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TRP 9742: Removal of Residual Elements in the Steel Ladle by a Combination of Top Slag and Deep Injection Practice

Authors:

S. Street, K. S. Coley and G. A. Iron

Performing Organization

McMaster University
Department of Materials Science and Engineering
1280 Main Street
Hamilton, Ontario L8S 4L7
Canada

Abstract

The objective of this work was to determine if tin could be removed from liquid steel by a combination of deep injection of calcium and a reducing top-slag practice. Calcium forms an intermetallic with tin, Ca_2Sn , but it is much less stable than CaO or CaS . The premise of the proposal was that the intermetallic could be formed during deep injection, and prevented from rapidly reverting to the steel by maintaining reducing conditions in the top slag. The work consisted of three types of experiments:

1. Injection of calcium wire into 35-kg heats melted in an induction furnace to study the kinetics of tin removal under various conditions of temperature, oxygen activity and sulphur content.
2. A program to study the solubility tin in the slag as a function of oxygen potential, temperature and slag composition.
3. Two full-scale plant trials were carried out at Dofasco Inc. as a result of the promising results from the laboratory studies.

In the injection into the induction furnace, it was found that 7 to 50% of the tin was removed from initial tin contents of 0.1% Sn, using 8 to 16 kg calcium/tonne steel. The extent of tin removal was found to increase with greater calcium injection, lower oxygen activity in the steel and lower temperature. The presence of sulphur (up to 0.012% S) did not impede the removal of tin, although S was also removed during the injection. Novel composite wires, containing calcium and flux, were also effective in removing tin, and were even more effective in S removal. In the injection trials, reversion was not observed probably because most of the slag was ejected from the crucible during injection.

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The following conditions are recommended for tin removal, based on results obtained from the first two stages of experiments:

1. Low oxygen potential to ensure a high calcium activity and avoid reversion from the slag.
2. High basicity to increase the calcium activity in the slag, which will enable it to hold more tin.
3. Low temperature benefits the injection process.

Two trials were carried out at the Ladle Metallurgy Furnace in Dofasco's EAF plant. Calcium consumption in their normal practice is 0.25 kg Ca/tonne steel, and this was increased to 0.5 and 1.1 kg Ca/tonne steel in the two trials. Unfortunately, virtually no tin was removed in the trials. It is believed that the addition was too small, compared to the levels used in the induction furnace injections, 8 to 16 kg Ca/tonne steel.

The current costs of calcium wire and calcium granules are approximately 11 and 5.50 USD/kg contained calcium. If 10 kg calcium/tonne steel were required to remove tin, then this would add \$110 or 55/tonne steel, respectively. Considering these prospective costs, it is not worthwhile to pursue this process further, even though it may be technically feasible.

(RDP standard Form, Form 298)

AISI/DOE Technology Roadmap Program

Final Report

Removal of Residual Elements in the Steel Ladle by a Combination of Top Slag and Deep Injection Practice

By

S. Street, K.S. Coley and G.A. Irons

**Steel Research Centre
McMaster University
Hamilton, ON**

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EXECUTIVE SUMMARY & RECOMMENDATIONS

Tin is one of the problematic residual elements in liquid steel that is continually increasing due to the recycling of tinplate. Currently, there is no cost-effective way to remove the tin, and judicious blending with low-residual scrap is generally the current practice. The objective of this work was to determine if tin could be removed from liquid steel by a combination of deep injection of calcium and a reducing top-slag practice. Calcium forms an intermetallic with tin, Ca_2Sn , but it is much less stable than CaO or CaS . The premise of the proposal was that the intermetallic could be formed during deep injection, and prevented from rapidly reverting to the steel by maintaining reducing conditions in the top slag. The work consisted of three types of experiments:

1. Injection of calcium wire into 35-kg heats melted in an induction furnace to study the kinetics of tin removal under various conditions of temperature, oxygen activity and sulphur content (Chapter 2).
2. A fundamental study of the slag/metal equilibrium slag under controlled atmosphere as a function of slag composition and oxygen potential (Chapter 3).
3. Two full-scale plant trials were carried out at Dofasco Inc. as a result of the promising results from the laboratory studies (Chapter 4).

In the injection into the induction furnace, it was found that 7 to 50% of the tin was removed from initial tin contents of 0.1% Sn, using 8 to 16 kg calcium/tonne steel. The extent of tin removal was found to increase with greater calcium injection, lower oxygen activity in the steel and lower temperature. The presence of sulphur (up to 0.012% S) did not impede the removal of tin, although sulphur was also removed during the injection. Novel composite wires, containing calcium and flux, were also effective in removing tin, and were even more effective in sulphur removal. In the injection trials, reversion was not observed probably because most of the slag was ejected from the crucible during injection. Thus, these trials were not a true test of the reversion.

The original aim of the fundamental study of slag/metal kinetics was to measure the reversion kinetics to determine whether tin reversion at the end of injection would be a problem within the time-scale that applies to the full-scale process. The laboratory injections showed that this was of little significance; therefore, the objective was modified to study the solubility of tin in the slag as a function of oxygen potential, temperature and slag composition. These variables had a significant effect on the tin solubility:

1. Low oxygen potentials favored high tin solubility.
2. High basicity favored high tin solubility.
3. The temperature effect on tin solubility was complex; increasing temperature increased solubility up to about 1500°C, but the solubility decreased with further increases in temperature. This effect was related to the reaction that controlled the calcium activity. At lower temperatures lime dissociation controlled it, whereas at higher temperatures calcium carbide fixed the calcium activity.
4. In a steel ladle, where the carbon activity is much lower, calcium carbide would not be present, and the solubility would increase with increasing temperature.

All of the above noted effects are related to control of the calcium activity, which is in support of the original premise behind this study; that calcium activity is the important parameter. If the activity can be kept high, oxygen potential will not be important. This is supported by results from laboratory injections; however, results from plant trials show that it is extremely difficult to impose a high calcium activity independent of the oxygen potential.

In light of the aforementioned effects the following conditions are recommended for tin removal:

1. Low oxygen potential to ensure a high calcium activity and avoid reversion from the slag.
2. High basicity to increase the calcium activity in the slag, which will enable it to hold more tin.
3. Low temperature benefits the injection process. This finding is at odds with observation 4 regarding tin solubility, but the effects on the injection process outweigh this factor.

Due to the success of the induction furnace injection, Dofasco very kindly consented to carry out a small number of full-scale trials at no cost. Two trials were carried out at the Ladle Metallurgy Furnace in Dofasco's EAF stream. Calcium consumption in their normal practice is 0.25 kg

calcium/tonne steel, and this was increased to 0.5 and 1.1 kg calcium/tonne steel in the two trials. Unfortunately, virtually no tin was removed in the trials. It is believed that the addition was too small, compared to the levels used in the induction furnace injections, 8 to 16 kg calcium/tonne steel.

The current costs of calcium wire and calcium granules are approximately 11 and 5.50 USD/kg contained calcium. If 10 kg calcium/tonne steel were required to remove tin, then this would add \$110 or 55/tonne steel, respectively. Considering these prospective costs, it is not worthwhile to pursue this process further, even though it may be technically feasible.

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The experiments at McMaster could not have been accomplished without the assistance of Mr. Owen Kelly, Dr. Dorel Anghelina, Ms. Marta Bailey, Mr. Dominic Roos and Ms. Karen Wolnik.

The support and expertise of Dofasco for the full-scale trials was tremendous, particularly from Dr. Stanley Sun, Messrs. Keith Smith, Tom Vert, Steve Waterfall, and Sajar Sagar.

Finally, several companies generously devoted supplies: Remacor, AlumiCa, Minteq, Heraeus Electro-nite, and Dofasco.

1.0 INTRODUCTION

The objective of this work was to determine if tin could be removed from liquid steel by a combination of deep injection of calcium and a reducing top slag practice. This research was conducted at McMaster University during the period of May 1998 to August 2001.

The American Iron and Steel Institute (AISI) and the American Department of Energy (DOE) funded the project. From within the AISI three companies, Dofasco, US Steel, and Weirton Steel sponsored the work. The project was designated project number 9742 under the AISI Technology Roadmap Program sub group Primary Operations.

As outlined in the initial research proposal to AISI, shown in Appendix 1, the project was divided into two sections. These results are reported in the following sections:

- A study of reaction kinetics during calcium injection with and without a top slag (Chapter 2).
- A fundamental study of slag metal equilibria under a controlled atmosphere, as a function of slag composition, and oxygen potential (Chapter 3).
- The results of the studies at McMaster were encouraging, so plant trials were also conducted at Dofasco (Chapter 4).

2.0 INJECTION TRIALS

A series of laboratory trials were performed to investigate the potential for removing residual elements from steel. The aim of these trials was to evaluate the influence of experimental variables such as temperature, slag composition, injection rate, oxygen content, and initial tin content on the extent of tin removal. Between May 1998 and April 2001 a total of ten injection experiments were undertaken.

2.1 Equipment

This section provides descriptive and photographic details of the equipment used to perform the injection experiments. Preparation of experimental consumables is described in section 2.3.

The induction furnace is shown in Figures 2.1. The furnace has a 75-kW power supply, and operates over a range of frequencies in the kHz range. MgO crucibles were used.

Control of the furnace atmosphere during melting and injection was maintained by running high purity argon from bottles. The gas train consisted of a regulator, flexible tubing, and a ball valve. Pressure relief of the chamber during heating was achieved through a gas bubbler that minimised potential air ingress.

The furnace chamber has a number of ports that were utilized during the trials. The chamber ports for gas inlet, pressure relief, gas outlet, wire injection, sampling, and hopper additions can be seen in Figure 2.2.

Wire was feed into the furnace using a unit adapted from a welding wire feeder. The feeder is shown in Figures 2.2 and 2.3. The initial seating of the wire into the feeder at the start of a run was somewhat awkward; however, with experience it was found that the straighter the wire, the easier the task. The wire feeder has a variable feed rate and could handle wire of different diameters; however, none larger than 5 mm were used. Figure 2.4 a and b show the wire seated in the feeding unit.

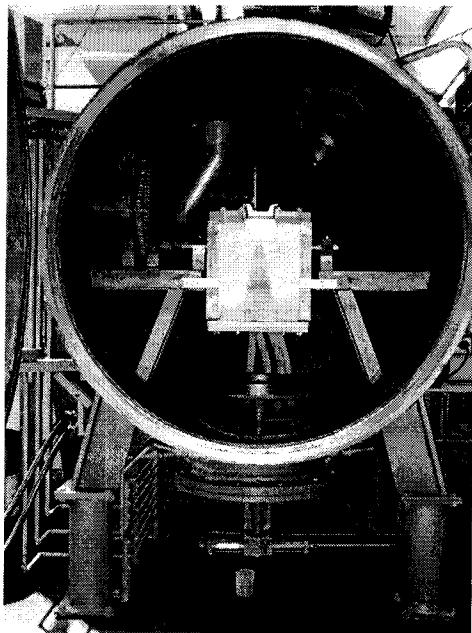


Figure 2.1: Internal view of induction furnace chamber used for injection experiments.

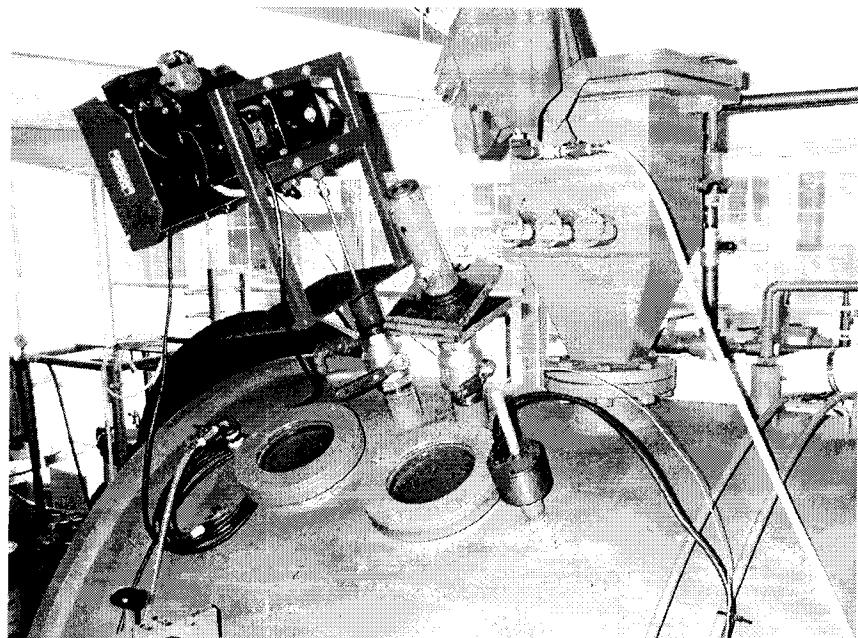


Figure 2.2: Induction furnace chamber ports. Top left clockwise: wire injection, hopper additions, pressure measurement/gas inlet, gas outlet (back right), 2 viewing ports, and pressure relief.



Figure 2.3: Wire feeding unit located on top of furnace chamber.

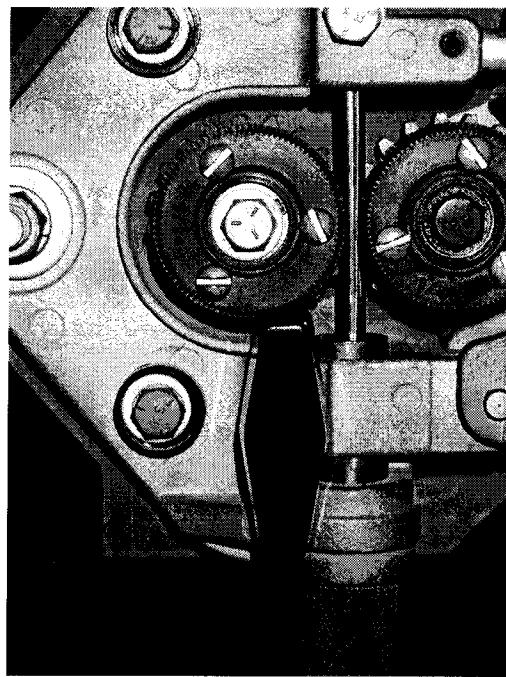


Figure 2.4a: Steel-clad calcium wire (5 mm diameter) seated in wire feeder.

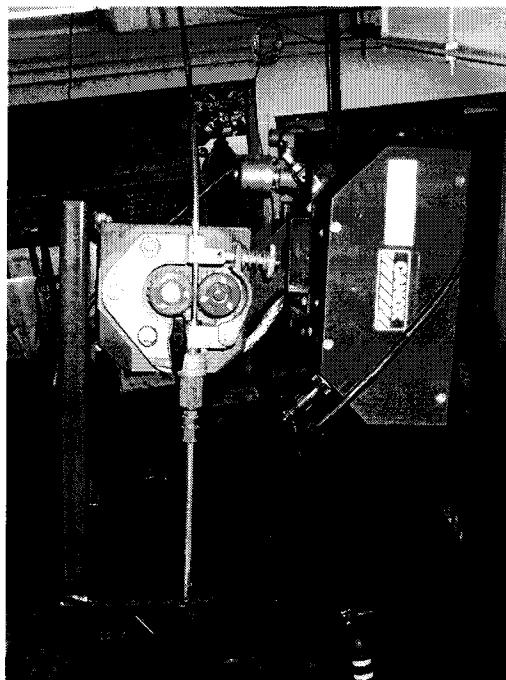


Figure 2.4b: Steel-clad calcium wire (5 mm diameter) seated in wire feeder.

2.2 Experimental Procedure

The same experimental procedure was followed for all trials, except for minor adjustments. Approximately 40 kg of steel bars were grit blasted to remove existing oxide scale. The cleaned steel was then loaded into the induction furnace crucible. Required additions such as aluminum, residual element additives (tin), and fluxing agents were bagged and placed into the hopper compartments above the induction furnace. Steel-clad calcium wire was loaded into the wire feeder located on top of the furnace. To achieve minimum oxygen levels in the melt, the furnace chamber was evacuated and backfilled with argon; this procedure was carried out twice before heating began. Once the steel was melted, and left to come to a uniform temperature for that given power level, a temperature/oxygen activity measurement was made. From these readings corrections of the oxygen activity and bath temperature were made. This was followed by the addition of the residual elements. At this stage a metal sample was taken. This metal sample was used for the initial starting point chemistry. Typically fluxing agents were then added to the bath. Because of the size of the hoppers, and the time taken for melting, flux additions were added 0.5 kg at a time. Once a sufficient slag layer developed another temperature and oxygen

measurement was taken. Wire injection then began. After a given time interval, injection was halted and metal samples were taken. Wire injection and sampling continued until only a small length of wire was left. Approximately 10 cm of wire was left out of the wire feeder so that it could be easily removed after the experiment. After the injection was finished, and the last of the metal samples had been taken, the furnace power was switched off and the heel was left to air cool.

2.3 Materials

The source of the materials used in the experiments is listed in Table 2.1.

Table 2.1 Source of consumable materials used in the injection experiments.

Material	Source	Comments
Steel	Dofasco Inc.	CC040A Grade, contact Bruce Farrand
Steel bars	Kubes Steel Ltd	Cut from material supplied by Dofasco
Tin	Various	Reagent grade
Al	Various	Reagent grade
Flux ^{#1}	Remacor	Doug Ashton, phone (905) 335-0200
Flux ^{#2}	AlumiCa	Gilles Turcotte, phone (613) 797-8589
Wire	Minteq	Rick Baum, phone (610) 250-3314
Wire ^{#2}	Made at McMaster	See Appendix II
Crucibles	Morganite	North Haven, CT, Size 509
Probes	Heraeus Electro-Nite	Ai-102 S080
Samplers	Blasch Precision Ceramics	Immersion samplers A-777 BP93/20-H

Dofasco kindly provided the steel for the experiments. An ultra deep drawing grade of steel was chosen because of its low alloy content. Table 2.2 lists the nominal composition of the steel used. Approximately 400 kg of material was cut from a hot mill end plate. The steel was then cut, by an outside contractor, into smaller more manageable pieces (20 mm H 20 mm H 160 mm). To remove oxide scale the steel bars were grit blasted prior to each trial.

Table 2.2 Residual content of Dofasco's CC040A grade steel (wt%).

C	P	S	Si	Al	Cu	Ni	Cr	Mo	Sn	Sb	Pb	Nb	V	Ti	N	B
0.05	0.00	0.00	0.00	0.03	0.01	0.00	0.02	<0.0	0.00	<0.0	NM	0.00	0.00	0.00	0.00	0.00
5	37	89	78	8	72	98	12	01	52	01		01	13	22	45	01
0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	DL	0.00	DL	NM	DL	0.00	0.00	0.00	DL
5	07	23	27	61	61	26	38		37				04	32	06	

N.B. above data supplied by Dofasco, data is not the chemical analysis of the actual steel used.

The slag was conveniently developed using a calcium aluminate-type flux rather than reagent grade fluxes, so that the experiments would duplicate industrial ladle slag practice. Remacor also kindly supplied a briquetted flux material (Newslag 366). Typical analysis for the flux material is shown in Table 2.3.

Table 2.3 Calcium aluminate briquettes – Newslag 366 from Remacor (typical analysis).

Al ₂ O ₃ (%)	MgO (%)	SiO ₂ (%)	FeO (%)
30	5-6	1-2	<0.4

Minteq donated 100 m of 5-mm diameter wire in July 1998 and provided a second donation of 50 m in August 2000. Table 2.4 lists specifications of the calcium wire.

Table 2.4 Steel-clad calcium wire from Minteq.

Ca content	Ca purity	Steel cladding
0.017 lb/ft	Typical +98%	1006 grade

Experiments were performed using MgO crucibles. The crucibles were approximately 300 mm in depth and 190 mm in diameter, giving an internal working volume of 7500-8500 cm³. New crucibles were used for each trial.

The melt temperature and oxygen content of the molten steel bath were simultaneously measured using single-use Electro-Nite probes. Readings were indicated on an Electro-Nite Co. Celox Lab Model 3000 monitor in Celsius degrees for temperature and ppm for oxygen content.

Metal samples were taken using immersion samplers that produced pins 12.7 mm diameter and up to 57 mm length.

Prior to each of the injection experiments some material preparation was required.

- As mentioned above it was necessary to grit blast oxide scale from the steel bars.
- The additives (Al, Sn, and FeS) were weighed and then bagged into packages. The packages fit into the feed hopper above the furnace chamber.
- The calcium wire was removed from its storage drum and straightened. This usually required 3 to 4 people and was performed the day before the trial in hallway, shown in Figures 2.5. In trials 7 and 8, a calcium-containing wire, made within the department, was used instead of using the commercial calcium wire from Minteq. Details of this will be discussed in a separate section.

