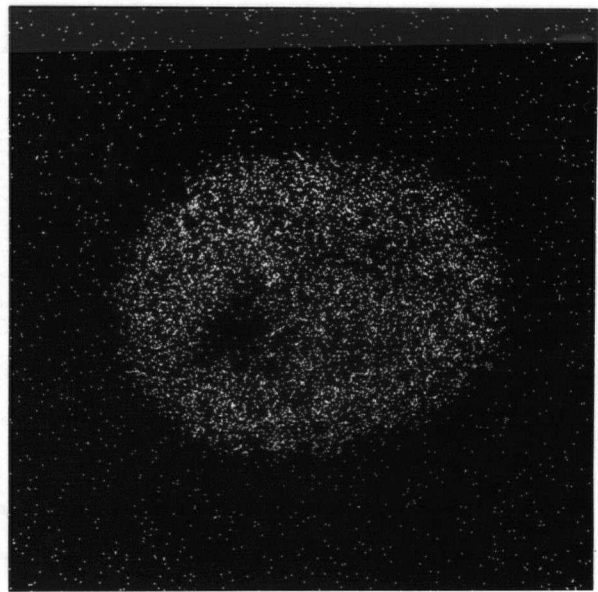
#### 4.4.2 Inclusions In The Liquid Steel

During the investigation it was observed that metallographic sections taken from small ladle samples contained pure CaS in rims around the aluminates and pure MnS type III. On the other hand, samples from large ingots revealed CaS rims containing some MnS and pure MnS type III. This suggests that the solid solution (Ca,Mn)S only develops if the MnS is given enough time to form during solidification (see also the phase diagram, Figure 8). The presence of pure MnS could be explained if all calcium reacts with either oxygen or sulphur in the bath.

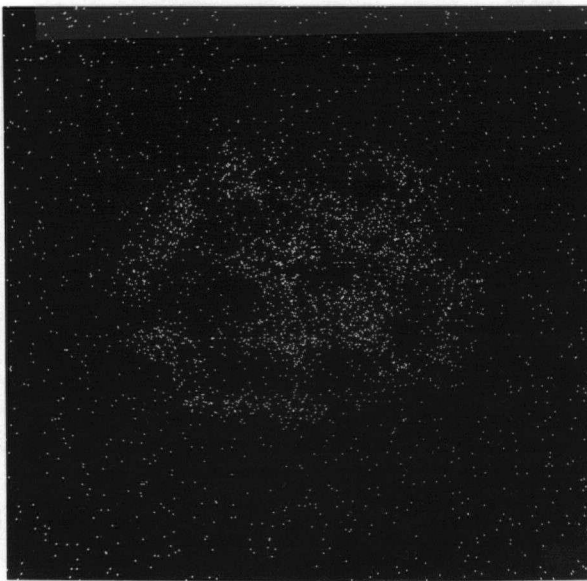
No investigation of the inclusions in a calcium treated liquid steel has been published. Therefore, a calcium containing steel was prepared in the induction furnace and pin samples taken from the liquid. An inclusion from one of the pin samples is shown in Figure 18. As the pin samples solidify immediately when they are drawn from the bath, the 20  $\mu\text{m}$  inclusion clearly existed in the liquid steel. The sulphide is pure CaS although the steel contained roughly 1% weight Mn. It is interesting that the CaS is present as "islands" in the aluminate, and not as a peripheral rim as expected in a normally solidified steel.



