METAL PENETRATION IN SAND MOLDS FOR STEEL
CASTINGS

Annual Report

RECEIVED
MAY 21 1996
OSTI

J. O. Barlow, D. M. Stefanescu, A. M. Lane, W. C. Schreiber,
M. Owens, and T. S. Piwonka

April 1996

Work Performed Under Contract DE-FC07-94ID13324

For
U. S. Department of Energy
Assistant Secretary for
Energy Efficiency and Renewable Energy
Washington, D.C.

Prepared By
The University of Alabama

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (423) 576-8401.

Available to the public from the U.S. Department of Commerce, Technology Administration, National Technical Information Services, Springfield, VA 22161, (703) 487-4650.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

METAL PENETRATION IN SAND MOLDS FOR STEEL CASTINGS

Annual Report for the Period
September 1994 to September 1995

By

J.O. Barlow, D.M. Stefanescu, A.M. Lane, W.C. Schreiber, M. Owens, and T.S. Piwonka

April 1996

Work Performed Under Contract No. DE-FC07-94ID13324

Prepared for the

U.S. Department of Energy
Under DOE Idaho Operations Office
Sponsored by the Office of the Assistant Secretary
for Energy Efficiency and Renewable Energy
Office of Industrial Technologies
Washington, D.C.

Prepared by
The University of Alabama
Tuscaloosa, Alabama 35487-0200

1 20-40

10-07
Hank

Executive Summary

Progress during the First Year

1. Case studies of samples of penetration provided by consortium members showed examples of what were clearly mechanical-type penetration defects, and examples of what appeared to be chemical penetration.
2. Sessile drop experiments on a variety of mold substrate materials using carbon, stainless, and manganese steels showed that manganese steel wets silica strongly, indicating that silica is not a suitable mold material for this family of alloys. Contact angles were lower for steels than for cast irons. Magnesite appeared to be the best overall mold material, although zircon flour also performed well.
3. A simplified one-dimensional model has been developed which predicts the diffusion rates which could cause chemical penetration has been developed. It shows that, contrary to the case of cast iron, chemical penetration is a possibility in medium and low carbon steels, as diffusion of carbon to the casting surface may not always occur quickly enough to protect the surface from an oxidizing reaction.
4. Modifications have been made to the mass spectrometer gas chromatograph train to allow accurate determination of the water content of gas at the mold/metal interface. Initial gas measurements indicated that the gas generated at the interface in steel castings is 80% hydrogen-20% carbon monoxide, instead of the 50% hydrogen-50% carbon monoxide mixture found in cast iron.

Table of Contents

1. Introduction	3
2. Case Study Of Steel Penetration In Sand Molds	4
3. Sessile Drop Experiments	10
4. Simplified Model To Predict Chemical Reaction At The Interface	14
5. Atmosphere At The Mold/Metal Interface	23
6. Conclusions And Future Work	24
7. Referneces	25
8. Appendix: Modifications To The GC And The MS	26

1. Introduction

Following the completion of work to determine the causes of penetration in cast iron (funded jointly by the American Foundrymen's Society, a consortium of foundries and foundry suppliers, and the Department of Energy under Cooperative Agreements DE-FC07-92ID13163 and DE-FC07-93ID13232) the Mold/Metal Interface Committee of the American Foundrymen's Society recommended that the work be extended to cover steel castings. Estimates of the cost of penetration defects indicate that it costs ferrous foundries \$60,000,000 annually. A consortium of steel foundries and suppliers was formed to contribute funds, program guidance, and casting defect examples, and additional funds are being supplied by the Department of Energy. This report describes activities carried out during the first year's technical effort on the program.

Past work to determine the cause of penetration in ferrous castings has identified two major causes of the defect: mechanical and chemical penetration.¹ Most of the work which has been reported has examined penetration in steel castings, and it has been assumed that causes of penetration in steel and causes of penetration in cast iron were the same. However, an extensive research project into the causes of penetration in cast iron² revealed that penetration in cast iron is *always* caused by mechanical means. Chemical penetration, which has been shown to occur when the surface of the casting becomes oxidized and the iron oxide formed reacts with silica to form fayalite, a low-melting point compound, cannot occur in cast iron, because the iron contains so much carbon that there is always carbon present to react preferentially with any oxygen which may approach the mold surface (oxygen would be present in the air or in the moisture used to bond green sand molds).