- In the earlier trials the briquetted calcium aluminate flux was pre-melted. This was carried out by heating 1 to 1.5 kg of the flux in a small graphite crucible in a high frequency induction furnace. The molten slag was poured onto a steel "I" beam for cooling. The slag was then crushed and bagged before the trial.

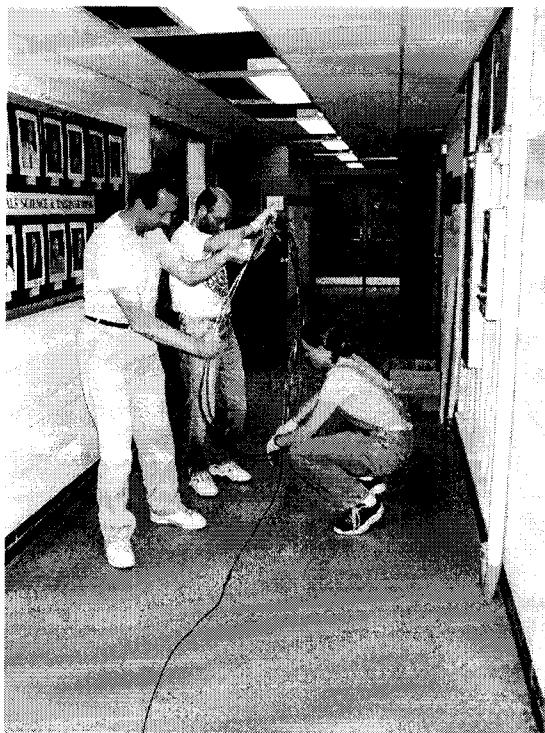


Figure 2.5: Uncoiling and straightening clad wire prior to injection experiments.

2.4 Chemical Analysis

In the majority of trials only metal samples were taken. After separating the metal from the sampler it was surface cleaned using a bench grinder. A sample approximately 15 mm in length was then cut from the rod using the automated cutting machine. The cutting wheel left a high quality surface, which only required minimal grinding before chemical analysis. Chemical analysis was then performed using an inductively coupled plasma spectrometer by sparking the metal samples. In cases where sulphur and carbon analysis were required smaller metal samples were analyzed using a LECO analyzer.

In some trials slag samples were also retrieved. These were analyzed using a number of standard techniques including ICP (solution) and EDS.

2.5 Injection Trial Results

A detailed summary of each injection is contained in Appendix II. Table 2.5 summarizes the injection conditions and some of the key experimental results.

Table 2.5 Summary of Injection Conditions and Results

Injection	1	2	3	4	5	6	7*	8*	9	10
Steel Weight (kg)	36.3	35.8	36.4	36.8	36.6	36.4	36.8	37.1	37.1	37.2
Initial										
<u>O</u> (ppm)	14.5	15.8	30.0	78.9	26.5	5.9	7.4	1.5	4.7	4.7
<u>S</u> (ppm)	n.a.	n.a.	n.a.	n.a.	n.a.	116	122	45	125	
%Sn	0.084	0.104	0.125	0.106	0.006	0.058	0.102	0.102	0.106	0.095
Temp (°C)	1672	1618	1750	1722	1752	1640	1615	1625	1618	1594
Weight Ca fed (g)	91.2 ¹	282.	444.	535.	535.	427.	413.	624.	541.	497.
Duration (s)	n.a. ¹	247.	430.	470.	450.	390.	486.	748.	474.	425.
kg Ca/tonne Fe	n.a.	7.88	12.2	14.5	14.6	11.7	11.2	16.8	14.6	13.4
kg Ca/tonne/min	n.a.	1.91	1.70	1.85	1.95	1.80	1.38	1.35	1.85	1.89
Final										
<u>O</u> (ppm)	12.1	5.4	12.4	32.0	7.6	9.0	1.4	n.a.	3.2	25.4
<u>S</u> (ppm)	n.a.	n.a.	n.a.	n.a.	n.a.	45	7	7	27	
%Sn	0.078	0.062	0.089	0.092	0.005	0.048	0.076	0.067	0.053	0.068
Temp (°C)	1614	1658	1645	1645	1678	1671	1555	n.a.	1614	1653
%Sn removed	7.1	40.4	28.8	13.2	16.7	17.2	25.5	34.3	50.0	28.4
%S removed	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	61.1	94.3	84.4	78.4
%O removed	16.6	65.8	58.7	59.4	71.3	-52.5	81.1	n.a.	31.9	-440.
Utilization ²	1.61	3.58	1.98	0.65	0.05	0.57	1.56	1.40	2.44	1.36
Scavenging Eff. ³	0.078	0.143	0.065	0.025	0.046	0.040	0.116	0.100	0.092	0.057

* In-house wire used (19.7 g Ca/m), compared to Minteq wire (25.3 g Ca/m)

¹ It was unclear how much wire entered the steel

² Utilization is the percentage of injected calcium that was used for tin removal according to stoichiometry.

³ Scavenging Efficiency is percentage change in tin in the steel divided by the grams of calcium injected.

The change in the tin content of the steel during wire injection is shown in Figure 2.5. In all cases there was some removal. Table 2.5 shows that the percentage removal varied between 7 and 50%.

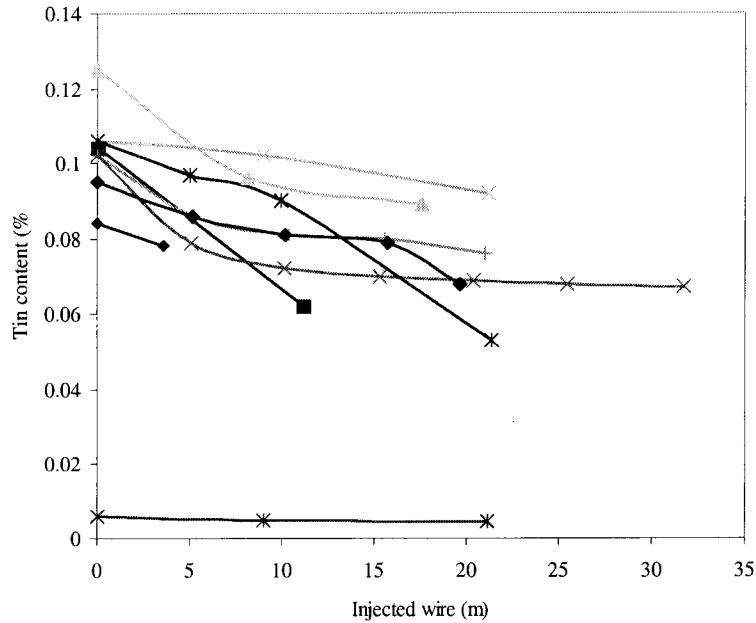


Figure 2.6: Change in tin content of steel due to injection of calcium wire. Note: wire used in trials 7 and 8 had a different calcium load.

The experimental results show that the greater the amount of injected calcium the greater the amount of tin removed from the steel. The relationship between total injected calcium and tin removal is shown in Figure 2.7.

The steel temperature was difficult to control for many of the injection experiments because once the injection started, it was not possible to insert a thermocouple. Figure 2.8 illustrates the trial temperature variation during each injection. Nevertheless, sufficient experiments were performed over a range of temperatures that it was possible to see a trend that lower temperatures favour greater tin removal. This trend is shown in Figure 2.9 in which the average temperature is plotted against the extent of tin removal.

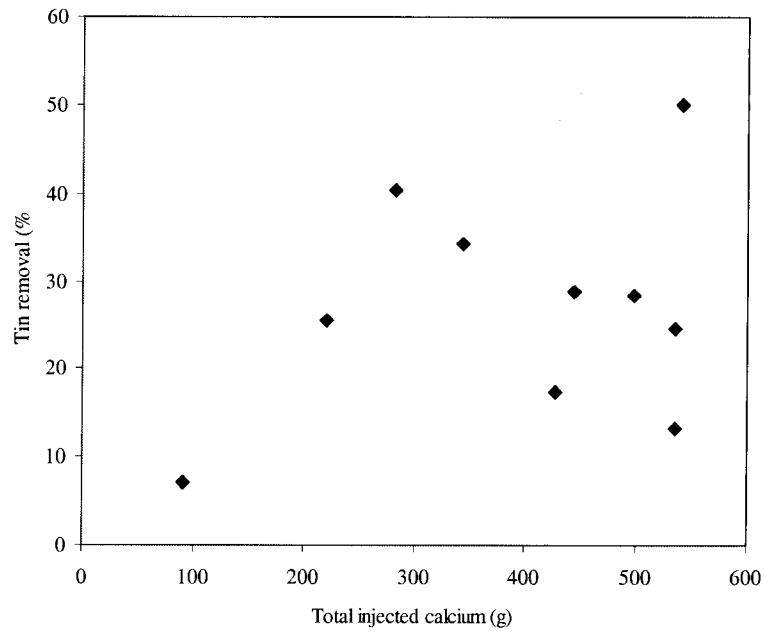


Figure 2.7: Relationship between total injected calcium and tin removal.

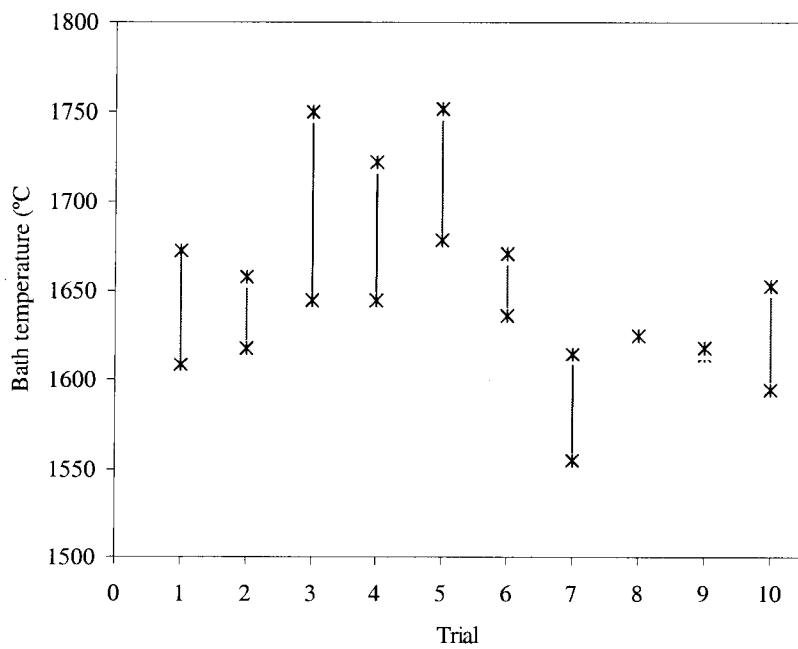


Figure 2.8: Inter-trial melt temperature variation.

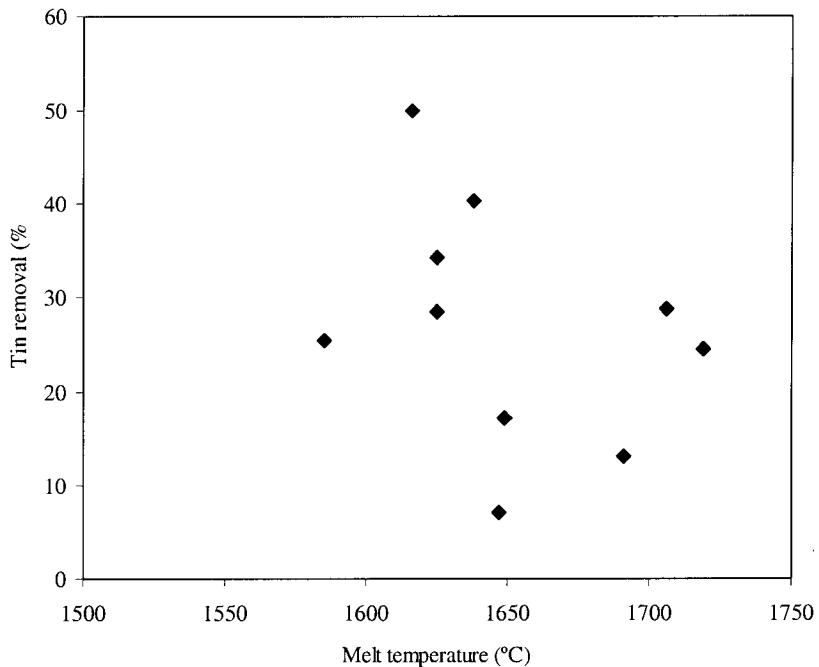


Figure 2.9: Relationship between average melt temperature and tin removal.

The oxygen activity in the steel was often difficult to control. Figure 2.10 shows the range of oxygen activity for each trial. As the experimental program progressed, techniques were developed to keep the oxygen level as low as possible. Table 2.5 also shows that calcium generally reduced the oxygen activity between 16 and 80%. As expected, lower oxygen activity favors the removal of tin, as shown in Figure 2.11.

One of the objectives of this work was to investigate the possibility of reversion of tin from the slag phase back to the steel. Where possible metal samples were taken up to 50 minutes after wire injection had stopped. The change in the tin content of the metal after injection had stopped is shown in Figure 2.12. This data suggests that limited reversion may occur. As discussed in Appendix II, in most cases the slag was ejected from the crucible once the injection started, so that this data is not a true test of reversion from the slag to metal.

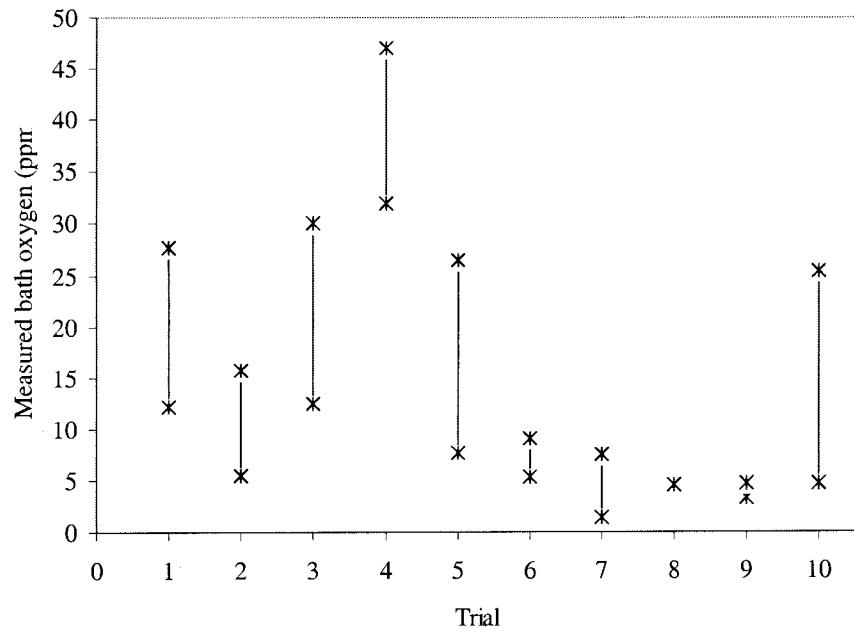


Figure 2.10: Inter-trial variation in the measured bath oxygen content.

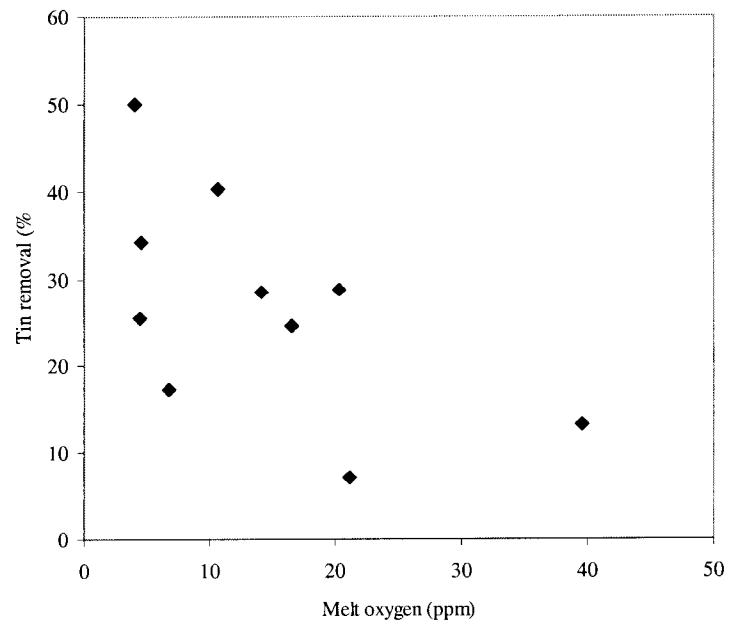


Figure 2.11: Influence of bath oxygen content on tin removal.

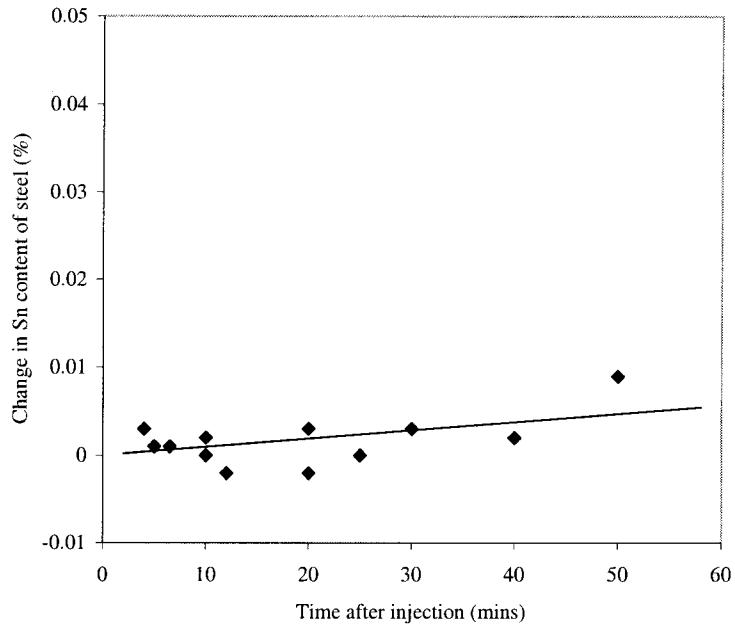
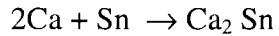


Figure 2.12: Change in tin content of steel after calcium wire injection had stopped.

2.6 Discussion of Injection Trials

The utilization of the calcium for tin removal was very low (Table 2.5) compared to the stoichiometric reaction:



It was generally in the range of 0.5 to 4%. Low utilization was also obtained in previous work with the same equipment by Lu *et al*^[1]. They attributed the low utilization to poor penetration of the calcium wire into the steel as shown in Figure 2.13. The calcium contained in the wire rapidly heats and melts at some distance below the top of the bath. As could be expected the penetration depth on such a small scale will be limited. Using an empirical relationship developed by Mucciardi^[2] the penetration depth for the feed rates used in the injection trials is estimated to be approximately 0.05 m.

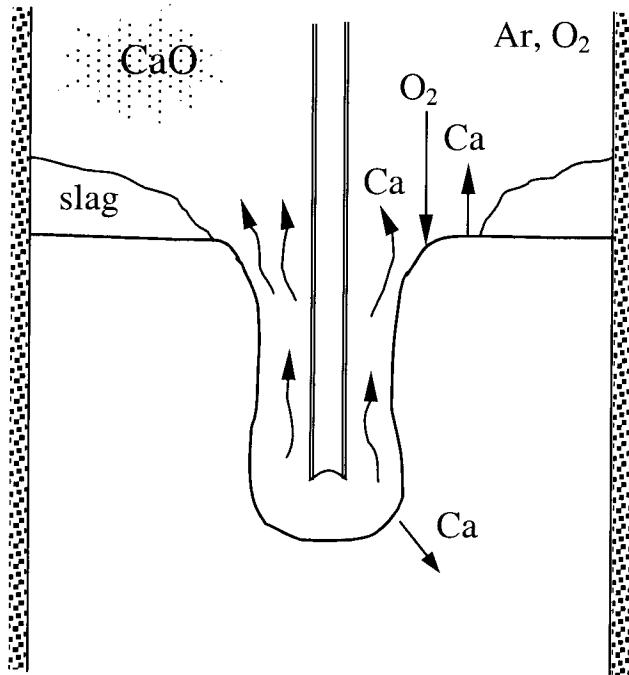
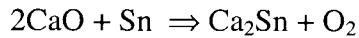


Figure 2.13: Reaction mechanisms during the injection of calcium wire into a steel bath.