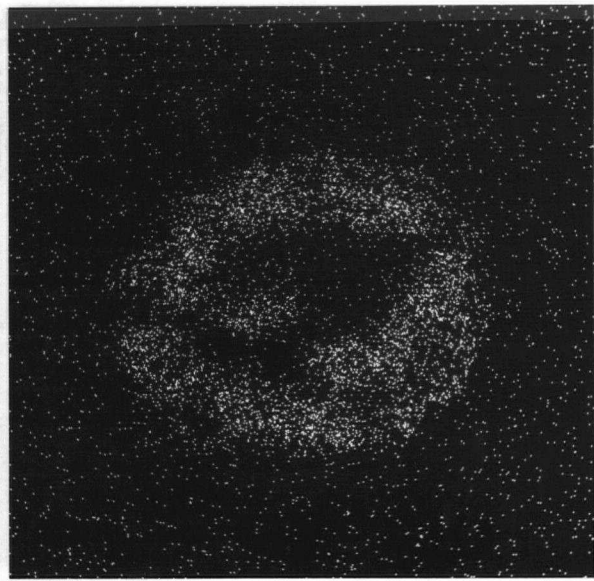
10  $\mu\text{m}$



Ca



Al



S

Figure 18 - Inclusion in pinsample taken from the liquid steel. Light microscope and SEM X-ray images.

Although the evidence is scanty, a possible precipitation sequence for the sulphides can be suggested. In the liquid bath calcium sulphide precipitates in or on the calcium aluminates. As solidification of the steel proceeds, Mn will segregate and reach such a level that MnS start precipitating. The MnS can either form a solid solution with existing solid CaS or form individual MnS type III sulphides. If all calcium in solution has already reacted with either oxygen or sulphur no calcium will be left to form high content manganese (Mn,Ca)S. This will happen if the total steel content of calcium is smaller than 2.5 times the total content of sulphur in weight percent, since approximately half the calcium is bound as sulphide.

The hypothesis is supported by the thermodynamic data, as seen in the following reaction, where K is calculated at 1600°C:



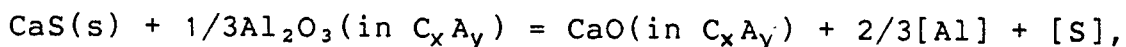
It appears unlikely that the equilibrium can be approached at high MnS activity, while low MnS activity and corresponding high CaS activity could lead to equilibrium conditions.

In an industrial steel, it is therefore not surprising that no high content manganese (Mn,Ca)S inclusions can be found. The beneficial effects of solid solution hardening of MnS inclusions (see Figure 9) can thus not be expected, unless very high contents of calcium are present.

V. CONCLUSIONS

The conclusions of this investigation are:

- 1) The principal mechanism of removal of calcium aluminates during VAR remelting is rejection to a free surface. The aluminates are hence collected on the periphery of the ingot.
- 2) Approximately one third of the calcium sulphide is removed together with the aluminates by rejection to a free surface.
- 3) Two thirds of the calcium sulphide reacts to form calcium oxide according to the the following reaction:



with the calcium oxide being rejected with the original oxide phases, and the sulphur reacting with available sulphide formers, for instance Mn, during ingot solidification.

- 4) The content of calcium in the remelted ingot will be 5 - 10 ppm regardless of the electrode calcium content. Therefore, the calcium treatment is more important for desulphurization than for inclusion shape control.

- 5) The results of this study are not in agreement with previous work which attempts to establish the composition of the calcium aluminates as a function of the steel content of sulphur, aluminium and calcium. Specifically it is found that the influence of oxygen content has not previously been sufficiently taken into account.