However, because steel castings contain less carbon than iron castings, it is logical to assume that some penetration may be caused by chemical means. In addition, a variety of alloys used to make steel castings, including stainless and manganese steels. These highly alloyed materials may have quite different surface properties than cast iron, which would make penetration more likely.

The objectives of this program are to extend the findings of the work on penetration in cast iron to steel castings, and to

1. Determine the conditions when chemical penetration can be expected in steel castings;
2. Determine the conditions when mechanical penetration can be expected in steel castings;
3. Develop a quantitative model of penetration in steel castings which can be used to predict the probability of a given alloy, pouring conditions, and mold composition leading to penetration.

2. Case Study of Steel Penetration in Sand Molds

2.1. Introduction

As an initial stage of determining the causes of penetration in steel castings, samples of penetration were submitted by the industrial sponsors. The pouring conditions, compositions, and mold and core characteristics were recorded. Metallographic specimens of the penetration samples were prepared, and both optical and SEM analysis of the samples were performed.

2.2. Materials Studied

Table 2-1 shows the casting description and pouring conditions for the industrial samples of penetration supplied by the sponsors. Table 2-2 lists the chemical compositions of the penetration samples. Samples 4, 6, 7, and 13 are stainless steels, and the remaining samples are low alloy steels. Table 2-3 lists the mold and core conditions for the penetration samples.

Table 2-1. Casting description and pouring conditions for case study of steel penetration.

No.	Casting description	Casting weight (lb)	Metallostatic head* (in.)	Defect frequency (%)	Pouring ladle	Pouring temp. (°F)
1	Rectangular box w/ cores	800	N/A	N/A	3000 lb. Bottom pour, 1.5" nozzle	N/A
2	Ring	2900	N/A	N/A	8000 lb.	N/A
3	Valve wafer body	2270	N/A	N/A	Bottom pour, 2" nozzle	N/A
4	Bonnet	N/A	14 - 36	>50	Bottom pour, 1.5" nozzle	2800-2810
5	N/A	N/A	43	100	Bottom pour, 1.5" nozzle	2840-2880
6	Blade ring	12500	43	100	N/A	2820
7	Ring	N/A	5 - 7	40	1000 lb. teapot	2825
8	N/A	N/A	12	First time	9000 lb. bottom pour with 2" nozzle	2800
9	N/A	87	N/A	N/A	N/A	2925
10	N/A	193	N/A	N/A	N/A	2825
11	N/A	140	N/A	N/A	N/A	2875
12	N/A	203	N/A	N/A	N/A	2925
13	Ring	N/A	20	2	N/A	2800

*Density of the metal can be approximated as 7000 kg/m³ to give 1 in. metallostatic head equals 0.25 psi, or an actual density of the material may be used. To reference the metallostatic head to another material use:

$$h_{ref} = h_{met} \frac{\rho_{met}}{\rho_{ref}} \quad (2.1)$$

where, h_{ref} is the height of the reference material in in., h_{met} is the metallostatic head in. in., ρ_{met} is the density of the metal (approximately 7000 kg/m³), and ρ_{ref} is the density of the reference material in kg/m³.

Table 2-2. Chemical analysis of castings for case study of steel penetration.