(If higher feeding rates were used, steel would have been ejected from the crucible). It is evident that most of the calcium will vaporize and escape through the plume region around the wire. Experimentally, the extent of calcium vaporization was demonstrated by the very short period that it was possible to observe the injection process due to the blanketing of the calcium fume. The extent of the calcium fume generated by vaporization during the injection trials is clearly shown in Figure 2.14.

Calcium has even more affinity for oxygen than it has for tin, so the exchange reaction:



favours the reverse reaction. Accordingly, the temperature and oxygen potential are important for the efficiency of calcium utilization.

The scavenging efficiency, defined as the fraction of the tin removed from the melt, divided by the amount of calcium injection, is strongly dependent on the temperature as seen in Figure 2.15.

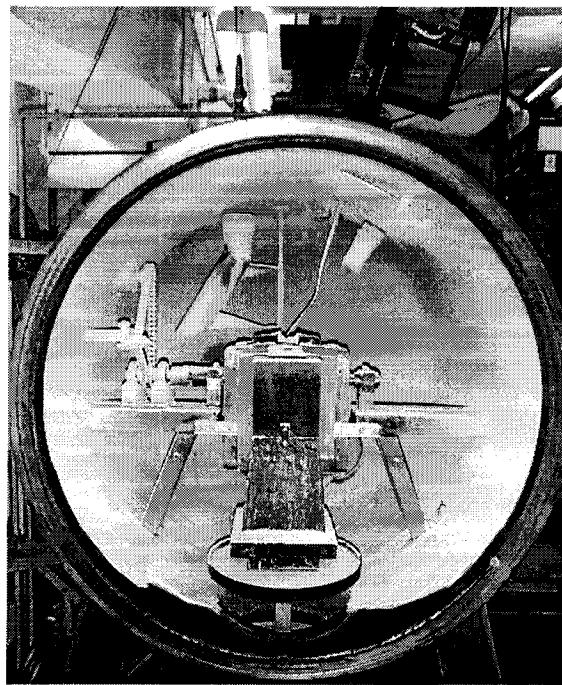


Figure 2.14: Induction furnace, after injection, showing extensive CaO fume coating.

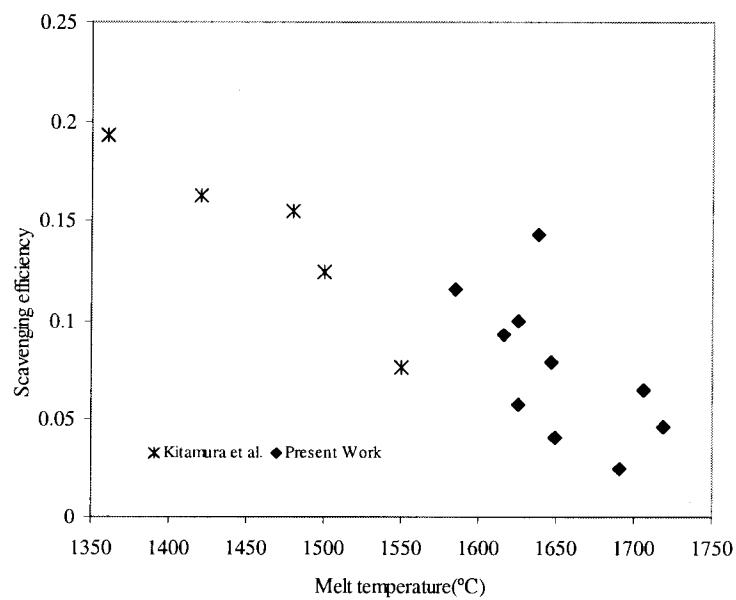


Figure 2.15: Influence of melt temperature on tin removal, indicated as scavenging efficiency, up to 1.5% Ca additions, compared with the work of Kitamura *et al.*^[3]

The amount of calcium added was obviously an important parameter. Figure 2.7 shows the percentage removal of tin as a function of the amount of calcium added, showing a trend of greater removal with more calcium addition. This trend is consistent with previous work conducted around 1600°C as shown in Figure 2.16.

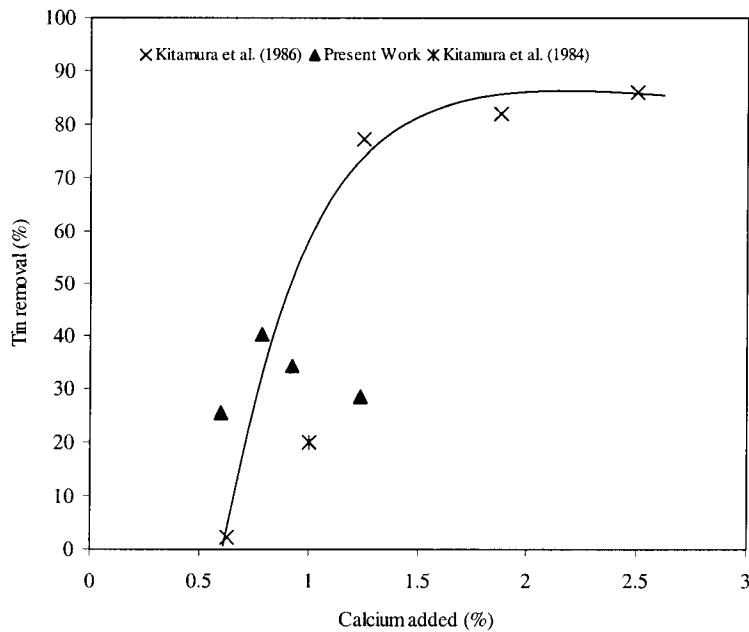


Figure 2.16: Relationship between total calcium added and removal of tin at temperatures between 1585 and 1625°C, compared with the work of Kitamura *et al.* (1986)^[3] and (1984)^[4].

It was speculated that sulphur might interfere with tin removal. This proved to be unfounded; Table 2.5 shows that tin and sulphur can be removed simultaneously. Figure 2.17 shows the percentage of tin and sulphur in the melt during injection. If these elements were both diffusing to the calcium bubble interface and being completely converted to reaction products, then the percentage elimination would be identical. Generally, Table 2.5 and Figure 2.17 show that the sulphur elimination is greater. This means that the chemical conditions for tin removal are not as good as those for sulphur.

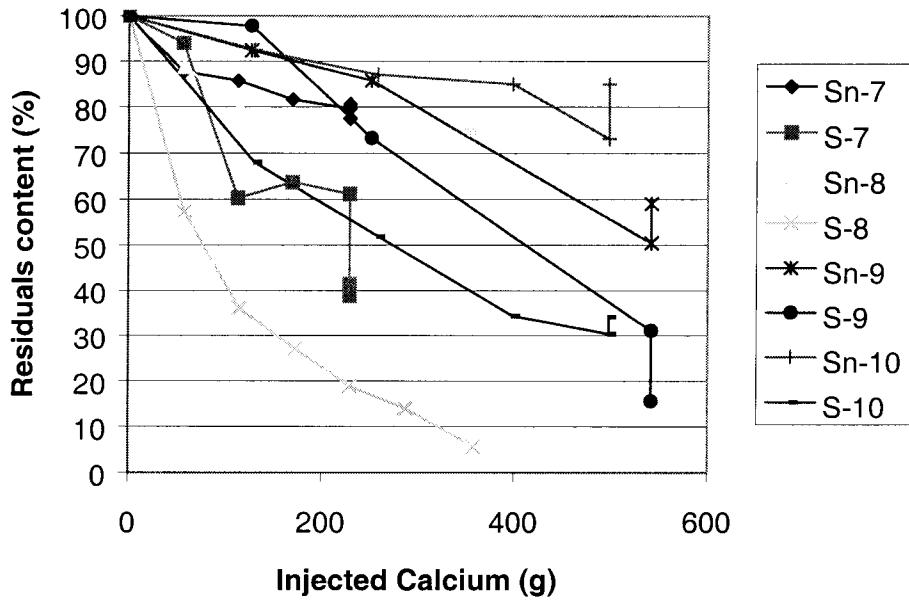


Figure 2.17: Percentage of the tin and S in steel during the injection of calcium. The numbers in the legend refer to the injection number.

Injections 7 and 8 used the in-house wire that contained calcium and the flux. Figure 2.17 shows that the sulphur elimination during these two injections was better than the other ones. The reason for this is likely that the calcium vapour produced very reducing conditions that made the flux much more effective than a slag on top of the steel with limited slag/metal surface area and more oxidizing conditions. This calcium-flux composite wire may be very effective to reach low sulphur contents required in many modern grades of steel. A project to optimize this could be the subject of future work.

2.7 Conclusions on Wire Injection Trials

1. It was found that 7 to 50% of the tin content of steel could be reduced from initial contents of approximately 0.1% Sn by injection of calcium wire into 35 kg heats of steel.
2. The extent of tin removal was found to increase with:
 - i) greater calcium injection
 - ii) lower oxygen activity in the steel

- iii) lower temperature.
- 3. The presence of sulphur, (up to 0.012% S), that also reacts with calcium did not impede the removal of tin, although sulphur was also removed during the injections.
- 4. Composite wires, containing calcium and flux, were also effective in removing tin. The results suggest that the composite wires were even more effective in sulphur removal.
- 5. Reversion of tin from the slag to the steel after injection was not observed. The likely explanation is that most of the slag was ejected from the crucible during the injection, and unable to participate in reversion.

3. SLAG METAL REACTION EXPERIMENTS

A series of experiments were planned to study the reversion of Sn species from the slag phase back to the metal. The experiments were to be performed at varying temperatures and atmospheres to investigate the influence of oxygen potential on reaction kinetics. However, initial injection experiments indicated that reversion was not a major issue and that the priority should be changed to investigate the thermodynamic effect of the slag on tin removal. The experimental objective was changed to investigate Sn solubility in slag. The aim of these experiments was to investigate the influence of slag chemistry, oxygen potential, and temperature on the slag-metal equilibrium.

3.1 Experimental

Gas-slag-metal experiments were performed in a vertical tube furnace under controlled temperature and atmospheres. The experiments were initially conducted using graphite crucibles containing 10 g of Sn and 30 g of pre-melted slag. The reaction crucible was raised into the tube furnace while cold. After sealing the furnace the system was left to reach equilibrium once the reaction temperature had been reached.

Small graphite reaction crucibles were used to contain typically 1.0 g of Sn and 3.0 g of pre-melted and crushed slag. The reaction crucible was then placed on a support tube/rod, the position of the support tube being controlled by a airtight lock nut. After re-sealing the bottom furnace flange that held the support tube/crucible, the furnace was left to flush for 2 hours to ensure the correct atmosphere was attained. The reaction crucible was then raised into the furnace hot zone and left for a set time. Following the reaction time the crucible was rapidly lowered into the water cooled cooling chamber. Cooling of the crucible was aided by continuously flushing the chamber with Ar gas for typically 15 minutes before removing. Gas samples were periodically tested by gas chromatography to determine the gas composition in the furnace which was ultimately used to determine the oxygen partial pressure.

3.1.1 Equipment

This section provides descriptive and photographic details of the equipment required to perform the gas-slag-metal reaction experiments. The furnace arrangement for the experiments is shown in Figure 3.1, and schematically in Figure 3.2. The tube furnace was a commercial model, PYROX VT70. Utilizing 6 lanthanum chromite elements, the furnace has an upper working limit of 1750°C. High purity alumina tubes, 34" in length by 3" O.D, were used as furnace tubes.

Temperature control was achieved through a single B type thermocouple. The thermocouple was inserted through the furnace roof and ran parallel to the alumina tube. The thermocouple was connected to a programmable Eurotherm controller (model 2416)

3.1.2 Materials

Experiments were performed using graphite crucibles. These crucibles were generally made within the department from bulk graphite. New crucibles were used for each trial. The dimensions of a single well crucible are shown in Figure 3.3. Slags were prepared by pre-melting fluxes. If pre-melting was carried out in a graphite crucible, care had to be taken with heating to ensure CaC_2 was not formed.

3.1.3 Sample Analysis

Slag and Sn were separated from the graphite crucible after cooling. Larger pieces of slag, free of graphite and any obvious metallic Sn, were then crushed in a shatter mill. Crushed slag was then passed through a sieve (-250 Mesh) before preparing for chemical analysis.

A fusion method to prepare the slag for wet chemical analysis was provided by the chemical lab at Dofasco.

In a Pt crucible mix:

0.25 g of sieved slag

1.0 g lithium tetraborate/lithium metaborate

3 drops lithium bromide solution (non-wetting agent)

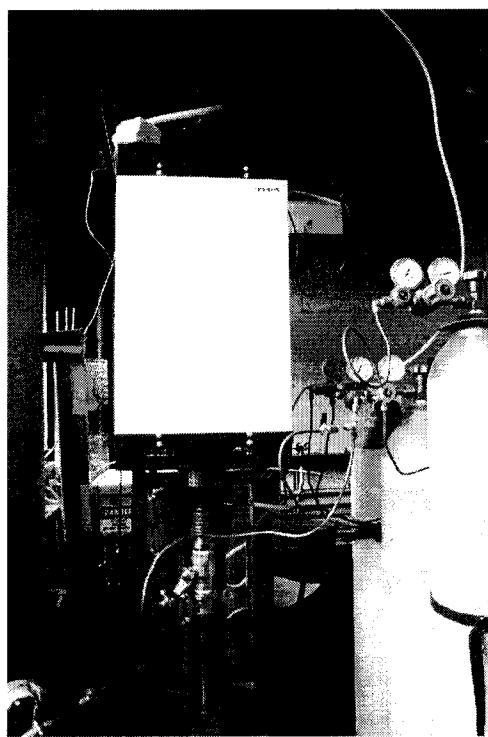


Figure 3.1: High temperature tube furnace for gas-slag-metal experiments.

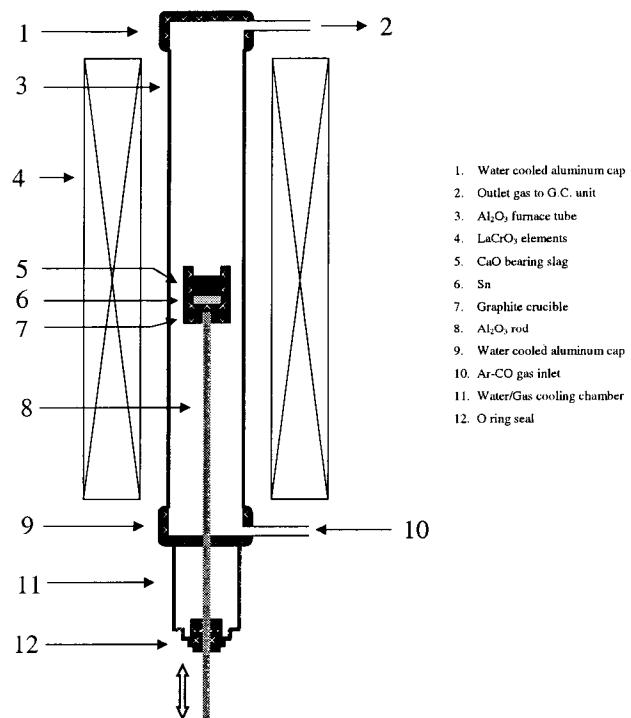


Figure 3.2: Schematic diagram of tube furnace used for slag-metal experiments.

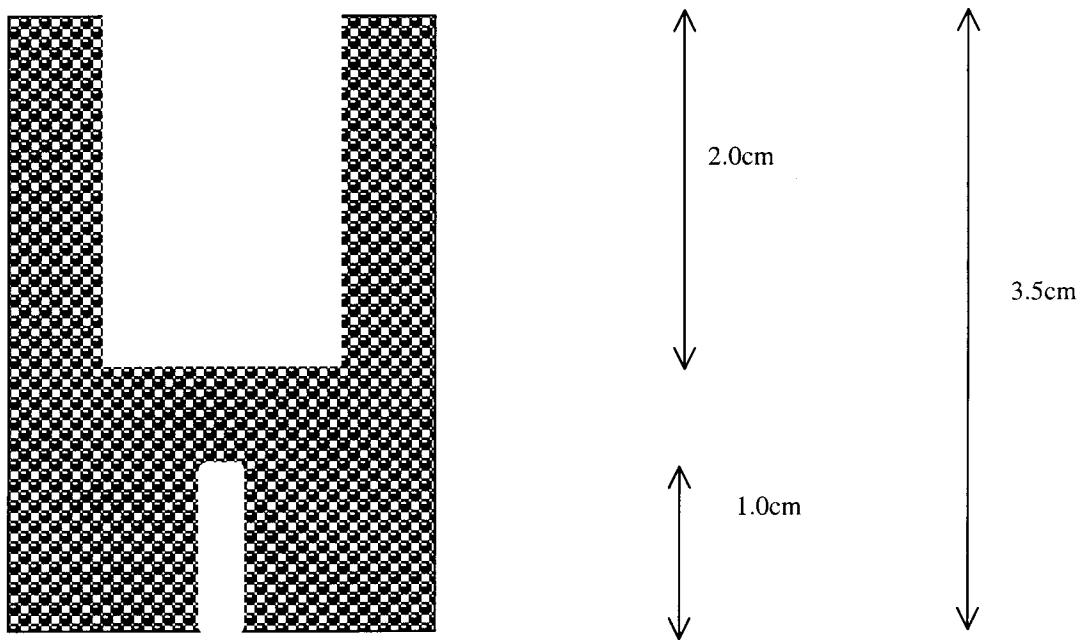


Figure 3.3: Single well graphite crucibles used to contain 1 g Sn and 3 g slag for gas-slag-metal reaction experiments.

Using Pt tipped tongs gradually heat the crucible over a bunsen burner flame. Heat crucible until the mixture is completely molten. While still molten, tip the contents of the crucible into a beaker containing:

75 ml of HNO_3 5% solution.

Leave until completely dissolved in the acid, then bulk up to 100 ml in a volumetric flask.

Sn was determined from the 0.25 g to 100 ml sample while for the Ca, Al and Si determination because of much higher concentrations a 1:10 aliquot was required.

Assuming 0.25 g to 100 ml:

$\% \text{Sn in slag} = \text{solution ppm H} 0.04$

3.1.4 Experimental Description

A series of experiments were conducted to investigate the slag-metal equilibrium between pure tin metal and a range of slag compositions. Experimental variables were slag chemistry, reaction temperature, and oxygen potential.

Initially 5 slag chemistries were selected (designated A through E). Nominal compositions for the slags are shown in Table 3.1. These slags were high in CaO and were chosen to replicate typical ladle slags. As the research program expanded the number of slags also increased.

Table 3.1. Slag compositions studied.

Slag/Component	CaO (wt%)	Al ₂ O ₃ (wt%)	SiO ₂ (wt%)
A	52	44	4
B	57.3	37.2	5.5
C	51	46	3
D	57	34	9
E	59	41	0
F	50	43.6	6.4
G	50	50	0
H	47.5	47.5	5
I	45	45	10
J	32.5	32.5	35
K	17.5	17.5	65

Slags G through K were used to look at the effect of increasing SiO₂ while maintaining a constant CaO/Al₂O₃ ratio. Slag compositions determined by analysis after equilibration, for slags A to E, are shown in Figure 3.4.

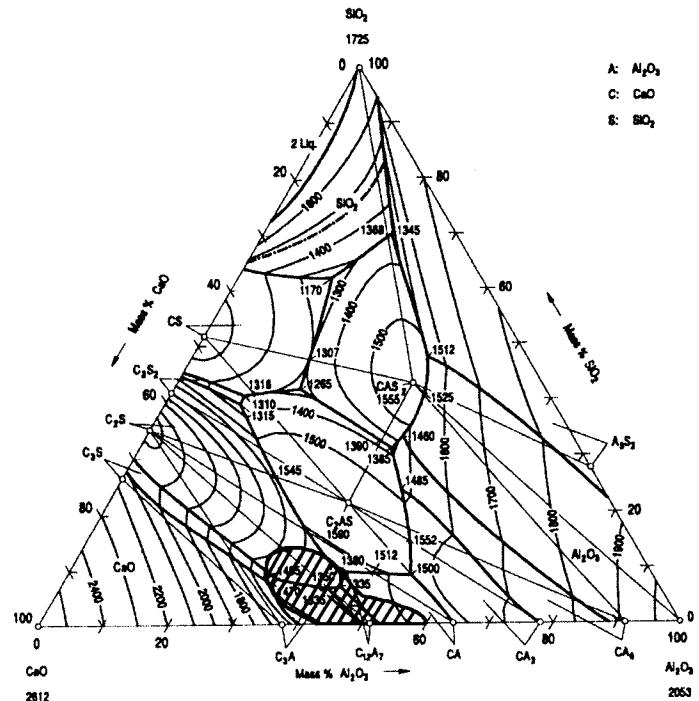


Figure 3.4. Composition of slags used in initial experimental phase, hatched region indicates slags A through E.