BIBLIOGRAPHY

1. L.E.K. Holappa: Int.Met.Rev., 1982, v. 27, no 2, pp. 53-76.
2. J.W. Robison: Scaninject III, Lulea, June 1983, paper 35.
3. T. Ototani: Ibid, paper 36.
4. P. Dewsnap: I and SM, Aug 1982, pp 15-17.
5. K. Krone, J. Kruger, H. Winterhager: "Beitrag zum Schmelzen von NiCr - Basislegierungen im Hochvakuum." Forschungsberichte des Landes Nordrhein - Westfahlen, nr 1825, Westdeutscher Verlag, Koln und Opladen, 1967.
6. V.I. Kazakov, A. Ya. Golubev, B.V. Sokolov, V.A. Boyarshinov: Metal Science and Heat Treatment, v. 18, Jan-Feb 1976, pp 35-39.
7. M. Wahlster, H. Spitzer: Stahl Eisen, v. 92, Sep 1972, nr 20, pp 961-972.
8. A. Mitchell: Electroslog and Vacuum Arc Remelting Processes. To be published.
9. D. Ya. Povolotskii, R.I. Grechin, A.V. Rechkalova, Yu. V. Kofman, V.E. Roshchin: Steel USSR, Dec 1973, v. 3, nr 12, pp 1004-1007.
10. S. Schiller, H. Forster, G. Jasch: Metallurgia, Nov 1980, v. 47, nr 11, pp 554-569.
11. C. Doenecke: "Einfluss des Elektronenstrahl-schmelzens auf die chemischen Veränderungen und die mechanischen Eigenschaften hochfester Baustähle." PhD. thesis, Technischen Universität Clausthal, 1971.
12. P. Loevenstein: Powder Metallurgy Superalloy Aerospace Materials for the 1980's, v. 1, Switz., 18-20 nov. 1980, pp 1-28.
13. W.H. Sutton: Proc. 7th Int. Conf. Vacuum. Met., 1982, Tokyo, Japan, pp 916-923.
14. F.B. Pickering: "Inclusions", The institution of Metallurgists, Monograph nr 3, London, 1979.
15. R. Kiessling: "Non metallic inclusions in steel", 2nd ed, The metals society, London, 1978.
16. H. Nordberg (editor): "Swedish symposium on Non-Metallic

Inclusions in Steel" Uddeholms AB, Sweden 1981.

17. T.J. Baker, J.A. Charles: JISI, sep 1972, pp702-706.
18. H. Takada, I. Bessho, T. Ito: Trans. ISIJ, v. 18, 1978, pp 564-573.
19. H. Fredriksson, M. Hillert: Scand. J. Met., v. 2, 1973, pp 125-145.
20. W.J.M Salter, F.B Pickering: JISI, July 1967, v. 207, pp 992-1002.
21. D.C. Hilty, J.W. Farell: I and SM, v. 2, 1975, Part I: May pp 17-22, Part II: June pp 20-27.
22. O. Haida, T. Emi, K. Sanbongi, T. Shiraishi, A. Fujiwara: Tetsu-to-Hagane, 1980, v. 66, no 3, pp 48-56.
23. G.M. Faulring, S. Ramalingam: Met. Trans. B, v. 11B, 1980, pp 125-130.
24. B.S. Hemmingway: J. Phys. Chem. 1982, v. 86, pp 2802-2803.
25. C. Leung: PhD thesis 1977, The University of Michigan.
26. R. Kiessling, C. Westman: JISI, July 1970, pp 699-700.
27. G. Eklund: Jernkontorets Annaler, v. 154, 1970, pp 321-324.
28. O. Kubashevski, C.B. Alcock: "Metallurgical thermochemistry", 5 ed, Pergamon Press 1979.
29. D.R. Stull, H. Prophet et.al.: JANAF Thermochemical Tables, 2nd ed, and supplements: J. Phys. Chem. Ref. Data v. 3-11, 1974-1982.
30. E. Schurmann, R. Schmidt: Arch. Eisenhüttenwes. v. 46, nr 12, 1975.
31. D.L. Sponseller, R.A Flinn: Trans. Met. Soc. AIME, 1964, v. 230, pp 876-888.
32. S. Kobayashi, Y. Omori, K. Sanbongi: Trans. ISIJ, v. 11, 1971, pp 260-269.
33. S. Gustafsson, P.O. Mellberg: Scand J. Met. v. 9, 1980, pp 111-116.
34. S. Gustafsson, Y. Li: Supplement IV in "On the Transformation of Inclusions when adding strong Deoxidizers": Dissertation by S. Gustafsson.