No.	C	Mn	Si	Cr	Ni	S	P	Al	Other
1*	0.26	0.82	0.42	0.07	0.03	N/A	N/A	0.051	Ti 0.003
2	0.18 max	0.4-0.7	0.6 max	2.0- 2.75	0.5 max	0.045 max	0.04 max	N/A	0.9-1.2 Mo, 0.5 max Cu, 0.1 W max
3	0.3 max	1.0 max	0.6 max	0.5 max	0.5 max	N/A	N/A	N/A	0.3 Cu max, 0.2 max Mo, 0.03 V max, resid. ≤ 1.0
4	0.08 max	1.5 max	2.0 max	18-21	9-12	0.04 max	0.04 max	N/A	2-3 Mo
5*	0.25	1.28	0.47	0.12	0.06	0.031	0.025	0.026	0.02 Mo, 0.1 Cu, 0.0003 B, 0.007 Sn, 0.002 Ti, 0.01 V, 0.012 Zr, 0.002 Ce, 0.003 Mg
6	0.06 max	1.0 max	1.0 max	11.5-14	3.5-4.5	0.04 max	0.04 max	N/A	0.4-1 Mo
7	0.08 max	1.5 max	2.0 max	18-21	9-12	0.04 max	0.04 max	N/A	2-3 Mo
8	0.20 max	0.5-0.8	0.6 max	1.0-1.5	0.5 max	0.045 max	0.04 max	N/A	0.45-0.65 Mo, 0.5 max Cu, 0.1 max W, resid. ≤ 1.0
9*	0.28	1.6	0.5	0.2	0.2	N/A	N/A	N/A	0.10 Mo
10*	0.25	0.80	0.50	0.60	0.654	N/A	N/A	N/A	0.20 Mo
11*	0.30	0.80	0.50	0.60	0.65	N/A	N/A	N/A	0.20 Mo
12*	0.22	1.1	0.5	0.2	0.2	N/A	N/A	N/A	0.10 Mo
13	0.08 max	1.5 max	2.0 max	18-21	9-12	0.04 max	0.04 max	N/A	2-3 Mo

* spectral analysis

Table 2-3. Mold and core characteristics for case study of steel penetration

No.	Mold			Core		
	sand	coating	binder	sand	coating	binder
1	60 GFN NJ Silica	Sprayed alcohol/zircon	1.5% Pep-Set	60 GFN NJ Silica	Brushed alcohol/zircon	1.5% Pep-Set
2	Silica	N/A	N/A	Silica	N/A	N/A
3	Silica	N/A	N/A	Silica	N/A	N/A
4	60% reclaim/40% new silica or 50% zircon/50% new silica	Sprayed alcohol/zircon	1.5% Pep-Set or 0.9% Pep-Set	60% reclaim/40% new silica or 50% zircon/50% new silica	Brushed alcohol/zircon	1.5% Pep-Set or 0.9% Pep-Set
5	55-58 GFN W&D silica & 3% black Fe oxide (magnetite)	1st coat: brushed alcohol/zircon; 2nd coat: sprayed alcohol/zircon	1.1% Phenolic Urethane No-Bake (60:40) and 3.5% catalyst	N/A	N/A	N/A
6	N/A	N/A	N/A	zircon	none	Baked for 1 hr
7	60 GFN Reclaimed	Sprayed Alcohol mold wash	No Bake	N/A	N/A	N/A
8	60 GFN Silica 60% Reclaim 40% new	Alcohol Zircon (Brushed)	Pep-Set	N/A	N/A	N/A
9	70 GFN Silica, 4% Iron Oxide (2% reg., 2% Sperox), 2.5% Kiln Clay	Vinsel, wax, low hexa	4.5% Resin (Shell)	N/A	N/A	N/A
10	70 GFN Silica, 4% Iron Oxide (2% reg., 2% Sperox), 2.5% Kiln Clay	Vinsel, wax, low hexa	4.5% Resin (Shell)	N/A	N/A	N/A
11	70 GFN Silica, 4% Iron Oxide (2% reg., 2% Sperox), 2.5% Kiln Clay	Vinsel, wax, low hexa	4.5% Resin (Shell)	N/A	N/A	N/A
12	53 GFN Lake Sand	N/A	1% Furan 941, 25-30% catalyst (binder (Sulfonic Acid))	N/A	N/A	N/A
13	60 GFN: 60% Reclaimed, 40% New Silica	Sprayed Alcohol/Zircon	1.5% Pepset	60 GFN: 60% Reclaimed, 40% New Silica	Brushed Alcohol/Zircon	1.5% Pepset