3.2 Results

Although it was not measured it was also assumed that no concentration gradients existed in the slag phase. Crushed master slag, contained in the graphite crucibles, inserted into the hot zone melted in less than 60 s. Note: some high SiO_2 content slags at elevated temperatures exhibited signs of SiO_2 reduction by the graphite crucibles.

Chemical analysis of the slags indicated that the method of preparation was good. Slag chemistries were close to their target compositions and there was little variation between slags of the same group.

Analysis of the slag samples where reaction time was the experimental variable showed that slag-metal equilibrium was not attained in a manner consistent with the reported dissolution behavior of Sn at low oxygen potentials. It was found that the Sn content of the slags rapidly rose before decreasing again; a typical example is shown in Figure 3.5.

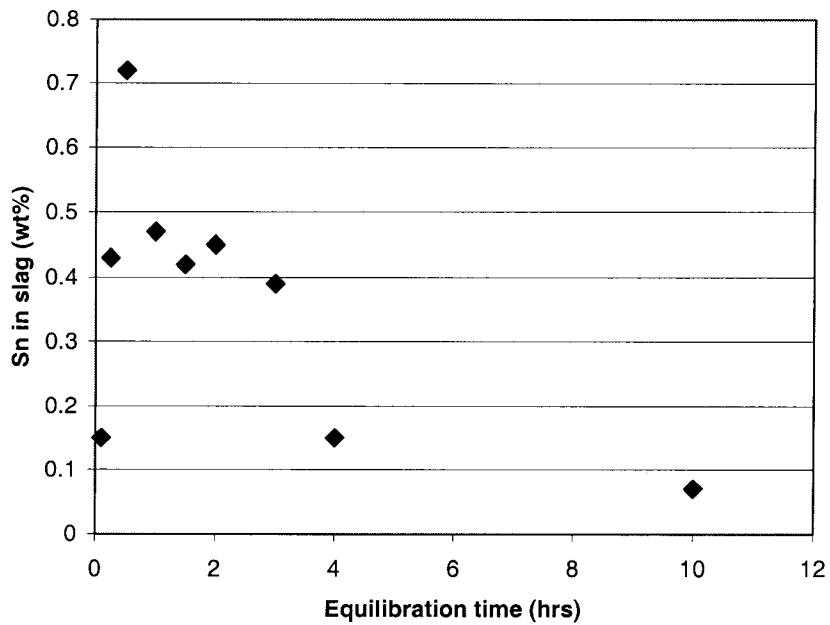


Figure 3.5. Typical variation in Sn content of CaO bearing slag. Reaction experiments performed before installation of sample vacuum chamber.

For the slag systems studied it appeared that at low oxygen potentials, the area of most interest in this study, equilibrium was only attained for reaction times in excess of 4 hours. The observed behavior is thought to be due to a greater than expected oxygen content of the metal during the initial stages of the experiments. In addition, low gas flow rates through the furnace may not have flushed the oxygen rich atmosphere surrounding the packed material within the crucible. Under these conditions it could be expected that the Sn would dissolve oxidatively in the slag before being reduced by the graphite and attaining final equilibrium with the system. This appears to be the most likely explanation with a similar experimental influence being observed in 2 other studies within our laboratory (Wall-Bonnet M.Eng. thesis 2001 and Pyke B.Eng. thesis 2001) and also reported by external researchers (Rankin, Met. Trans. B 1986). As a result of initial injection experiments (see Chapter 2), experimental priorities were directed towards measurement of slag metal partitioning rather than kinetics. Therefore, further work was only performed on those samples that had been produced in the 10 and 16 hour runs where equilibrium had been attained.

3.2.1 Effect of pO₂

Rather than present the results of analysis of a range of slags equilibrated, under different oxygen partial pressures, with tin for 10 hours at 1873 K in the main report, it is included in Appendix 3, Table A3-1. Only the important features of the data are presented here in graphical form. The Sn content of the slags equilibrated at 1600°C for 10 hours were not only greater than expected (0.02 to 0.99 wt%), but also lacked any clear dependence on the system oxygen potential, as shown in Fig. 3.6. Closer examination of the quenched slags showed that many of the samples contained metallic Sn. The Sn being present as metallic spherules or veins throughout the slag as illustrated in Fig. 3.7. The formation of these Sn veins suggest that dissolved Sn may precipitate on cooling, which also suggests that Sn⁰ is at least one of the dissolved species. This would be independent of oxygen potential and would lead to a distortion of the results at low oxygen potentials. It was intended that the using a sample preparation procedure including crushing and sieving would have been adequate to remove any metallic Sn. However, it is likely that some metallic Sn reported to the -250 Mesh fraction, and hence the Sn contents of the slags would be artificially high. Only data from those slags that were clear and glassy, and obviously free of metallic Sn are discussed further in this work.

3.2.1.1 Discussion of the Effect of pO₂

The dissolution behavior of a minor element, such as Sn, can be investigated by examining the dependency of the distribution ratio on the oxygen potential such as outlined by Nagamori and Mackey^[5]. For the experimental procedure employed in this study, the Sn content in slag is used in place of the distribution ratio since the metallic phase contains only Sn.

Oxygen potentials were controlled using CO and Ar gas mixtures in equilibrium with the crucible graphite, where the p_{O₂} value is calculated by^[6]



$$\Delta G^0 = -114,400 - 85.8T \text{ (J/mol)} \quad (3.2)$$

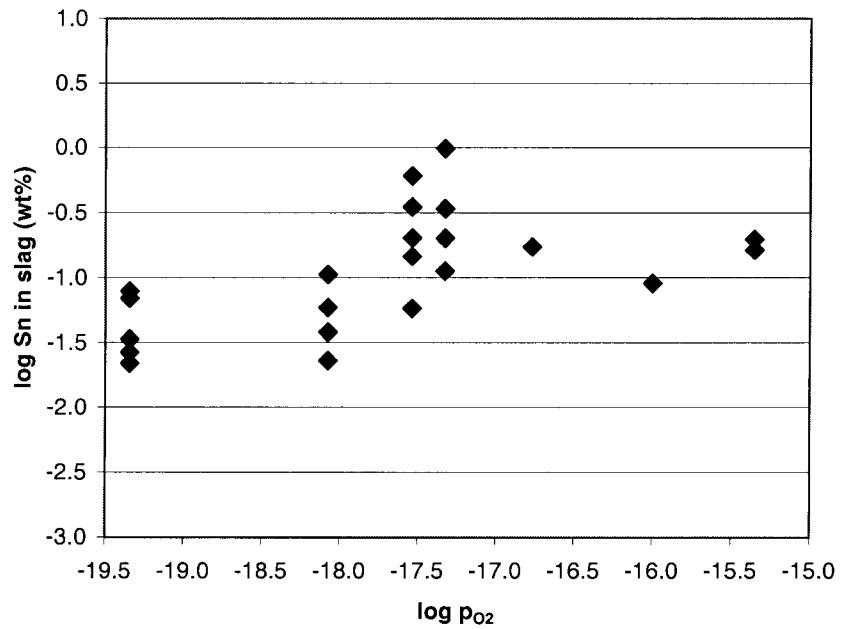


Figure 3.6: Sn content in slags (A-E) at varying oxygen potentials. Equilibrated for 10 hours at 1600°C.

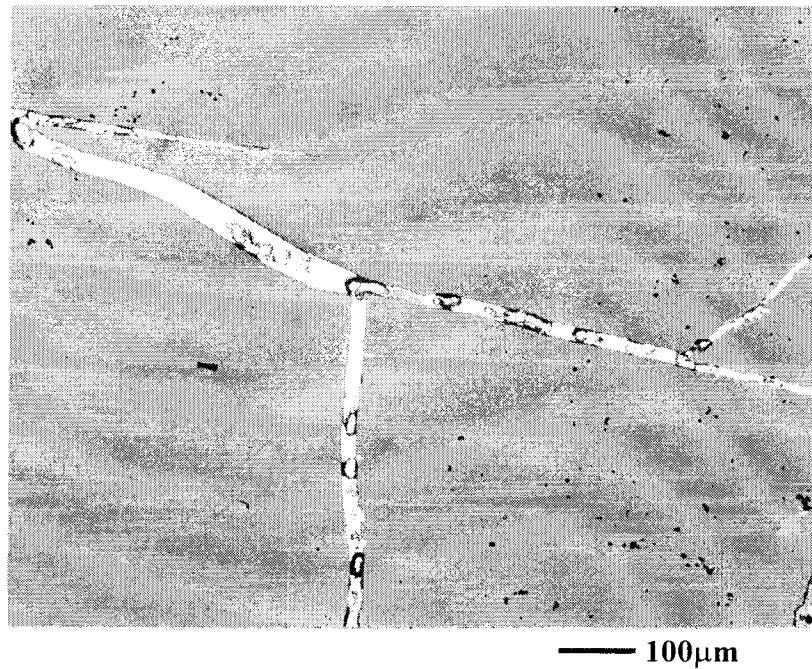


Figure 3.7: Slag sample showing tin veins.

Equilibrium experiments were performed using CO/(CO + Ar) ratios of between 0.01 and 1. At 1600°C this is equivalent to oxygen potentials between $4.52 \text{ H} 10^{-20}$ and $4.52 \text{ H} 10^{-16}$.

The Sn content of the slags are shown along with the data of Isawa et al^[7] in Fig. 3.8. From this figure it would appear that Sn dissolution in the slag system studied occurs along similar mechanisms to that identified previously.

The variation in Sn content at fixed oxygen potentials can be ascribed to the different slag compositions used. This appears to be related mainly to calcium activity and is discussed further in section 3.2.3. Isawa et al utilized a single slag composition that had a fixed CaO activity of 0.62, while the present study utilized a range of compositions. Although studying higher oxygen potentials Takeda et al found that Sn solubility is highly dependent on slag composition as shown in Fig. 3.9^[8].

The CaO activity of the slags (a_{CaO}) used in the study were calculated according to^[9]

$$\log a_{\text{CaO}} = 12.5\Lambda - 10 \quad (3.3)$$

where Λ is the optical basicity of the slag. Data to calculate Λ were those recommended by Mills^[10]. The relationship between the Sn content of the slag and the CaO activity at low oxygen potentials is shown in Fig. 3.10. In general, under low oxygen potential conditions as lime activity increases the Sn content of the slag increases.

These data show a significant scatter about the trend line taken from the data of Isawa et al^[7]. It could be argued that the scatter appears no greater than other similar studies. However, the CaO activity in itself is not the control factor as shown in equation 3.4. The significant factor is the Ca activity, which at the lower oxygen potentials employed in this study will be in equilibrium with CaC_2 ^[14].



$$\Delta G^0 = -353,970 (\pm 1670) + 79.28 (\pm 1.26)T \text{ (J/mol)} \quad (3.5)$$

The calcium activity operating under the conditions of this investigation can be calculated from^[11]

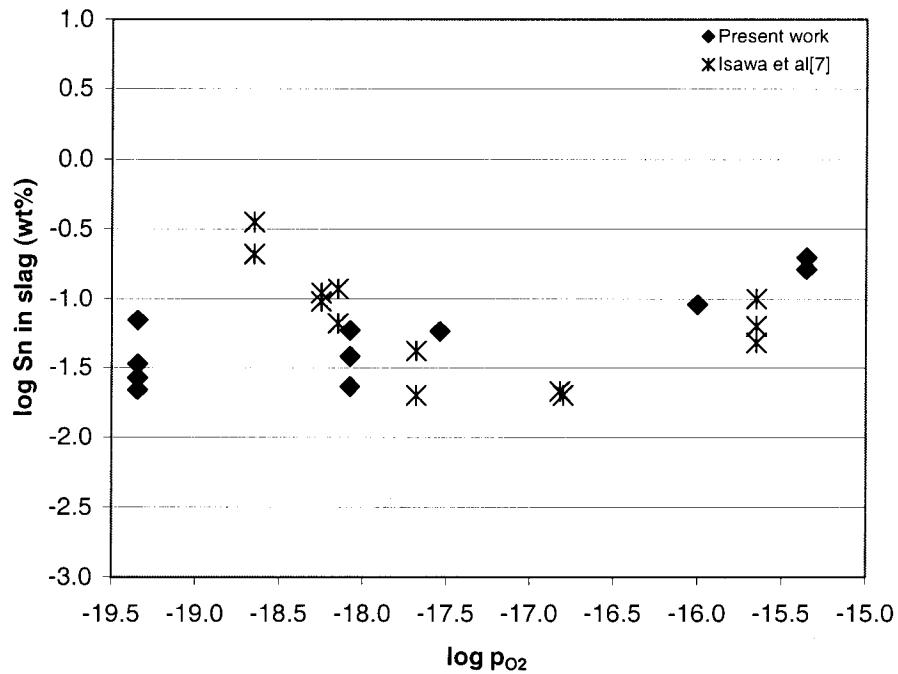


Figure 3.8: Tin solubility as a function of oxygen partial pressure at 1600°C.

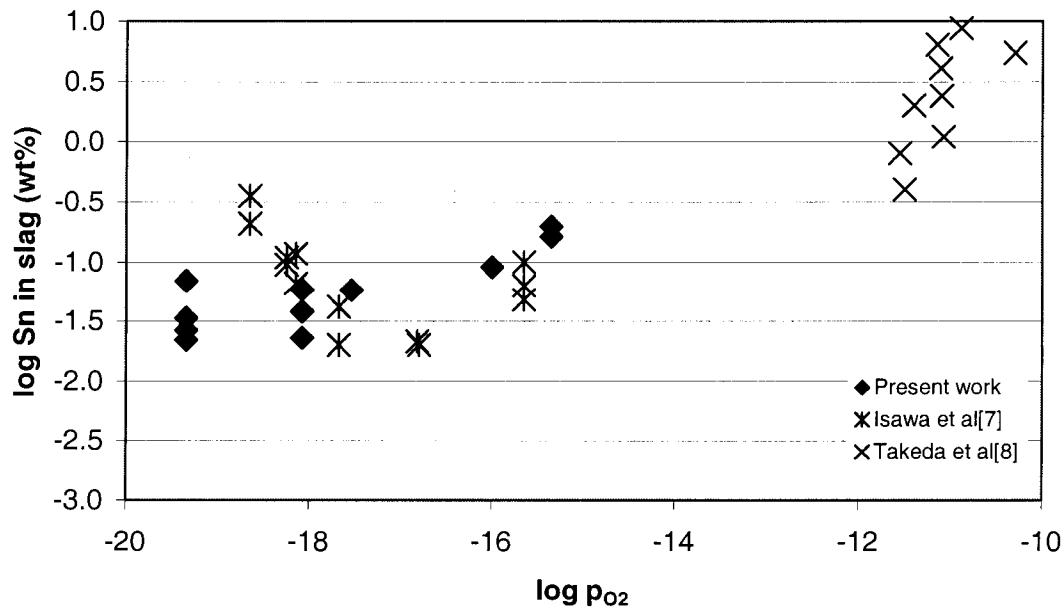


Figure 3.9: Comparison of tin solubility in the present work with that of Takeda at higher oxygen potentials.

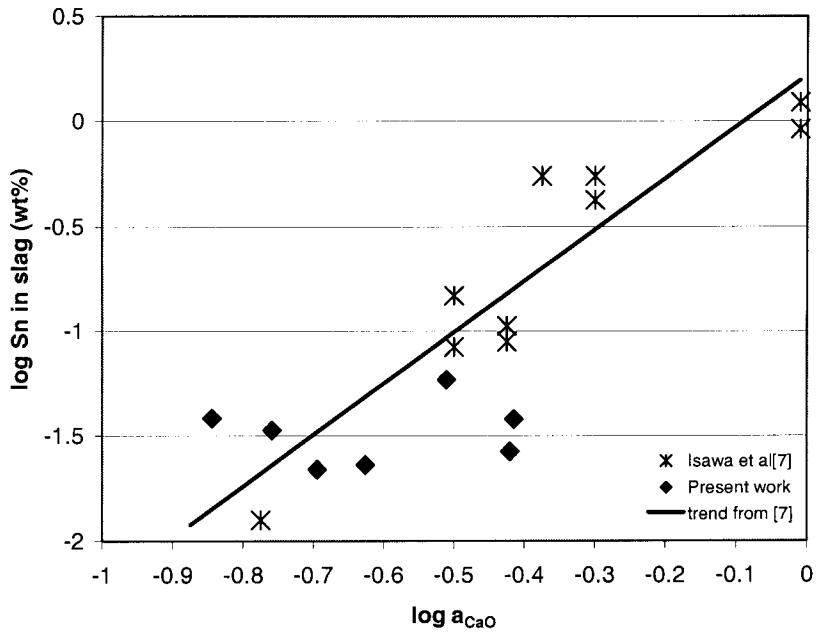


Figure 3.10. Influence of slag CaO activity on Sn content in slag.



$$\Delta G^0 = -628,000 + 118T \text{ (J/mol)} \quad (3.7)$$

at the higher oxygen potentials where reaction 3.6 is controlling, and by^[6]



$$\Delta G^0 = 60,250 + 26.28T \text{ (J/mol)} \quad (3.9)$$

at the lower oxygen potentials when reaction 3.8 is controlling.

Figure 3.11 shows the relationship between the calcium activity and the Sn content of the slags where the activity has been calculated where CaC₂ controls the calcium activity. The results from the study are compared against earlier experimental data of Kohler and Engell^[12] and the theoretical estimations of Wakasugi and Sano^[13]. When considered in this way the results of the present study are remarkably close to both previous studies^[7,12,13].

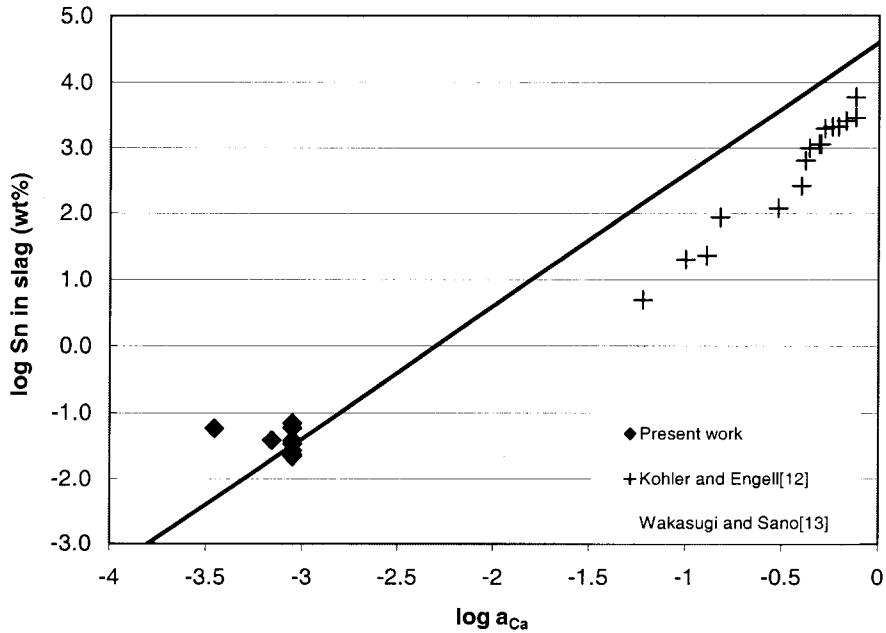


Figure 3.11: Influence of Ca activity on the Sn content of Ca based slags.

If it is assumed that at low oxygen potentials Sn exists in slag as solely Ca_2Sn , then the activity coefficient of Ca_2Sn ($\gamma_{\text{Ca}_2\text{Sn}}$) can be determined. Where the activity of Ca_2Sn can be calculated using equations (3.10) and (3.11).

There is little thermodynamic data on the intermetallic compound Ca_2Sn . One of the few studies is that by Min and Sano^[14] who calculated that $\gamma_{\text{Ca}_2\text{Sn}}$ was 150. The activity coefficient determined in this study is about one order of magnitude greater than that of Min and Sano^[14]. This discrepancy can be explained by the slightly higher free energy of formation employed by Wakasugi and Sano^[13], which was used in this study, compared with that used by Min and Sano in calculating the activity coefficient of Ca_2Sn .