35. T. Ototani, Y. Kataura, T. Degawa: Trans ISIJ, v. 16, 1976, pp 275-282.
36. M. Joyant, C. Gatellier: "Determination experimentale de la solubilité de CaO dans l'acier liquide a 1600°C" IRSID report, 1983.
37. O. Haida, T. Emi, K Sanbongi, T. Shiraishi, A Fujiwara: Tetsu-to-Hagane, 1978, v. 64, pp 1538-1547.
38. P.O Mellberg, S. Gustafsson: "Thermochemical behaviour of calcium in steel refining" Shanghai symposium on injection metallurgy, Nov 1982.
39. G.K. Sigworth, J.F. Elliott: Metal. Sci. v. 8, 1974, pp 298-310.
40. G.G. Mikhailov, E.P. Baibulenko: Steel USSR, Aug 1981, pp 443-444.
41. K. Sanbongi: Trans ISIJ, v. 19, 1979, pp 1-10.
42. P.T. Carter, T.G. Macfalane: JISI, v. 185, 1957, pp 54-62.
43. R.A. Sharma, F.D. Richardson: JISI, v. 198, 1961, pp. 386-390.
44. R.W. Nurse, J.H. Welch, A.J. Majundar: Trans. British Ceramic Soc., v. 64, 1965, pp 409-418.
45. R.H. Rein, J. Chipman: Trans. AIME, v. 233, 1965, pp 415-425.
46. J. Cameron, T.B. Gibbons, J. Taylor: JISI, v. 204, 1966, pp 1223-1228.
47. G.J.W. Kor, F.D. Richardson, *ibid*, v. 206, 1968, pp 700-704.
48. S.X. Dou: J. Phys. Chem, 1981, v. 85, pp 3859-3863.
49. M. Allibert, C. Chatillon, K.T. Jacob, R. Lourtou: J. Am. Ceramic Soc., v. 64, no 5, 1981, pp 307-314.
50. I. Eliezer, N. Elizer, R.A. Howald, P. Viswanadham: J. Phys. Chem., v. 85, 1981, pp 2835-2838.
51. N. Eliezer, R.A. Howald, B.N. Roy: J. Phys. Chem. v. 86, no. 14, 1982, pp 2803-2804.
52. "Handbook of Chemistry and Physics", 53 ed., 1972-1973, Published by the Chemical Rubber Co.

53. O. Redlich, A.T. Kister, C.E. Turnquist: Chem Eng. Progr. Symp. Ser., 1952, v. 48, nr 2, pp 49-61.
54. G.H. Geiger, D.R. Poirier: "Transport phenomena in metallurgy", Addison-Wesley Publishing co, 1973.
55. M. Olette: Proc. 4th Int. Conf. Vacuum Met., sec. 1., pp 29-34.
56. E.S. Machlin: Trans AIME, v. 218, 1960, pp 314-326.
57. R.G. Ward: JISI, Jan 1963, pp 11-15.
58. I. Langmuir: Phys. Rev. v. 2, series 2, no 5, 1913, pp 329-332.
59. F. Reyes-Carmona: PhD thesis, UBC 1983.
60. C.O. Ingamells: Anal. Chim. Acta. v. 52, 1970, pp. 323-334.
61. I.S. Basheina, J.B. Headridge: Analyst, v. 106, Feb 1981, pp 221-226.

APPENDIX A - NOTATION

$\alpha$	=	condensation coefficient
$\gamma$	=	activity coefficient
$a$	=	activity
$A$	=	$\text{Al}_2\text{O}_3$
$c$	=	concentration
$C$	=	$\text{CaO}$
$C_x A_y$	=	$x\text{CaO} \cdot y\text{Al}_2\text{O}_3$
$f$	=	Henrian activity coefficient
$h$	=	Henrian activity
$H$	=	integral enthalpy of mixing
$K$	=	equilibrium constant
$m$	=	evaporated mass
$M$	=	molecular weight of evaporated species
$p$	=	vapour pressure
$p^0$	=	vapour pressure of pure element
$S$	=	evaporation area
$t$	=	time
$T$	=	temperature
$X$	=	atomic fraction

In chemical reactions:

[ ]	=	in metallic solution
(s)	=	solid
(l)	=	liquid
(g)	=	gaseous

APPENDIX B - DETERMINATION OF CALCIUM IN STEEL BY ATOMIC  
ABSORPTION SPECTROPHOTOMETRY

This method was applied using a Perkin and Elmer Model 306 Atomic Absorption Spectrophotometer (AAS). The method is a modification of the procedure described by Hilty and Farrell<sup>21</sup>.