The dissolution behavior of Sn in calcium bearing slags at higher oxygen potentials is shown in Fig. 3.12. Although there is some difference in the slag systems it would appear reasonable to claim that Sn dissolves oxidatively as SnO rather than as SnO_2 . For the range of oxygen potentials studied it is reasonable to say that Sn dissolves according to Equation 3.10. However,

as the higher oxygen partial pressure range is of little interest in the present study, no further discussion of oxidative dissolution is included in this report

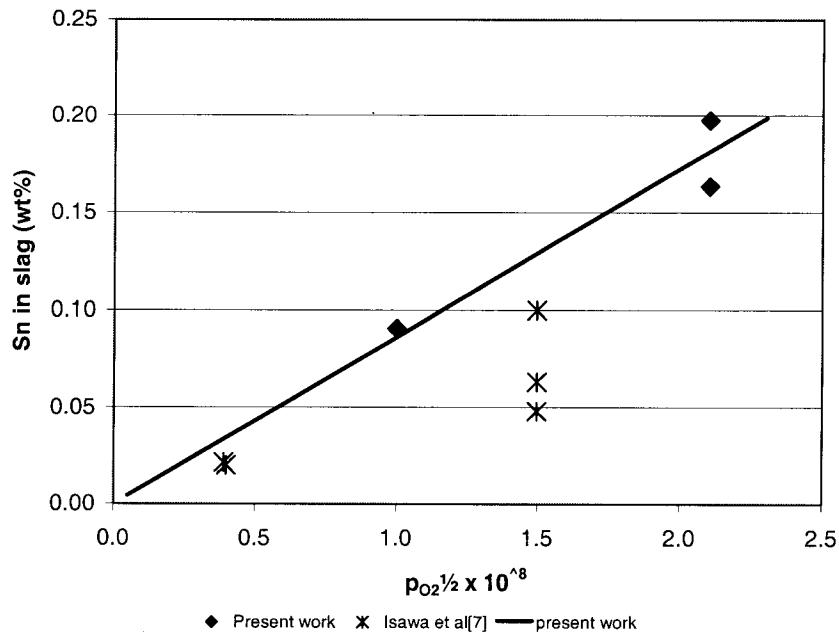


Figure 3.12: Influence of oxygen potential on Sn content of Ca bearing slags.

3.2.2 Effect of Temperature

Figure 3.13 shows the effect of temperature on the tin solubility in slags E and F. The raw data for this figure can be found in Table A3-2. The data does not show a simple trend with temperature but both slags exhibit a “spike” in tin solubility at an intermediate temperature. This feature is also exhibited by several other slags examined in this study which can be seen by examination of Table A3-2. One possible reason for the spike is illustrated in Figures 3.14 and 3.15.

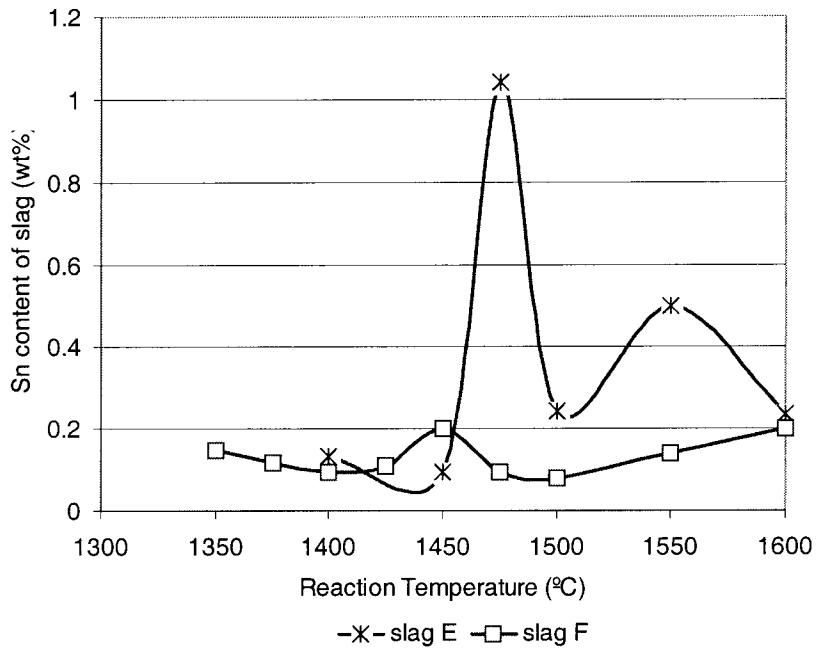


Figure 3.13: Influence of reaction temperature on the Sn content of CaO-bearing slags. Equilibrated for 16 hours under pure Ar.

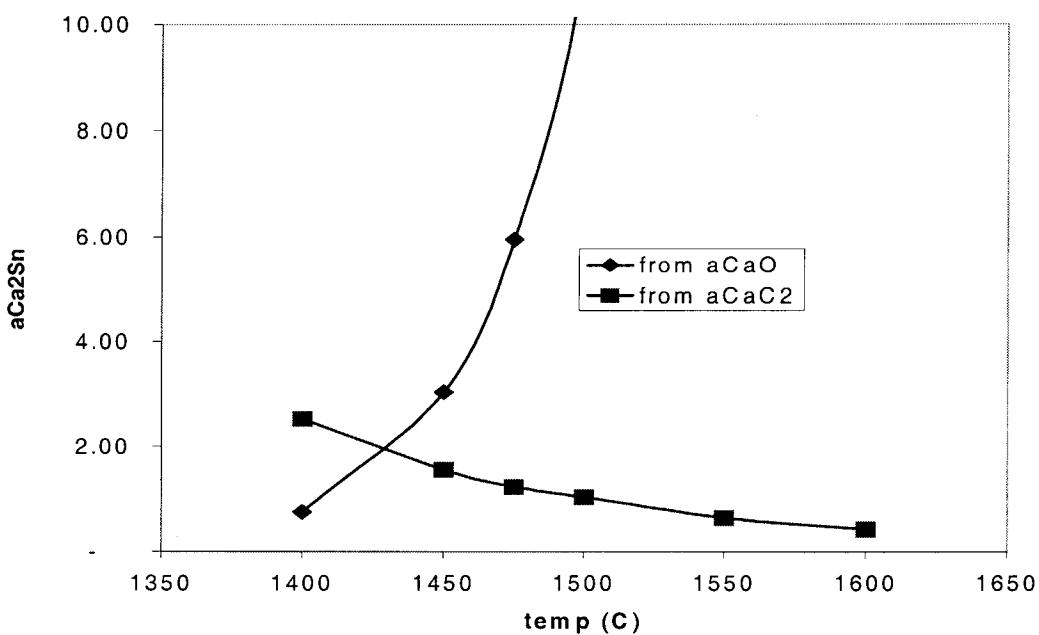


Figure 3.14: Activity of Ca₂Sn, as a function of temperature, calculated from equilibrium with both CaO in the slag and CaC₂ for slag E.

In these figures, both reactions that can fix the calcium activity are considered, reactions 3.6 and 3.8. At higher temperatures the calcium activity is fixed by reaction 3.8 and at lower temperatures by reaction 3.6. As the temperature is increased from 1300EC to about 1450EC the Ca_2Sn activity increases because CaO becomes less stable with increasing temperature, thereby increasing the calcium activity. At temperatures in excess of about 1450 or 1500°C CaC_2 controls the calcium activity and the activity of Ca_2Sn begins to decrease with temperature. From Figure 3.15 it can be seen that both slags exhibit a maximum in Ca_2Sn activity between 1450EC and 1500°C. In the case of slag E, this maximum is considerably greater than unity, therefore, the system becomes supersaturated with respect to Ca_2Sn , which may explain the extreme nature of the spike in Figure 3.13. The spike for slag F is neither so large, nor is it at the temperature indicated in Figure 3.15. This result could be a consequence of the lower Ca_2Sn activity generated by slag F. In fact, this slag never becomes supersaturated in the temperature range considered.

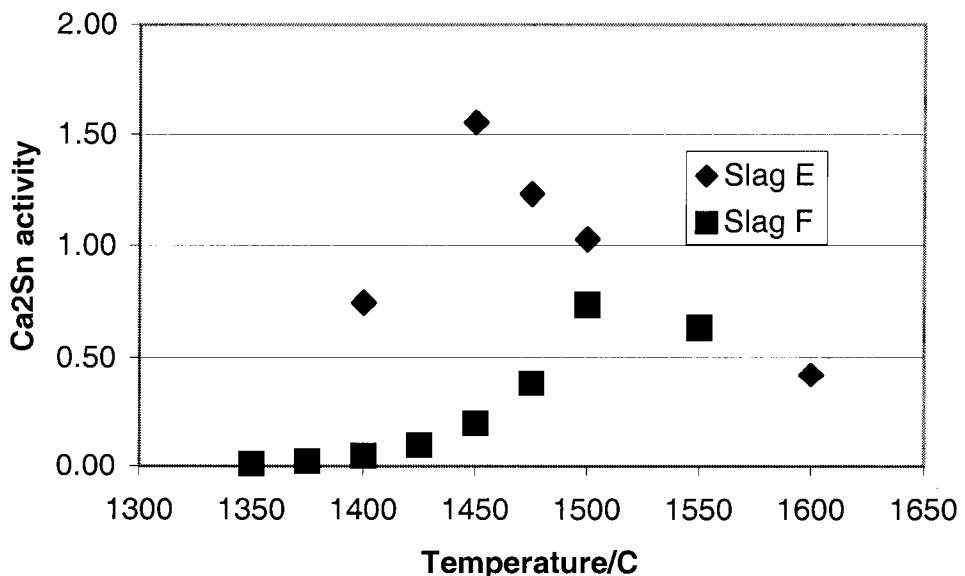


Figure 3.15: Activity of Ca_2Sn as a function of temperature for slags E and F.

Examination of the effect of temperature suggests that the major effect is on the activity of calcium, which in turn is the major factor in controlling the Ca_2Sn activity. With respect to the

injection situation, the activity of calcium in equilibrium with the slag will have little bearing on the de-tinning efficiency, because the calcium is injected as metal. The only possible influence of the slag calcium activity is in retaining tin in the slag after the intermetallic has floated from the melt. However, evidence from laboratory injection trials suggests that reversion is not an issue. Therefore, the major relevant effect is the ability of the slag to dissolve Ca_2Sn . This is considered as a function of slag composition in the next section.

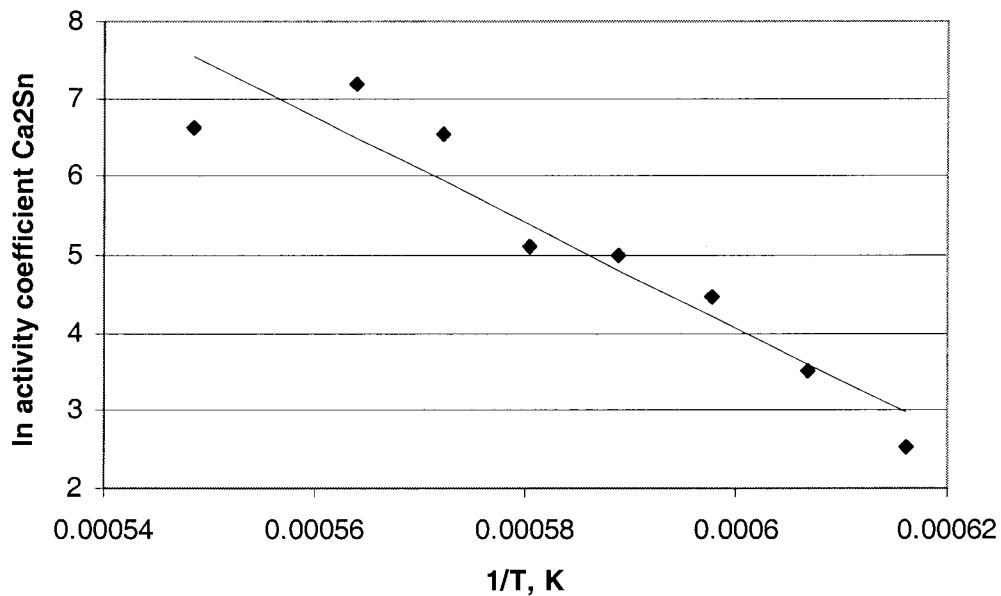


Figure 3.16: Natural logarithm of the activity coefficient, γ (Ca_2Sn), as a function of reciprocal temperature for slag F.

If we examine γ (Ca_2Sn) as a function of temperature, for only those slag F samples with a Ca_2Sn activity of less than unity, we see in Figure 3.16 that the natural logarithm of γ (Ca_2Sn), is a linear function of $1/T$. Analysis of the slope for slags F and C yields heats of mixing between -500 and -600 kJ/mol . These exothermic heats of mixing are not consistent with the positive deviation from ideality observed for Ca_2Sn solubility in these slags. It should be noted that the calculation of the activity coefficient is highly dependent on the calculated activity of Ca, over which there is considerable uncertainty.

3.2.3 Effect of Slag Composition on Tin Solubility

The results of equilibration of a wide range of ladle furnace-type slags with pure tin are presented in Table A3-3. The main features of this data will be considered in this section. These data indicate that the primary effect of slag composition on tin solubility, is on the activity of calcium. However, once the activity of calcium is accounted for, we see a two order of magnitude variation in the activity coefficient for Ca_2Sn . In addition, it appears that higher silica slags exhibit lower activity coefficients. Therefore, if another means of fixing a (Ca) is employed, it may be better to use a high silica slag. This sensitivity of the result to the calculated calcium activity should also be recognized; therefore, care should be taken before reading too much into this result.

3.3 Conclusions on Slag Metal Experiments

1. Tin solubilities in typical ladle metallurgy slags are similar to those found by Sano and co-workers for fluorspar based slags.
2. The effect of oxygen potential is in good agreement with that found by Sano et al indicating dissolution in the form of Ca_2Sn .
3. High basicity favored high tin solubility.
4. The temperature effect on tin solubility was complex; increasing temperature increased solubility up to about 1500°C, and the solubility decreased with further increases in temperature. This effect was related to the reaction that controlled the calcium activity. At lower temperatures lime dissociation controlled, whereas at higher temperatures calcium carbide fixed the calcium activity.
5. All of the above noted effects are related to control of the calcium activity which is in support the original premise behind this study; that calcium activity is the important parameter. If this can be kept high oxygen potential will not be important. This is supported by results from laboratory injections; however, results from plant trials show that it is extremely difficult to impose a high calcium activity independent of the oxygen potential.

4. FULL-SCALE PLANT TRIALS

4.1 Introduction

The injections into the induction furnace were very promising, so it was decided to extend the scope of the work to include a limited number of full-scale plant trials of the process to determine its feasibility. Dofasco very kindly agreed to act as the host site for a small number of trials at no cost.

4.2 Equipment

The trials were carried out in Dofasco's EAF stream in Hamilton. Steel was melted in an AC EAF with a heat size of 165 tonnes. The steel was transported to the Ladle Metallurgy Furnace (LMF), equipped with complete facilities of heating, slag addition, alloying, and CaSi wire injection. The 16 mm OD wire (containing about 30% Ca, and 0.3 kg alloy/m), was injected at a constant speed of 225 m/min. The injection occurred with an open atmosphere.

The CaSi cored wire is believed to reach depths of the order of 2.3 m, depending on the specific conditions (cored wire characteristics, injection rate, and steel temperature).

4.3 Procedure

The steel was tapped free of steelmaking slag into the ladle (using the EBT) system, then transferred to the LMF for slag addition (typically dry lime and calcium aluminate). The amount of slag was increased to about 25 kg/t, so that sulfur removal could be accomplished with the alumina lining operating at low temperatures. Aluminum for deoxidation also contributes to slag formation. Argon was blown through two porous plugs. Using these procedures Dofasco routinely achieves CaO saturation and the reducible oxide content (FeO + MnO) in the slag less than 1.0 wt. %.

The current trials were conducted with tin addition (made at the LMF), the lowest sulphur content available, and increased Ca consumption (normal practice is 0.25 kg Ca/tonne Fe). The reagent composition and its injection rate were kept constant, so that to increase the amount of calcium injected, 3 to 5 injection sequences were performed in each trial. Both reactions (sulfur

and tin removal) were monitored with timing, steel/slag samples, and temperature/ O_2 measurements.

4.4 Results

Two trials were conducted, and the conditions and results are summarized in Table 4.1. Due to the injection sequence, the total duration of the treatment was 5 to 6 times the actual injection time.

It was disappointing that virtually no tin was removed in these two trials, even though the oxygen and sulphur contents were very low. It is believed that the reason is that not enough calcium was added, 0.5 and 1.1 kg Ca/tonne Fe, compared to 8 to 16 kg Ca/tonne Fe in the induction furnace injections. Logistically, it was too difficult for Dofasco to significantly increase the amount of calcium injected; it would have required more than 1 hour at the LMF. If tin is to be removed, extra wire feeders or higher capacity powder injection need to be utilized.

During these trials, the sulphur content was dramatically reduced. However, very little desulphurization occurred during the injection, rather it occurred during the following holding/bubbling period. Therefore, it was concluded that desulphurization occurred primarily by a slag/metal reaction, not at the calcium bubble interface. The reaction may have been facilitated by the powerful deoxidation effect of the calcium. This finding is consistent with those at LTV Steel. Furthermore, at LTV, they found that powder injection was much better at desulphurization than was wire injection. It may be surmised that pneumatic injection of particles provides more interfacial area for reaction. Removal of sulphur and tin require the same types of reaction mechanisms to occur; sulphur or tin diffuses to the bubble interface where it forms a reaction product. In the injections at McMaster, it was found that the extent of removal of tin and sulphur were similar (Figure 2.22), supporting this supposition. Therefore, tin removal may be more efficient with powder injection than with wire injection, and the cost may be lower.

Table 4.1 Conditions and Results for Full-Scale Injection Trials

Trial	1	2
Steel Weight (tonne)	161.5	166.9
Initial		
O (ppm)	2.8	<1
S (ppm)	223	99
%Sn	0.0695	0.0337
Ca (ppm)	1	1
%Si	<0.01	0.02
%Al	0.0123	0.0489
Weight Ca fed (kg)	86.4	185.4
Duration (min)*	4.26 (22)	9.16 (54)
Kg Ca/tonne Fe	0.534	1.11
Kg Ca/tonne Fe/min ¹	0.125	0.121
Final		
O (ppm)	<1	<1
S (ppm)	30	6
%Sn	0.0654	0.0335
Ca (ppm)	33	44
%Si	0.13	0.2
%Al	0.0378	0.0630
%Sn removed	5.9	0.59
%S removed	87.	94.0
%O removed	57.	N/A
Utilization ²	5.2 H 10 ⁻²	1.2 H 10 ⁻³

* The injection time is given followed by the total time in brackets. The sequences were:

Trial 1: 28.8 kg, 10.5 min wait, 28.8 kg, 10.5 min wait, 28.8 kg;

Trial 2: 11.4 kg, 11 min wait, 43.5 kg, 12.5 min wait, 43.5 kg, 12.5 min wait, 43.5 kg, 8.5 min wait, 43.5 kg.

¹ This figure is based on injection time, not total time.

² Utilization is the percentage of calcium that was used for tin removal according to stoichiometry.

4.5 Conclusions on Full-Scale Trials

1. Virtually no tin was removed from the steel in two trials at Dofasco because not enough calcium could be added for logistical reasons. In these trials 0.5 and 1.1 kg Ca/tonne Fe, compared to 7–16 kg Ca/tonne Fe in the induction furnace injections.
2. To implement de-tinning by calcium injection facilities (either powder or wire injection), must have the capability to injection 10 to 20 kg Ca/tonne Fe in a matter of minutes to meet normal production schedules.

5. GENERAL DISCUSSION AND EVALUATION OF PROGRESS ON MILESTONES

5.1 Introduction

The original proposal was aimed at developing a method to remove tin from liquid steel by a combination of calcium injection and top slag. The study consisted of two primary components; one aimed at investigating the kinetics of reversion of tin from the top slag and the other studying the effect of calcium injection. These components are described in detail in Appendix 1.

5.2 Evaluation of Progress

5.2.1 Part 1 Slag/Metal Experiments

In this part of the project the objective was to investigate the kinetics of tin reversion as a function of, oxygen potential, slag composition and temperature, with a view to minimizing the effect of reversion on the overall process. It was also an aim of the programme to determine whether high fluoride slags were required to remove tin. It was demonstrated early in the programme that high fluoride slags were not necessary. However preliminary experiments in Part 2 of this study indicated that reversion was not a significant problem. It was therefore decided, after one year of the project, to modify the programme, to investigate the solubility of tin in the slag as a function of the same variables, in order to optimize the minimum tin levels that could be achieved by the proposed process. It was not decided to abandon research on tin reversion but to give priority to thermodynamic aspects of the research. However, there was insufficient time available to pursue reversion studies and these were never undertaken.

The programme has achieved its revised aims in terms of evaluating tin solubility as a function of oxygen potential, slag composition and temperature. Both temperature and slag composition affect the tin solubility, but the major effect as highlighted in Chapter 3, is the effect on the calcium activity. The primary reaction for tin removal is



The importance of this equation as the primary mechanism for tin removal was the premise on which this project was based and borne out by both parts of the study.

5.2.2 Part 2 Tin Removal by Deep Injection of Calcium

The aim of this study was to investigate tin removal from 40 Kg melts by a combination of calcium injection and top slag. The aims of this study were: 1) to determine the global kinetics of the process and in combination with data from part 1, develop a predictive model to describe detinning of steel and 2) to evaluate the feasibility of the process with a view to going to full scale plant trials. Issues of importance were seen as, the slag composition, oxygen potential, temperature, and competition with other elements such as sulphur. Development of a predictive model proved to be out-with the scope of the project. However, all other aspects were completed. Early experiments indicated little involvement of the slag in laboratory injections; however it was also found that significant quantities of tin could be removed, even when it would not be expected from the bulk oxygen content of the steel. This vindicates the original premise of this study, that equation (5.1) is the important detinning reaction. This means that, provided a high local calcium activity can be maintained at the reaction site, the bulk oxygen content is of little importance. This part of the study also indicated that competition with sulphur did not significantly inhibit tin removal. The promise shown in this part of the study led to plant trials being undertaken at Dofasco.

5.2.3 Full-Scale Plant Trials

Plant trials did not result in measurable tin removal, which is contrary to the findings of the laboratory trials. It appears that, with the amount of calcium that we were able to inject, in the plant trials, it was not possible to overcome the effects of oxygen and sulphur. This is discussed in detail in Chapter 4, and it may be possible to employ injection rates that will remove tin from steelmaking ladles, but as stated in that chapter, it is unlikely to be economic.

5.3 General Comments and Recommendations

Most of the revised milestones for this project were achieved, and the basis of the proposal, that a local calcium activity capable of removing tin, can be fixed independent of oxygen, has been demonstrated to be true in the case of laboratory injections. However, it was not possible to

maintain a high calcium activity in full scale trials. The only possibility for this to be feasible in the future, would appear to be by the use of powder rather than wire injection of calcium.

REFERENCES

1. Lu D, Irons GA, Lu WK. A Kinetic Study of Calcium Wire Injection into Steel 1988: Proc Intl Symp on Calcium Treatment, ISM 23-30.
2. Mucciardi F, Guthrie RIL. Aluminum Wire Feeding in Steelmaking 1983: Trans Iron and Steel Society of AIME 3: 53-59.
3. Kitamura K, Sakurai T, Takenouchi T, Iwanami Y. Removal of Impurities from Carbon Steel by the Addition of CaC_2 1986: ISS Steelmaking Conf 69:269-275.
4. Kitamura K, Funazaki M, Iwanami Y. Takenouchi T. Production of Low Phosphorous Stainless Steel by the Reducing Dephosphorization Process, Transactions ISIJ 1984: 24: 631-638.
5. Nagamori M, Mackey PJ. Met Trans B 1977: 8B: 39-46.
6. Turkdogan ET. Physical Chemistry of High Temperature Technology 1980: Academic Press, New York: 5-24.
7. Isawa T, Wakasugi T, Noguchi K, Sano N. Steel Research 1987: 58: 7: 296-302.
8. Takeda Y, Yazawa A, Chit PP, Ujiie H. Matl Trans JIM 1990: 31: 9: 793-801.
9. Gaskell DR. Met Trans B 1989: 20B: 113-118.
10. Slag Atlas, 2nd Ed 1995: ed. VDEh, Verlag Stahleisen GmbH: 10-11. Gaskell DR. 4th Intl Conf on Molten Slags and Fluxes 1992: Sendai: ISIJ: 204-209.
11. Wakasugi T, Sano N. Met Trans B 1989: 20B: p431-433
12. Kohler M, Engell HJ. 2nd Int Symp on Metallurgical Slags and Fluxes 1984: TMS - MetSoc AIME: 483-496.
13. Wakasugi T, Sano N. Steel Research 1989: 60: 1: 1-5.
14. Min DJ, Sano N. Met Trans B 1988: 19B: 433-439.

APPENDIX I

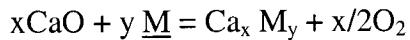
ORIGINAL PROPOSAL –

REMOVAL OF RESIDUAL ELEMENTS IN THE STEEL LADLE BY A COMBINATION OF TOP-SLAG AND DEEP INJECTION PRACTICE

Executive Summary

The level of undesirable residual elements (Cu, Sn, Ni, Mo, P) is increasing to an unacceptable level and it is anticipated that other elements such as (Pb, As, Sb, Bi) will become a problem in the future. At present this problem is avoided by steelmakers by careful selection of scrap, but this may not be possible in the future.

There have been a number of processes proposed in the past, for the removal of residuals, but none has been seen as sufficiently attractive for adoption by the industry. One such process involves the use of high calcium fluoride fluxes under highly reducing conditions for the removal of Sn, Pb, Sb, As and Bi. The thermodynamics of this process have been thoroughly investigated and successful removal of the elements, M, can be achieved by the reaction:



This equation shows that it is the calcium activity in the slag that is important and that it may be possible to dispense with calcium fluoride. The current proposal seeks to modify this process to use non-fluoride-bearing fluxes and to tackle some of the questions that must be answered before the process can be applied in practice. The critical issues are seen as:

Reaction Kinetics

Slag Composition

Oxygen Potential.

The proposed research will employ calcium injection to ensure an extremely low local oxygen potential and rapid reaction kinetics, in combination with a top slag to absorb the reaction products.

Each of these critical components will be studied independently.

The rate of reversion from the top slag at higher oxygen potentials is seen as critical to the process and will comprise a major part of this study. Data from this phase of the investigation will then be used in conjunction with kinetic data from injection experiments to develop a model of the entire process. With positive results from this phase of the work, plant trials will be proposed.

Because of the importance of the recycling of tin-plate, the research will initially focus on tin, but will be extended to include lead, arsenic antimony and bismuth.

Introduction

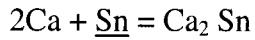
As more and more steel is recycled, and in particular as more and more steel from consumer products is recycled, the level of undesirable residual elements (Cu, Sn, Ni, Mo, P) is increasing to an unacceptable level. In addition it is anticipated that other elements such as (Pb, As, Sb, Bi) will become a problem in the future. There have been a number of methods proposed to remove residual elements^[1-6]. However these processes have not been adopted by the industry, generally because they involve one or other unpalatable aspect: the use of sulphide based fluxes that are difficult to handle and increase the sulphur levels in the steel; processes that produce volatile sulfides or chlorides^[1-4] causing handling difficulties; or processes that require high fluoride fluxes^[6] which have health and safety problems, and also cause severe refractory attack.

Of the elements listed above phosphorous is controlled fairly successfully at present by the use of oxidizing conditions. Whilst reducing conditions would also be effective, they create slag disposal problems. The only feasible methods for copper reduction are based on the formation of copper sulphide which have not been viewed with much enthusiasm from the steel industry, tin could also be removed by such methods and has the advantage of forming a volatile sulphide so removal could be enhanced by vacuum treatment. For lead, arsenic, antimony and bismuth it seems that only reducing conditions can be used and Nakamura *et al*^[6] and Sano and co-workers^[7-10] have proposed a process that employs highly reducing fluoride-based fluxes. Whilst this process is not without its problems, it is closest to conventional techniques for processing liquid steel and is therefore likely to be more readily accepted by the industry. One of the main drawbacks of this process is the seeming requirement for a high fluoride slag. However, the applicants do not believe that a high fluoride slag

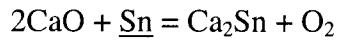
is essential, and it is the development of this process to employ more conventional ladle slags that is the subject of the present proposal. This process is also expected to work well for tin^[6, 7] which is an important element from the point of view of the recycling of tin plate and therefore will be the main focus of this study.

Technical Background and Technical Hurdles

The elements lead, arsenic, antimony and bismuth can only be removed from steel under reducing conditions^[9] and in addition it is probably more attractive to remove tin under reducing conditions. Sano and co-workers have proposed that high fluoride fluxes can be employed under strongly reducing conditions to remove these elements, and these workers have carried out a significant amount of work on the thermodynamic aspects of this process^[7-11]. They have shown that the important reaction for de-tinning is

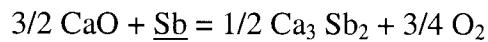
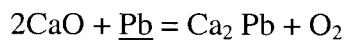


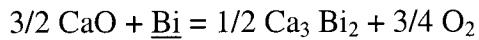
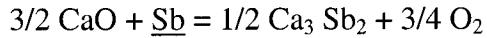
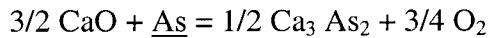
From Equation 1 it is clear that the higher the calcium activity the lower will be the level of tin that can be achieved. In Sano=s process the calcium activity is achieved via a lime-bearing calcium fluoride flux, therefore, Equation 1 should be rewritten as:



which shows that a low oxygen potential is important in achieving removal of Sn. In fact Sano and coworkers have shown that if the oxygen potential is held at a sufficiently low level slag/metal partition ratios (%Sn in slag /% Sn in metal) of as high as 10^4 can be achieved^[7]. This was also found by Breitzmann *et al*^[12] who used calcium metal under high pressure, to measure partition ratios for a range of residuals.

Sano and co-workers^[7, 8] studied several residual elements and demonstrated that the following reactions could be used to remove, Pb, Sb, As and Bi from liquid steel.





The conditions to remove these elements are very similar making the development of this technique attractive because of its flexibility of application. Therefore work in the present application which will focus on tin will be extended to include these other elements, which have been predicted to be a problem in the future.

Despite the apparent attractiveness of such a process there are questions that require to be answered and problems to solve before it could be applied on an industrial scale.

1. Are the kinetics of such a process sufficiently fast? Whilst extensive thermodynamic investigations indicate that the process is feasible there has been no study of the kinetics.
2. Is it necessary to employ high fluoride fluxes? High fluoride fluxes are viewed as a health hazard and cause accelerated refractory attack. In addition, they present problems from the point of view of disposal. All thermodynamic studies show that lime saturated slags provide the optimum conditions^[7,8] and Equation 2 indicates that it is the CaO activity in combination with a low oxygen potential that provides the driving force. Therefore the driving force for residual element removal will be the same for any lime saturated slag, fluoride bearing or not, provided the fluoride does not have a strong influence on the activity coefficient for $\text{Ca}_x \text{M}_y$.
3. Can a sufficiently low oxygen potential be achieved? The very high partition ratios measured by Sano required an oxygen potential of 10^{-24} and to achieve acceptable partitions 10^{-22} would be required.
4. Can magnesium be used as a substitute for, or in addition to calcium and what are the relative advantages?

Providing an answer to question 1 is seen as the primary objective of the proposed research which will focus on the kinetics of removal of Sn and ultimately will be extended Pb, Sb, As and Bi. However questions 2 and 3 represent critical issues that must be addressed if such a process is to be feasible. For the reasons discussed above it is likely that fluoride can be eliminated from the slag without a great detrimental effect on partition ratio for any of the residual elements under consideration. The only question being whether the fluoride has a beneficial effect on the activity coefficient for Ca_2Sn , however, available evidence^[8] suggests that it does not for other similar compounds. Calcium fluoride has been shown to accelerate a number of slag/metal reactions and therefore removal of the fluoride may adversely affect the reaction kinetics. This issue will be tackled as part of the kinetic study. Typical ladle slags will be employed in the reaction kinetics study to illustrate whether or not acceptable removal levels can be achieved without calcium fluoride. In addition, slags with small quantities of calcium fluoride will be used to assess the effect of fluoride on the reaction kinetics. It is likely that the use of a top-slag by itself will not be sufficient to ensure reasonable kinetics; therefore, deep injection of calcium as the main de-tinning reagent will be employed. This is expected to yield benefits other than enhanced kinetics and may indeed be critical to the success of the process. The role of deep injection will be discussed in more detail below.

The maintenance of a low oxygen potential, or more correctly a high calcium activity is essential to this type of process^[7, 8, 12]. There is some difficulty in achieving oxygen potentials that will give very high partitions when carrying out kinetic studies in the laboratory, because the reactions normally used in controlled atmosphere furnaces, CO/CO_2 or CO/C do not provide a sufficiently low oxygen potential. Sano used Ar/CO gas mixtures in equilibrium with solid carbon and managed to achieve $\text{pO}_2 = 10^{-21}$ but this would require an extremely gas-tight system which would not be compatible with sampling during kinetic measurements. However, it is possible to establish extremely low localized oxygen potentials during injection of calcium or magnesium^[13]. It is likely that the oxygen potential at the slag/metal interface will be influenced by oxygen from the atmosphere and therefore it may be difficult to ensure good slag/metal partition ratios. On the other hand if deep injection of calcium is employed it is the calcium activity at the interface between the injected calcium and the melt that is critical in removal of residuals.

Nakamura has shown acceptable levels of de-tinning with high calcium fluxes^[6] and one of the current applicants^[13] has demonstrated that, during calcium injection for inclusion modification, calcium activities of greater than 0.01 with respect to pure calcium vapor at 1 atmosphere, can be achieved at the reacting interface. Such values would provide a partition coefficient of about 100 for Sn. In the case of reference 13 calcium activities would probably have been higher if they were not controlled by reaction with sulphur and oxygen in the steel. This raises the question of interference, by or with, other refining reactions. Calcium treatment is used for inclusion modification and desulphurisation, and it is likely that sulphur could interfere with the reaction to remove residuals by consuming calcium and lowering the calcium activity in the melt. Therefore the present study will seek to investigate interferences between injection to remove tin and sulphur in the melt.

On the assumption that reaction 2 can be made to occur deep in the melt, the role of the slag then becomes different from the case where it is the primary refiner. The slag will have to absorb Ca₂Sn and prevent tin from reverting back into the metal. It is not necessary that the absorption is a chemical process, the physical "trapping" of Ca₂Sn may well be sufficient, but the properties of the slag will have to favor the capture of the intermetallic. If the oxygen potential is sufficiently high there will be a driving force for reversion of the tin. In this case a slag with sluggish reaction kinetics is desired, which would seem to be in conflict with the requirement for rapid absorption. This study will examine the effect of slag composition on reversion, in an attempt to find the optimum balance between capture of the intermetallic containing the residual element in question, and subsequent reversion of that element. It is possible that a fluid, active, slag is required in the early stages of the process, but that additives should be made to "stiffen it up" at the end. This possibility will also be considered.

The non-ferrous industry has shown that magnesium is extremely effective in the removal of Bi by a process similar to that proposed here^[14], and in the Kroll-Betterton Process a combination of magnesium and calcium is more effective than either in isolation. Therefore magnesium will also be included in the present study as a possible reagent and the simultaneous injection of magnesium and calcium will be investigated.

Benefits of Proposed Research

The "problem" of residuals has been discussed for a number of years, but in general steelmakers have managed to avoid the problem by selecting appropriate scrap. Whether the problem can be circumvented for the foreseeable future is not clear, nor is the cost of avoiding the problem as opposed to confronting it. Therefore it is not possible for the applicants to put a dollar value on the outcome of this proposal but it is clear that current trends will serve to make the problem worse, and a solution of the type proposed more attractive.

As the percentage of the world's steel from electric steelmaking increases, the ability of steelmakers to pick and choose scrap will decrease, and the capacity to control residuals will be required to provide a level of flexibility. In addition, the proposed process will increase the percentage of total product that can be recycled, a requirement that is continually being increased by governments.

Possible Problems

The only foreseeable problem with "making the proposal work" is the achievement of a sufficiently low oxygen potential (see above). However, calculations indicate that the requirements are no more arduous than for best-practice desulfurization^[13].

A more major difficulty with the adoption of such technology is slag disposal. The intermetallics produced by the proposed process produce poisonous gases (such as arsenine and stibnene) on contact with water. Therefore some steps would be required to "stabilize" these compounds rendering them harmless. The applicants are aware of this problem but do not propose a solution, on the grounds that once the process has been shown to work a solution can be found. It is also true to say that for many of the residuals this problem or similar will arise regardless of the technology.

Research Programme

The research programme will be conducted in three phases, two laboratory based and one in-plant. The details of the plant study are dependent on the results from the laboratory work but will essentially be a validation stage. The applicants are not tied to a particular steelmaker with respect to

this study but have had an informal offer from Mr. Debo Aichbhaumik of Weirton Steel (a tin plate producer) to carry out trials.

The laboratory studies to be carried out in parallel, will comprise:

1. a fundamental study of slag metal reversion kinetics under a controlled atmosphere, as a function of slag composition, and oxygen potential;

and 2. a study of reaction kinetics during calcium injection with and without a top slag.

1. Slag-Metal Reaction Study

The main purpose of this part of the study is to determine the ability of ladle slags to hold tin removed by calcium injection. This will enable optimum slag compositions to be chosen for the injection experiments in Phase 2. As the transport mechanisms are likely to be the same as for removal this will also give information useful in determining the extent to which the slag can be made to contribute to de-tinning.

Experiments will be carried out in a controlled atmosphere tube furnace to measure the kinetics and determine the reaction mechanism for reversion of residual elements from the slag. Slags that have been pre-saturated with tin using high tin iron will be exposed to tin-free iron. The use of a controlled atmosphere tube furnace will allow more control of the oxygen potential than would be possible in open crucible experiments. As conditions will be set to favour reversion (relatively high oxygen potentials) it should be possible to control conditions using CO/CO₂ and CO/C. This will allow the reaction to be studied as a function of oxygen potential. The oxygen potential will be varied in the range 10^{-10} to 10^{-16} using CO/CO₂ and CO carbon and will be monitored using a solid electrolyte probe. Slags will be studied in the composition range typical of current ladle metallurgy practice, with the inclusion of some slags containing up to 5% CaF₂. Experiments will employ 100 g of metal and 30 g of slag and the reaction will be followed by intermittent sampling of metal. In some instances smaller melts will have to be studied and the extent of reaction measured by quenching whole crucibles.

The first part of this phase will determine the reaction kinetics as a function of oxygen potential for a typical ladle slag, and will concentrate on tin. In order to fully understand the kinetics and to

determine the rate controlling step slag and metal height will be systematically varied in this part of the study.

The effect of slag composition on the reaction kinetics will be investigated. The composition variables that will be studied are lime to alumina ratio and calcium fluoride content of the slag. Reaction rate data will be analyzed as a function of slag viscosity and CaO activity. Data from this part of the study will be used to determine the most promising compositions to use as a top slag in Phase 2 of this investigation, the injection studies.

The final part of this phase will determine reversion rates for other residuals, Pb, As, Sb and Bi.

2. Pilot-Scale Injection Study

As discussed above, it is not possible to achieve sufficiently low oxygen activity and/or high enough calcium activity for effective residual removal at the slag/metal interface. However, injection of calcium is likely to achieve the necessary conditions.

In these experiments, calcium and CaSi will be injected into 40 kg heats of steel. The rate of removal of the residual elements will be studied as a function of the rate of solids injection, oxygen potential in the steel and freeboard of the crucible, and the type of top slag employed. From our previous work with calcium injection, it is not possible to inject the calcium deeply due to excessive splashing at this pilot-scale^[13]. Nevertheless, calcium will refine the steel. One of the most critical aspects of the study is to determine which types of top slags are most suitable for preventing reversion of the residual element from the slag back to the steel. The information from the slag/metal reaction studies outlined in the Part 1 will be valuable in this regard. In the initial part of this work, slags will be based on current practice in ladle metallurgy, but variations may be made in light of the findings from Part 1.

The oxygen potential is crucial to this study, so it will be measured with oxygen probes in the steel and the freeboard of crucible. In our previous work, it was found that the oxygen potential was considerably reduced by calcium injection. Therefore, the second injection in a heat may be carried out at lower oxygen potential.

The relationship between reversion rate and oxygen potential determined in Part 1 of this study will be used in the analysis of the results from this part. In an analogous manner to our previous work on desulfurization and inclusion modification with calcium, we will develop mathematical models to describe the refining reactions at the calcium vapor interface, and the reversion reactions at the top slag. We will also be able to scale-up these models to industrial ladle-scale to assess industrial practicality of these techniques. With promising results, and the willingness of member companies, we anticipate that full-scale plant trials will be conducted.

Schedule

Milestone	Time to complete from project start
Part 1.	
Equipment assembly and testing	0.5 year
Reversion tests with tin with various slags	1.0 year
Reversion test with Pb, As, Sb and Bi individually and various slags	2.0 year
Reversion tests with multiple elements	3.0 year
Part 2.	
Equipment assembly and testing	0.5 year
Tin removal experiments with Ca and CaSi and various top slags	1.0 year
Removal of Pb, As, Sb and Bi by Ca and CaSi injection	2.0 year
Plant trials at AISI member company	3.0 year

Budget

The following budget is estimated on an annual basis assuming that this is a contract, not a grant, giving AISI the rights to the intellectual property. The budget is in \$CDN converted to \$US in the last line.