All glassware was cleaned by immersion in 5% HNO<sub>3</sub> overnight prior to the final rinse in de-ionized H<sub>2</sub>O. The number of pieces of glassware used was minimized and filtration procedures eliminated to avoid contamination of the samples.

0.500g of clean drillings from each steel was weighed and transferred to a 50ml volumetric flask. Five portions of 0.5 g calcium free iron wire were prepared and transferred into 50 ml volumetric flasks. Samples and standards were dissolved with 7 ml concentrated HNO<sub>3</sub> and 5 drops concentrated HCl plus 1 to 10 ml H<sub>2</sub>O as needed to speed up the dissolution. In some cases cautious heating of the flasks was required to dissolve the sample. To both samples and standards 5 ml of a lanthanum chloride solution (29 g La<sub>2</sub>O<sub>3</sub> + 200 ml HCl diluted to 1000 ml) and 5 ml of a potassium solution (52 g KNO<sub>3</sub> + 100 ml HNO<sub>3</sub> diluted to 1000 ml) were added to counteract the depressing effects of aluminum and phosphorus and to counteract ionization interference.

Of a standard calcium stock solution containing 10 ppm Ca, 0.0, 0.5, 1.0, 3.0, and 5.0 ml were added to the standard solutions. All solutions were diluted to volume and particles present allowed to settle overnight before analysis.

The AAS analysis was done according to standard procedure using a nitrous oxide - acetylene flame.

APPENDIX C - STEEL COMPOSITIONSComposition of Electrode Steels (weight %)

	<u>V1</u>	<u>V2</u>	<u>V3</u>	<u>V4</u>	<u>V5</u>	<u>V6</u>
C	.41	.24	.17	.31	.42	.39
Mn	1.20	.46	1.06	1.14	1.08	.40
P	.009	.011	.007	.010	.007	.022
S	.0050	.0060	.0070	.0037	.0015	.0023
Si	.29	.12	.21	.29	1.68	1.00
Ni	1.88	2.64	.36	1.81	1.86	.31
Cr	.85	1.44	2.19	.84	.94	5.02
Mo	.25	.57	.94	.48	.40	1.25
V	.01	.10	.01	.07	.08	.92
Cu	.07	.18	.19	.18	.18	-
Al	.030	.030	.026	.053	.023	.024
Co	-	.05	.02	.03	.03	-
Ca	.0029	.0063	.0060	.0062	.0030	.0020
O	.0066	.0068	.0060	.0069	.0054	.0032

Composition of Ingot Steels (weight %)

	<u>V1R</u>	<u>V2R</u>	<u>V3R</u>	<u>V4R</u>	<u>V5R</u>	<u>V6R</u>
C	-	.25	.17	.32	.42	.36
Mn	-	.31	.70	.83	.78	.31
P	-	.012	.006	.009	.009	.022
S	.0015	.0052	.0060	.0031	.0012	.0021
Si	-	.13	.21	.27	1.70	1.00
Ni	-	2.69	.36	1.79	1.87	.31
Cr	-	1.45	2.20	.83	.95	5.02
Mo	-	.59	.95	.48	.41	1.25
V	-	.10	<.01	.07	.08	.92
Cu	-	.17	.17	.16	.17	-
Al	.017	.024	.022	.034	.021	.024
Co	-	.05	.02	.03	.03	-
Ca	.0006	.0005	.0007	.0006	.0008	.0002
O	.0022	.0014	.0021	.0014	.0016	.0025

APPENDIX D - UNCERTAINTY OF CHEMICAL ANALYSIS

The uncertainty of the chemical analysis is:

Oxygen	$\pm 5$ ppm
Sulphur	$\pm 5$ ppm
Aluminum	$\pm .005$ weight %
Calcium	$\pm 3$ ppm