Salaries (est. incl. fringe benefits)

Dr. G.A. Irons (12 days/yr @ \$1000)	\$12,000
Dr. K.S. Coley (12 days/yr @ \$1000)	\$12,000
Post-Doctoral Fellow	\$30,000
Graduate Student	\$15,000
Co-Op Community College Student for chem. analysis	\$12,000

Supplies (estimated at actual cost)

Part I experimental supplies (crucibles, thermocouples, etc.)	\$ 8,300
Part II experimental supplies (crucibles, thermocouples, repairs and modifications)	\$15,000
Chemical Analysis (Leco for C, S and O, spectrometer for residual elements)	\$ 5,000

Travel

Two investigators to ISS Conferences	\$ 3,000
Two investigators to industrial collaborator	\$ 3,000

Overhead

40% of Salaries and supplies, 2% of travel

TOTAL ANNUAL BUDGET \$142,820 CDN

CONVERTED TO \$US @ 0.75 \$107,115US

References

1. X. Liu and J.H. E. Jeffes; Ironmaking and Steelmaking, **15** (1988) pp 21-26.
2. X. Liu and J.H. E. Jeffes; Ironmaking and Steelmaking, **15** (1988) pp 27-32.
3. R. E. Brown, H. V. Divilio and R. J. Divilio; RI 8065, pp1-31, (1995) U.S. Bureau of Mines, Washington, DC.
4. R. Morales and N Sano; Ironmaking and Steelmaking, **9** (1982) pp 64-76.
5. T. Imai and N. Sano; Trans ISIJ, **28** (1982) pp 999-1005.
6. Y. Nakamura, N. Tokumitsu, K. Harashima and K Segawa; Trans ISIJ, **16** (1976) pp 623-627.
7. T. Isawa, T. Wakasugi, K. Noguchi and N. Sano; Steel Research, **58** (1987) pp 296-302.
8. T. Wakasugi and N. Sano; Steel Research, **60** (1989) pp 1-5.
9. Y. Ochifuji, F. Tsukihashi, and N. Sano; Met and Mater Trans B, **26B** (1995) pp 789-794.
10. F. Tsukihashi, K. Kuroda, S. Arakawa, and N Sano; Steel Research, **65** (1994) pp 53-57.
11. F. Tsukihashi, A Suzuki, and N Sano; Steel Research,
12. M. Breitzmann, H-J. Engell, and D. Janke; Steel Research, **59** (1988) pp 289-294.
13. D-Z. Lu, G. A. Irons, and W-K. Lu; Ironmaking and Steelmaking, **21** (1994) pp 362-371.
14. F. K. Ojebuoboh; JOM, 1992, pp 46-49.

APPENDIX II

DESCRIPTION OF INDUCTION FURNACE INJECTIONS

The following section outlines basic details of each individual injection trial.

INJECTION TRIAL 1

21st January 1999

80 lb of steel bars was melted over 1 $\frac{3}{4}$ hours under an argon atmosphere. Once melted an oxygen and temperature measurement was taken. 36 g of Sn were then added via the hopper, the target Sn level in the steel being 0.1%. Aluminum (54 g) was added to the melt to kill the steel. A metal sample was taken prior to the slag being added (1 kg). Further temperature and oxygen measurements were made to check the bath condition before the start of injection.

Wire injection was started, the planned injection rate being 3 cms⁻¹. The initial attempt at injection failed. Through the glass port it was possible to see that the wire had contacted frozen slag. Instead of passing through molten slag then reacting at some depth under the molten steel, the wire started to bend away from the melt as shown schematically in Figure AII.1.

A “breaker bar” was used to remove some of the frozen slag in the region where the wire was impacting the surface. Upon restarting the injection the wire successfully passed through the slag and into the steel. Immediately this was followed by the generation of large volumes of fume. It was also apparent that there was considerable splashing of the bath due to the number of ejected droplets hitting the glass viewing ports. During wire injection a distinctive red/pink glow emanated from the vicinity of the bath surface. Before the first minute of injection had ended it was not possible to see through the glass ports due to the extent of the fume generation.

After 1 minute the injection was halted so that a metal sample could be taken. This was followed by another minute of wire injection and another metal sample. Difficulties were encountered with the ongoing injection due to the wire being bent away from the melt by frozen slag. Further

attempts at clearing the blockage were made before restarting wire injection and sampling. In total 6 metal samples were taken over the coarse of injecting 10 m of wire.

Key data for trial 1:

Wire injection rate:	target 3 cms ⁻¹
Wire injected:	target 10 m
Bath temperature during injection:	1672°C to 1622°C to 1609°C to 1614°C
Oxygen content:	14.5 ppm to 27.8 ppm to 78.6 ppm to 12.1 ppm

Discussion of Trial 1

The brief discussion in this section is limited to those made from experimental observations. The extent of residual removal during this injection trial will be discussed later.

There appeared to be 3 areas of concern from the first trial. These were:

- unknown amount of calcium injected
- slag layer
- oxygen potential

10 m of wire was feed through the feeder, however, it was unclear as to how much of the wire successfully penetrated the steel. Much of the injection period was not accompanied by the distinctive red glow. Difficulties with the injecting arose due to the stop-start injection/sampling technique used and due to the slag layer freezing. It was identified that to some extent these problems could be lessened by using continuous wire feeding, reducing lateral movement of the wire through the use of a longer wire guide, and by improving slag fluidity.

The slag layer did not completely melt. Heat losses from the system were too great. Unlike the industrial situation where the slag is hotter than the bath, in the induction furnace it was readily apparent that the slag was considerably colder than the steel bath. The slag layer also developed an “open eye”, in this region steel was open to the furnace atmosphere. This developed because of the convex melt surface generated by induction heating and the low slag volume.

Examination of the crucible contents after the trial also showed that at some stage during injection/sampling the metal/slag interface was broken. The slag layer had frozen while the metal level dropped due to sampling. Suggested solutions to the slag layer problems included reducing heat losses through the use of a top layer of insulation, graphite susceptor rings around the slag layer, adding more slag, adding slag throughout the injection period, pre-fusing the slag, using a more fluid and/or lower melting temperature slag.

There was also some concern over the oxygen content of the steel bath. Lower oxygen contents were expected with increased experimental awareness and greater control over the melting time and bath temperature.

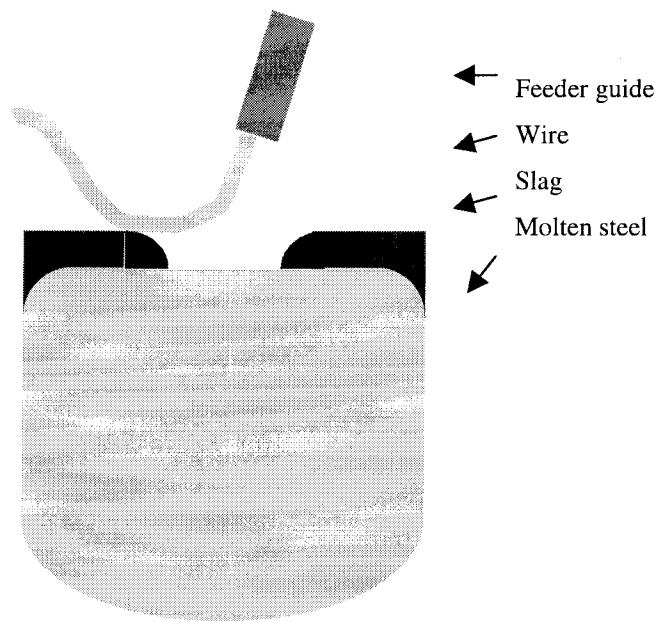


Figure AII.1. Schematic diagram of calcium wire being bent away by frozen slag during injection period of Trial 1.

INJECTION TRIAL 2

5th March 1999

78.8 lb of steel bars were melted over 1 $\frac{3}{4}$ hours under an argon atmosphere. Once melted an oxygen and temperature measurement was taken. 36 g of Sn were then added via the hopper, the

target Sn level in the steel being 0.1%. A metal sample was taken prior to the slag addition. Aluminum (54 g) was added to the melt to kill the steel together with 300 g of pre-fused flux. At 10 minute intervals slag was added twice more. The two 600 g additions bringing the total slag content up to 1.5 kg. Further temperature and oxygen measurements were made to check the bath condition before the start of injection, in response to the oxygen level (34.6 ppm) more Al was added.

Wire injection was started, the planned injection rate being 5 cms^{-1} . As before there was considerable fume generated, the injection producing numerous ejections of metal droplets and the distinctive red/pink colour. This continued until wire injection was stopped after 4 minutes and 7 seconds at which time a second metal sample was taken.

Key data for trial 2:

Wire injection rate:	target 5 cms^{-1}	measured 4.5 cms^{-1}
Wire injected:	target 10 m	measured 11.13 m
Injection time:	4 mins 07 sec	
Bath temperature during injection:	1618°C to 1658°C	
Oxygen content:	15.8 ppm [†] to 5.4 ppm	

† the real oxygen content would have been somewhat lower. More Al was added to the bath immediately following this probe measurement just prior to the start of injection.

Discussion of Trial 2

In attempt to solve some of the problems encountered in trial 1 a number of changes were made to the experimental plan for trial 2. A longer injection period was achieved in this trial. In total 11.13 m of wire was injected over a 4 minute period. This was most likely achieved through the use of a faster rate of wire injection (5 versus 3 cms^{-1}) and a continuous injection period. However, because the wire was feed without stopping there was no opportunity for taking metal samples other than at the start and end of injection. Hence for this trial only 2 metal samples were taken. Although the use of pre-fused slag appeared to help the formation of a molten slag

phase it was still evident that there was a considerable temperature gradient across the slag phase. During one of the stages of killing the steel aluminum shot added to the bath landed on the outer edges of the slag layer, as shown schematically in Figure AII.2. Given that the aluminum did not melt for a considerable time clearly indicates that the temperature at the top of the slag was not much more than 700°C (melting point of aluminum 660°C). It was also clear that a gap between the slag and metal phase had been generated during the slag melting stage. As the power was increased to provide more heat the metal top surface becomes more convex due to induction forces. However, as the power is lowered the metal surface flattens and can lead to the slag becoming “hung up” on the crucible wall if it has insufficient fluidity.

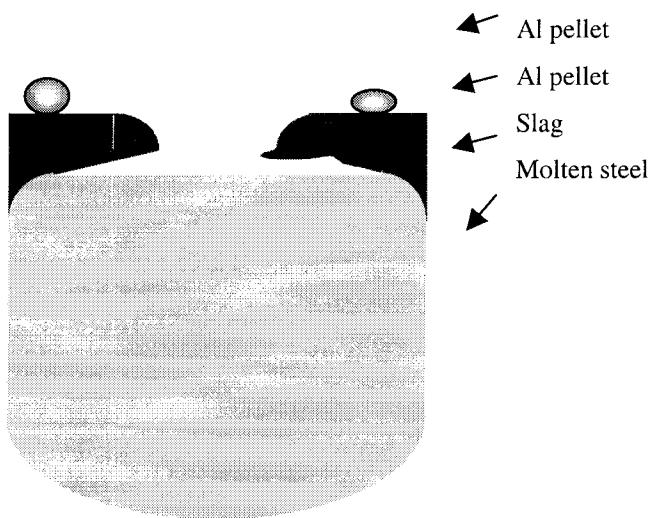


Figure AII.2. Schematic diagram illustrating frozen slag layer and unmelted Al pellets, indicating steep temperature gradients at top of crucible.

INJECTION TRIAL 3

7th April 1999

80.25 lb of steel was melted over 1½ hours under an argon atmosphere. Once melted an oxygen and temperature measurement was taken. 40 g of Sn was then added via the hopper, the target Sn level in the steel being ~0.1%. A metal sample was taken prior to the killing the steel with aluminum (60 g). At 10 minute intervals pre-fused flux was added to the bath. In total three

500 g additions were made bringing the total slag content up to 1.5 kg. Further temperature and oxygen measurements showed that the bath temperature was in excess of 1750°C. Although the bath temperature was still too high it was decided that there could be no further time delays. So after waiting 30 minutes wire injection was started. The planned injection rate was 5 cms⁻¹. As before there was considerable fume generated, the injection producing numerous ejections of metal droplets and the distinctive red/pink colour. This continued until wire injection was stopped after 3 minutes and 20 seconds at which time a second metal sample was taken. In an attempt to determine the potential reversion of Sn from the slag to metal phase a metal sample was taken after approximately 10 minutes after injection had been stopped. Metal samples were again taken at 25 and 40 minutes. To replenish the slag layer a final 500 g of pre-fused slag was added. The second period of wire injection was started. Wire was injected for another 3 minutes and 50 seconds, bringing the total wire injection time to 7 minutes 10 seconds. Metal samples were taken at intervals of approximately 1, 10, 20, 30 and 50 minutes after injection.

Key data for trial 3:

Wire injection rate:	target 5 cms ⁻¹	measured 4.1 cms ⁻¹
Wire injected:	target 20 m	measured 17.55 m
Injection time:	7 mins 10 sec	
Bath temperature during injection:	~1750°C to 1738°C and 1690°C to 1645°C	
Oxygen content:	30 ppm, 18.4 ppm to 12.4 ppm	

Discussion of Trial 3

The main aim of this trial was to investigate the potential for reversion of the residual elements (Sn) from the slag phase back to the steel phase. Taking metal samples over a given time period following wire injection facilitated this. In total 7 metal samples were taken specifically for the reversion test.

The main difficulty that arose in this experiment was the extreme bath temperatures. Prior to the first injection the bath was hotter than the probe could measure, i.e. $>1750^{\circ}\text{C}$. High bath temperatures cause several problems:

- higher oxygen content in the bath, the oxygen coming from the MgO crucible
- reduced wire penetration depth due to greater superheat.

Another problem encountered was the unknown amount of wire effectively injected in the second period. There was a large amount of wire leftover (5.31 m) and due to the large number of metal samples taken the bath height dropped leaving a “hung up” slag layer. The distance the wire then had to travel before impacting the metal surface was greater, it is likely that the wire had a much lower penetration depth due to the increased pre-heating.

INJECTION TRIAL 4

29th February 2000

81 lb of steel was melted over 2 hours under an argon atmosphere. Once melted an oxygen and temperature measurement was taken. 40 g of Sn was then added via the hopper, the target Sn level in the steel being $\sim 0.1\%$. A metal sample was taken prior to the killing the steel with aluminum (60 g). Over the next 40-minute period further Al was added in response to higher than anticipated oxygen levels. At 10-minute intervals pre-fused flux was added to the bath. In total three 500 g additions were made bringing the total slag content up to 1.5 kg. Further temperature and oxygen measurements showed that the oxygen content of the bath was still high, however, because of concerns over time delays the injection was started.

Wire injection was started, the planned injection rate being 5 cms^{-1} . As before there was considerable fume generated, the injection producing numerous ejections of metal droplets and the distinctive red/pink colour. This continued until wire injection was stopped after 3 minutes and 20 seconds at which time a second metal sample was taken. A further metal sample was taken at approximately $6\frac{1}{2}$ minutes after injection was stopped to test for Sn reversion.

The second period of wire injection was started. Wire was injected for another 4 minutes and 30 seconds, bringing the total wire injection time to 7 minutes 50 seconds. Metal samples were taken at intervals of approximately 1, 4, and 12 minutes after injection.

Key data for trial 4:

Wire injection rate:	target 5 cms ⁻¹	measured 4.5 cms ⁻¹
Wire injected:	target 20 m	measured 21.13 m
Injection time:	7 mins 50 sec	
Bath temperature during injection:	1722°C to 1707°C to 1645°C	
Oxygen content:	78.9 ppm to 47.3 ppm to 32.0 ppm	

Discussion of Trial 4

Because of concerns over the high bath temperatures generated during trial 3, considerable time was wasted on this trial decreasing the power level of the induction furnace to prevent over heating the bath. However, this generally resulted in the bath becoming sufficiently cold that the slag layer froze. Much of the time in this trial was spent between concerns over the bath being too hot, and the slag layer freezing. The result being that the steel was never fully killed. It was clear from this trial that it was difficult to melt 1.5 kg of slag without the use of insulating tops or graphite rings. Once molten the slag tended to insulate the steel heel. Frequent adjustments of the furnace power levels were clearly not the best solution. It is also likely that the slow heating cycle did not help the oxygen content of the bath.

INJECTION TRIAL 5

21st March 2000

80½ lb of steel was melted over 1¾ hours under an argon atmosphere. Adding aluminum (60 g) directly into the starting furnace charge negated previous experiences with high initial bath oxygen levels. Once melted an oxygen and temperature measurement was taken. The target Sn

level in the steel was 0.1% Sn. A metal sample was then taken. At 10-minute intervals pre-fused flux was added to the bath. In total three 500 g additions were made bringing the total slag content up to 1.5 kg. Further aluminum was added in response to a temperature and oxygen measurement that showed the oxygen content of the bath had increased slightly during the formation of the slag layer.

Wire injection was started, the planned injection rate being 5 cms^{-1} . As before there was considerable fume generated, the injection producing numerous ejections of metal droplets and the distinctive red/pink colour. This continued until wire injection was stopped after 3 minutes and 40 seconds at which time a second metal sample was taken. A further metal sample was taken at approximately 4 minutes after injection was stopped to test for Sn reversion.

The second period of wire injection was started. Wire was injected for approximately 4 minutes, bringing the total wire injection time to 7-8 minutes. Metal samples were taken at intervals of approximately 1½, 6, and 10 minutes after injection.

Discussion of Trial 5

Trial 5 was ran at higher than ideal bath temperatures. The consequence of the bath temperatures, in excess of 1700°C , was that the oxygen levels were also high. Even after the first injection period the oxygen content was still above 10 ppm. The second problem encountered in trial 5 was that during the second wire injection period the feeder wheels lost grip and were slipping on the wire. As a result for an unknown time the wire was feeding at a slower rate than 5 cms^{-1} , this would have produced shallower penetration depths for injection.

On cleaning the furnace after the trial it was also found that the Sn had not been added to the melt. This oversight meant that the initial residuals level was very low.

Key data for trial 5:

Wire injection rate:	target 5 cms^{-1}	measured not $>4.5 \text{ cms}^{-1}$
Wire injected:	target 20 m	measured 21.3 m
Injection time:	7-8 mins	

Bath temperature during injection:	1752°C to 1727°C to 1678°C
Oxygen content:	26.5 ppm to 15.3 ppm to 7.6 ppm

INJECTION TRIAL 6

17th April 2000

80.1 lb of steel was melted over 1¾ hours under an argon atmosphere. Aluminum (60 g) was included in the original charge to help kill the steel. Once melted an oxygen and temperature measurement was taken. 20 g of Sn were added to the bath from the hopper. The target Sn level in the steel was 0.05%Sn. A metal sample was then taken. At 10-minute intervals pre-fused flux was added to the bath. In total three 500 g additions were made bringing the total slag content up to 1.5 kg. Further aluminum (20 g) was added in response to a temperature and oxygen measurement that showed the oxygen content of the bath had increased slightly during the formation of the slag layer.

Wire injection was started, the planned injection rate being 5 cms⁻¹. As before there was considerable fume generated, the injection producing numerous ejections of metal droplets and the distinctive red/pink colour. This continued until wire injection was stopped after 3 minutes and 20 seconds at which time a second metal sample was taken.

The second period of wire injection was started. Wire was injected for approximately 3 minutes, bringing the total wire injection time to 6-7 minutes. Metal samples were taken at intervals of approximately 3 and 10 minutes after injection.

Discussion of Trial 6

Trial 6 consumed the last of the calcium steel clad wire supplied by Minteq in 1998. The available wire for this trial was a little shorter than previous trials that had used 20 m. This trial was also different from previous trials because the target Sn level was only 0.05%, compared to trials to date, which were 0.1% (trial 5's mishap excepted).

The only difficulty experienced with trial 6 was that from observations the second period of wire injection did not appear to work. It was assumed that the wire was being deflected away from the bath by frozen slag. The breaker bar was used in an attempt to clear an eye through the slag. After this the wire appeared to inject with its characteristic generation of metal droplet ejections and distinctive colours. Less emphasis was also placed on obtaining metal samples for reversion.

Key data for trial 6:

Wire injection rate:	target 5 cms ⁻¹	measured 4.5 cms ⁻¹
Wire injected:	target 17 m	measured 16.9 m
Injection time:	6-7 mins	
Bath temperature during injection:	1640°C to 1636°C to 1671°C	
Oxygen content:	5.9 ppm to 5.3 ppm to 9.0 ppm	

Notes on Sulphur Trials and Construction of Calcium Containing Wire

In the original research proposal made to the AISI it was suggested that there was potentially an inhibiting influence from S on the removal of Sn using calcium. Trials performed to date had very low S levels (90 ppm). The main focus of the following series of injection trials was to investigate the effect of S on the efficiency of Sn removal from the steel.

In conjunction with the study of the influence of S, trials 7 and 8 also looked at using a different source of calcium for refining. As mentioned previously trials 7 and 8 used calcium wire that was manufactured within the department, rather than commercially available wire. The following section outlines the procedure used to construct the wire.

Calcium Wire Construction Method

Table AII.1 lists the materials required in the construction of the calcium containing wire.

The inside of the steel tube was rinsed with alcohol to remove oil and residue. Calcium metal was mixed 50:50, by weight, with flux under an Ar atmosphere. Typically a 20 ft section of tubing required 240 g of mixed Ca metal + flux.

Table AII-1: Source of consumable materials used in the construction of the calcium wire.

Material	Source	Comments
Steel tube	T&T Liquids, Hamilton	$\frac{3}{8}$ " hydraulic tubing, 0.04" wall thickness
Ca	Alfa Aesar	Granules, +98.8%, -16 Mesh
flux	AlumiCa	Kwikflux 65, -14 Mesh

A procedure was developed that allowed a 20 ft section of tube to be packed in approximately 20 minutes. This required the help of 3 to 4 people. By utilizing the 3 floors of stairwell at the end of the JHE building it was possible to hold the tube in a vertical position. Mixed powders were then fed into the top of the tube while 2 people continuously tapped the side of the tube to aid filling.

The filled tube was then passed through the Fenn Swage machine located at McMaster. Tubes were swaged once, using a single pass, through a 0.215" swage block. A 20 ft section of tube was swaged to approximately 37 ft in about 10-15 minutes. Key points swaging of the tube were that the tube needed constant oil lubrication prior to entering the swage block, that the swaging process required 4 people, and that the tube was very hot after swaging.

To enable the swaged wires to be continuously injected 2 or more sections were joined. The facility workshop staff joined the tube ends by welding. A small pin was used to increase the strength of the joints.

INJECTION TRIAL 7

18th May 2000

81.1 lb of steel was melted over 1 $\frac{3}{4}$ hours under an argon atmosphere. Auminum (60 g) was included in the original charge to help kill the steel. FeS chips (2.96 g) were also added to the

original charge to provide a source of S, the target level being 120 ppm. Once melted an oxygen and temperature measurement was taken. Further aluminum (20 g) was added in response to a temperature and oxygen measurement. 40 g of Sn was added to the bath from the hopper. The target Sn level in the steel was 0.1%Sn. A metal sample was then taken. A single batch of pre-fused flux was added to the bath (250 g) to form the slag layer.

Wire injection was started, the planned injection rate being 5 cms^{-1} . Wire injection was carried out for periods of 2, 2, 2, and 2 mins 06 sec followed by metal sampling. The total wire injection time was 8 minutes and 6 seconds. Further metal samples were then taken at intervals of 5, 10 and 20 minutes after injection.

Discussion of Trial 7

Trial 7 was most notably different from previous trials because the in-house wire reacted less vigorous with the steel bath. Unlike trials with the commercial wire it was possible to view the injection process beyond 1 minute. This could have been due to the decreased Ca load per unit of wire and the thicker steel walls of the wire. Overall the calcium wire made within the department was injected into the bath without problems; the shallow slag layer may have aided this.

Key data for trial 7:

Wire injection rate:	target 5 cms^{-1}	measured 4.3 cms^{-1}
Wire injected:	target 20 m	measured 21.0 m
Injection time:	8 mins 06 sec	
Bath temperature during injection:	1615°C to 1555°C	
Oxygen content:	7.4 ppm to 1.4 ppm	

INJECTION TRIAL 8

28th June 2000

81.7 lb of steel was melted over 1¾ hours under an argon atmosphere. Aluminum (60 g) was included in the original charge to help kill the steel. FeS chips (6.1 g) were added to the melt to provide a source of S, the target level being 150 ppm. 40 g of Sn was added to the bath from the hopper. The target Sn level in the steel was 0.1%Sn. A metal sample was then taken. Further aluminum (20 g) was added in response to a temperature and oxygen measurement together with a single batch of pre-fused flux to the bath (250 g) to form the slag layer.

Wire injection was started, the planned injection rate being 5 cms⁻¹. Wire injection was carried out for periods of 2, 2, 2, 2, 2, and 2 mins 28 sec followed by metal sampling. The total wire injection time was 12 minutes and 28 seconds.

Discussion of Trial 8

Trial 8 consumed 3 sections of the in-house wire. As with trial 7 injection of the in-house wire was problem free. Again the reaction of the wire with the bath was much less vigorous than the commercial wire. Although it was observed that the furnace chamber frequently shook. The shaking was accompanied by a loud noise. This may have been due to explosive uplift of the bath from vaporizing calcium. This was not observed in any of the trials using commercial wire. Due to the number of metal samples taken it was not possible to measure the temperature and oxygen content the bath after injection had finished.

The difference between the reaction behavior of the commercial and in-house wire can be seen on the video recording taken of trials 7 and 8.

On cleaning the furnace after the trial it was also apparent that there was considerably less Ca fume coating the internals of the chamber compared the commercial wire. This was also noted for trial 7.

Key data for trial 8:

Wire injection rate:	target 5 cms ⁻¹	measured 4.2 cms ⁻¹
Wire injected:	target 30.4 m	measured 31.7 m
Injection time:	12 mins 28 sec	
Bath temperature during injection:	1625°C	
Oxygen content:	1.5 ppm	

INJECTION TRIAL 9

22nd August 2000

The aim of injection trial 9 was to compare the efficiency of removing residuals, including S, from the steel using the commercial wire versus the wire made within the department used in trials 7 and 8.

81¾ lb of steel bars was melted over 1¾ hours under an argon atmosphere. Included in the initial crucible load were 2.96 g of FeS and 60 g of Al. Once the molten heel had been produced 40g Sn was added via the hopper. This was followed shortly by an oxygen and temperature measurement. A metal sample was taken prior to the slag addition. Further Al (20 g) was added to the melt together with 250 g of calcium aluminate flux. A second oxygen and temperature measurement were taken; this was followed by another addition of Al (20 g) and another temperature and oxygen measurement to check the bath condition before the start of injection. Wire injection was started, the planned injection rate being 5 cms⁻¹. As in previous trials considerable fume was generated. Wire injection was stopped after 1 minute 52 seconds to allow a metal sample to be taken. This was calculated to be approximately the amount of calcium injected during trial 7. Injection was restarted until 3 minutes and 40 seconds where another metal sample was taken. In an attempt to maintain the slag layer a further 250 g of flux material was added to the crucible. After a few minutes injection was restarted and continued until 7 minutes and 54 seconds. After the wire injection was stopped a metal sample was taken, followed by a temperature and oxygen measurement, and then a final metal sample.

Discussion of Trial 9

Trial 9 was completed without any great difficulty. In particular the bath temperature and oxygen content were relatively constant. The commercial wire from Minteq reacted in the same manner as all previous injections. Wire from this trial was drawn from the second drum of wire delivered in August 2000. The initial stages of the injection were recorded on video and clearly show the difference between the commercial and in-house wire.

Key data for trial 9:

Wire injection rate:	target 5 cms ⁻¹	measured 4.5 cms ⁻¹
Wire injected:	target 20 m	measured 21.4 m
Injection time:	7 mins 54 sec	
Bath temperature during injection:	1618°C to 1614°C	
Oxygen content:	4.7 ppm to 3.2 ppm	

INJECTION TRIAL 10

18th October 2000

The aim of injection trial 10 was to compare the efficiency of removing residuals, including S, from the steel using the commercial wire versus the wire made within the department used in trials 7 and 8.

82 lb of steel was melted over 2 hours under an argon atmosphere. Included in the initial crucible load were 60g of Al. Once the molten heel had been produced 10.9 g of FeS was added by the hopper. After a further 5 minutes 40 g of Sn was added. This was followed shortly by an oxygen and temperature measurement. A further 25 g of Al was added. A metal sample was taken prior to the slag addition. Further Al (20 g) was added to the melt together with 250 g of calcium aluminate flux. A second oxygen and temperature measurement was taken to check the bath condition before the start of injection.

Wire injection was started, the planned injection rate being 5 cms^{-1} . As in previous trials considerable fume was generated. Wire injection was stopped after 1 minute 52 seconds to allow a metal sample to be taken. Injection was restarted until 3 minutes and 40 seconds where another metal sample was taken and again after 5 minutes and 40 seconds. In an attempt to maintain the slag layer a further 250 g of flux material was added to the crucible. After a few minutes injection was restarted and continued until 7 minutes and 5 seconds. After the wire injection was stopped a metal sample was taken, followed by a temperature and oxygen measurement, and then a final metal sample.

Discussion of Trial 10

The injection of wire in trial 10 proceeded without problem. Because the wire in the second drum had been sent in several pieces the length of wire used in trial 10 was 2 m shorter than usual. The main problem with trial 10 was that despite attempts to control bath temperature and oxygen both increased throughout the trial.

The increased amount of FeS added at the start was required because of the steel used for the heel had been desulphurized in a previous trial. The steel originally supplied by Dofasco had been consumed. We therefore used the steel from trial 5 in which the Sn had not been added and had lower starting levels of S than the bulk material supplied by Dofasco.

Key data for trial 10:

Wire injection rate:	target 5 cms^{-1}	measured 4.6 cms^{-1}
Wire injected:	target 18 m	measured 19.6 m
Injection time:	7 mins 5 sec	
Bath temperature during injection:	1594°C to 1627°C to 1653°C	
Oxygen content:	4.7 ppm to 13.2 ppm to 25.4 ppm	

APPENDIX - III

Table AIII-1: Analysis for Slags equilibrated with pure tin at different CO/Ar ratios

slag (10hrs @ 1600C)	CaO	Al ₂ O ₃	SiO ₂	Sn	log Sn	pO ₂	log pO ₂	log a CaO
A -1% CO	49.74	45.90	4.36	0.022	-1.66	5.00E-20	-19.30	-0.69
B-1%CO	56.60	37.21	6.19	0.027	-1.58	5.00E-20	-19.30	-0.42
C -1%CO	40.92	56.01	3.06	0.066	-1.16	5.00E-20	-19.30	-1.05
D -1%CO	51.89	37.20	10.91	0.034	-1.47	5.00E-20	-19.30	-0.76
E -1%CO	55.25	43.01	1.74	0.079	-1.10	5.00E-20	-19.30	-0.37
A - 5%CO	51.25	44.39	4.37	0.023	-1.64	8.37E-19	-18.08	-0.63
B - 5%CO	56.78	36.90	6.33	0.038	-1.42	8.37E-19	-18.08	-0.42
C 5%CO	45.73	51.13	3.14	0.038	-1.42	8.37E-19	-18.08	-0.84
D - 5%CO	57.63	30.74	11.62	0.058	-1.23	8.37E-19	-18.08	-0.51
E - 5%CO	55.46	42.61	1.92	0.106	-0.98	8.37E-19	-18.08	-0.36
A - 10%CO	51.44	44.39	4.17	0.350	-0.46	2.88E-18	-17.54	-0.61
B - 10%CO	56.93	37.03	6.04	0.20	-0.69	2.88E-18	-17.54	-0.40
C - 10%CO	45.03	51.90	3.07	0.058	-1.24	2.88E-18	-17.54	-0.87
D - 10%CO	57.27	30.79	11.94	0.146	-0.84	2.88E-18	-17.54	-0.53
E - 10%CO	56.74	41.50	1.77	0.604	-0.22	2.88E-18	-17.54	-0.30
A - 10%CO	51.48	44.25	4.27	0.340	-0.47	4.67E-18	-17.33	-0.61
B - 10%CO	57.15	36.96	5.90	0.113	-0.95	4.67E-18	-17.33	-0.39
C - 10%CO	45.04	51.96	3.00	0.202	-0.69	4.67E-18	-17.33	-0.87
D - 10%CO	59.25	29.58	11.17	0.339	-0.47	4.67E-18	-17.33	-0.42
E - 10%CO	56.53	41.64	1.83	0.985	-0.006	4.67E-18	-17.33	-0.31
C - 50%CO	44.29	52.56	3.15	0.091	-1.04	1.01E-16	-15.99	-0.91
A - 100%CO	52.88	43.07	4.05	0.198	-0.70	4.42E-16	-15.35	-0.54
B - 100%CO	59.67	34.40	5.93	0.163	-0.79	4.42E-16	-15.35	-0.26
A20%CO	51.96	43.98	4.07	0.173	-0.76	1.71E-17	-16.77	-0.59

Table AIII-1 shows how the tin solubility of a range of ladle slags varies with oxygen partial pressure. The oxygen partial pressure was controlled in these experiments by equilibrating an argon/carbon-monoxide gas mixture with graphite. In Table AIII-2 the effect of temperature at a constant CO/Ar ratio is examined for two typical ladle slag compositions. In this table the slag optical basicity is also presented, along with the calculated calcium activity based on equilibrium with CaO and with CaC₂. The calculated Ca₂Sn activity is based on the smaller of the two calcium activities. The liquid fraction of the slag is also included in this table.

APPENDIX - III

Table AIII-2: Analysis of Slags Equilibrated with Pure Tin as a Function of Temperature, Including Estimated Liquid Fraction and Calcium Activity in Equilibrium with CaO and CaC₂

slag	Temp (C)	Liquidity	CaO (wt%)	Al ₂ O ₃ (wt%)	SiO ₂ (wt%)	Sn (wt%)	X _{Sn}	opt. bas.	a _{CaO}	a _{Ca}	From CaO			From CaC ₂		
											log a _{Ca}	log a _{Ca}	log a _{Ca}	log a _{Ca}	log a _{Ca}	
E	1400	1	59	41	0	0.132	0.00076	0.789	0.728	0.00030	-3.519	0.000557	-3.254	0.00030	0.746	975
E	1450	1	59	41	0	0.095	0.00055	0.789	0.728	0.00088	-3.053	0.000632	-3.199	0.000632	1.553	2823
E	1475	1	59	41	0	1.04	0.00399	0.789	0.728	0.00148	-2.831	0.000671	-3.173	0.000671	1.230	205
E	1500	1	59	41	0	0.243	0.00141	0.789	0.728	0.00243	-2.615	0.000728	-3.138	0.000728	1.027	730
E	1550	1	59	41	0	0.50	0.00289	0.789	0.728	0.00632	-2.199	0.000796	-3.090	0.000796	0.635	219
E	1600	1	59	41	0	0.0998	0.00058	0.789	0.728	0.01560	-1.806	0.000885	-3.053	0.00089	0.421	728
F	1350	1	50	43.6	6.4	0.147	0.00087	0.741	0.185	2.46E-05	-4.609	0.000488	-3.312	0.000025	0.011	12.5
F	1375	1	50	43.6	6.4	0.117	0.00069	0.741	0.185	4.39E-05	-4.358	0.000557	-3.254	0.000044	0.023	33.3
F	1400	1	50	43.6	6.4	0.094	0.00056	0.741	0.185	0.00008	-4.115	0.000557	-3.254	0.000077	0.048	86.5
F	1425	1	50	43.6	6.4	0.111	0.00066	0.741	0.185	0.00013	-3.878	0.000594	-3.226	0.000132	0.098	149.3
F	1450	1	50	43.6	6.4	0.199	0.00117	0.741	0.185	0.00022	-3.649	0.000632	-3.199	0.000224	0.196	166.5
F	1475	1	50	43.6	6.4	0.094	0.00056	0.741	0.185	0.00038	-3.427	0.000671	-3.173	0.000375	0.382	689.7
F	1500	1	50	43.6	6.4	0.094	0.00056	0.741	0.185	0.00062	-3.210	0.000728	-3.137	0.000616	0.736	1325.3
F	1550	1	50	43.6	6.4	0.141	0.00083	0.741	0.185	0.00160	-2.795	0.000796	-3.099	0.000796	0.635	763

Table AIII-3 shows the effect of both temperature and slag silica content on tin solubility. It is assumed that only the liquid portion of the slag is available to dissolve tin. Therefore, the calculated mole fractions are based on the liquid fraction and the optical basicity and CaO activities are based on the composition of the liquid fraction. This data shows that silica has a significant effect on the tin solubility. However, when the activity coefficient for Ca₂Sn is examined there is not a large effect of silica and if anything the solubility increases with silica content. It appears that the major effect of silica is on the activity of calcium.

APPENDIX - III

Table AIII-3: Analysis of Slags Equilibrated with Pure Tin as a Function of Temperature and SiO_2 Content

slag	temp (C)	liquidity	CaO (wt%)	Al ₂ O ₃ (wt%)	SiO ₂ (wt%)	Sn (wt%)	X_{Sn}	opt. bas.	a _{CaO}	a _{Ca}	from CaO		from CaC_2	
											from CaC_2	from CaC_2	a _{Ca2Sn}	gamma Ca_2Sn
C	1350	0.5	51	46	3	0.232	0.0028	0.75	0.249	0.00033	0.00049	0.00033	0.01966	7.10
C	1450	0.73	51	46	3	2.433	0.0195	0.75	0.249	0.000302	0.00063	0.000302	0.355578	18.22
C	1475	1	51	46	3	0.056	0.0003	0.75	0.249	0.000505	0.00067	0.000505	0.69675	2094.43
C	1550	1	51	46	3	0.013	0.0001	0.75	0.249	0.002162	0.00080	0.000796	0.63538	8244.70
C	1600	1	51	46	3	0.100	0.0006	0.75	0.249	0.005341	0.00089	0.000885	0.42117	706.77
E	1350	0	59	41	0	0.236	1.0000	0.00	0.000	0.000000	0.000000	0.000000	0.000000	0.00
E	1425	1	59	41	0	0.247	0.0014	0.79	0.728	0.000521	0.00059	0.000521	1.52079	1065.69
E	1487	1	59	41	0	3.386	0.0192	0.79	0.728	0.001878	0.00069	0.000691	1.10278	57.30
G	1475	1	50	50	0	0.192	0.0012	0.75	0.266	0.000540	0.00067	0.000540	0.79551	681.33
G	1500	1	50	50	0	0.776	0.0047	0.75	0.266	0.000888	0.00073	0.000728	1.02705	218.08
G	1550	1	50	50	0	0.040	0.0002	0.75	0.266	0.002310	0.00080	0.000796	0.63538	2618.66
G	1600	1	50	50	0	0.911	0.0055	0.75	0.266	0.005707	0.00089	0.000885	0.42117	76.25
H	1475	1	47.5	47.5	5	0.438	0.0026	0.74	0.154	0.000313	0.00067	0.000313	0.26773	101.47
H	1500	1	47.5	47.5	5	0.398	0.0024	0.74	0.154	0.000515	0.00073	0.000515	0.51447	214.56
H	1550	1	47.5	47.5	5	0.059	0.0004	0.74	0.154	0.001340	0.00080	0.000796	0.63538	1787.78
H	1600	1	47.5	47.5	5	0.732	0.0044	0.74	0.154	0.003311	0.00089	0.000885	0.42117	95.75
I	1475	1	45	45	10	0.026	0.0002	0.72	0.092	0.000186	0.00067	0.000186	0.09404	600.79
I	1500	1	45	45	10	0.532	0.0032	0.72	0.092	0.000305	0.00073	0.000305	0.18072	57.01
I	1550	1	45	45	10	1.057	0.0063	0.72	0.092	0.000794	0.00080	0.000794	0.63240	100.76
I	1600	1	45	45	10	1.405	0.0083	0.72	0.092	0.001962	0.00089	0.000885	0.42117	50.59
J	1475	1	32.5	32.5	35	0.056	0.0003	0.64	0.009	0.000018	0.00067	0.000018	0.00088	2.75
J	1500	1	32.5	32.5	35	0.008	0.0000	0.64	0.009	0.000030	0.00073	0.000030	0.00169	36.31
J	1550	1	32.5	32.5	35	0.143	0.0008	0.64	0.009	0.000077	0.00080	0.000077	0.00593	7.30
J	1600	1	32.5	32.5	35	0.475	0.0027	0.64	0.009	0.000190	0.00089	0.000190	0.01941	7.20
K	1500	1	17.5	17.5	65	0.136	0.0007	0.56	0.001	0.000003	0.00073	0.000003	0.00002	0.02
K	1550	1	17.5	17.5	65	0.232	0.0012	0.56	0.001	0.000008	0.00080	0.000008	0.000006	0.05
K	1600	1	17.5	17.5	65	0.190	0.0010	0.56	0.001	0.000019	0.00089	0.000019	0.000019	0.19