Table 2-4. SEM analysis for case study of steel penetration

No.	Measurement position		Dist. from metal/sand interface (μm)	Composition, wt%		
	No.	Description		Si	Cr	Mn
1	-	bulk analysis	-	0.6	0	1.31
	1	matrix	high	0.22-0.27	0	1.59
	1	matrix	5	1.98	0.33	1.75
	1	matrix	3	3.91	0.37	1.55
	1	matrix	1	11.46	0	2.28
	2	oxidized matrix	-	0.56-0.59	0.39	1.03
	3	sand/matrix interf.	-	8.44-12.18	0-0.33	3.46
2	1	matrix	-	0.63-1.21	2.68-2.73	0
	2	oxidized matrix	-	0.76-0.8	1.49-4.14	2.43
	3	sand/matrix interf.	-	14.32-15.51	0	2.46-3.1
3	-	bulk analysis	-	0.53	0	0.87
	1	matrix	-	0.75	0	0.48
	2	oxidized matrix	-	0.17	0	1.46
	3	sand/matrix interf.	-	19.14	0	3.54
4*	-	bulk analysis	-	1.12-1.67	23.7-25.12	1.99-2.1
	1	matrix	high	1.59-1.66	20.9-24.14	1.7-1.98
	1	matrix	5	1.95	21.3	2.67
	1	matrix	3	1.22-3.2	22.4-22.06	1.68-4.2
	1	matrix	1	1.59-7.12	21.2-21.7	1.49-1.5
5	-	bulk analysis	-	0.53	0.45	1.29
	1	matrix	high	0.55	0	1.0
	1	matrix	5	0.54	0	1.56
	1	matrix	3	0.51	0	1.11
	1	matrix	1	1.25	0	1.78
6	1	matrix	high	0.54	11.57	1.52
	1	matrix	3	1.97	14.01	0
	1	matrix	1	4.08	24.82	0

* average of two samples

2.3. Results and Discussion

Table 2-4 displays the average compositions determined from the energy-dispersive x-ray spectrometry performed on the SEM.

2.3.1. Low alloy steels

The low alloy samples 1, 2 and 3 displayed an oxidized region (region 2) where the compositions did not vary significantly from the unoxidized matrix (region 1) as shown in Table 2-4, Fig. 2-1, and Fig. 2-5 (a) (Energy-dispersive x-ray spectrometry (EDS) on the SEM cannot detect the presence of oxygen.). Samples 1, 2, and 3 also displayed a region at the interface (region 3) which is rich in silica (Table 2-4 and Fig. 2-1 and Fig. 2-5 (a)). This layer is most probably fayalite. This indicates chemical penetration in the samples.

a) 25X

b) 400X

Fig. 2-1. Optical microstructures of chemical penetration region, sample 2, low alloy steel.

The other low alloy steels displayed no oxidized region. This would indicate that some type of mechanical penetration occurred. For sample 10 this can be attributed to a coating failure (Fig. 2-3). The metal outside of the coating appears the same as that on the interior of the casting as shown in Fig. 2-3. This indicates that the metal penetrates the coating but not

Fig. 2-2. Optical microstructure of low alloy steel where no chemical penetration is present (Sample 8, 100x).

Fig. 2-3. Optical microstructure showing a coating failure (Sample 10, 25x).

Fig. 2-4. Optical microstructure of penetration region, sample 4, stainless steel. 25X

Fig. 2-4 and Fig. 2-5 (b). This indicates mechanical penetration in the stainless steel samples. Sample 7 also penetrated due to a coating failure as in sample 10 (Fig. 2-3).

2.4. Conclusions

An oxidized region was found in three of the low alloy steel samples.

One type of mechanical penetration appeared to be a coating failure, where the metal penetrates the coating but not the mold.

Chemical penetration did not occur in any of the stainless steel samples.

the mold.

The oxidized regions generally occur in heavier castings (Table 2-1). This can be attributed to longer solidification times for the heavier castings so that the metal has significant time to react with the refractory and/or decarburize the steel.

2.3.2. Stainless steels

The stainless steel samples did not display the oxidized region or the layer at the interface, as shown in Table 2-4 and

a) sample 2, low alloy steel

b) sample 4, stainless steel

Fig. 2-5. SEM picture of penetration regions.

3. Sessile Drop Experiments

3.1. Experimental Method

The experimental method used is similar to that used by Stefanescu et al^{1,2} for determining the contact angles for cast iron, except that samples were submitted by the industrial sponsors. The samples were turned on a lathe to a diameter of 5 mm.

3.2. Materials Tested

A number of sessile drop experiments involving steel of various composition and different refractory substrates were performed. The substrates used were monolithic quartz, zircon (sand and flour), magnesite, and olivine. The steel samples included carbon steel, high manganese steel, and stainless steel.

The compositions of the steel samples are shown in Table 3-1. The substrates and the average particle diameters are given in Table 3-2. All of the sessile drop experiments were performed with a superheat of 150 °C and in an argon atmosphere.

Table 3-1. Compositions steel of samples used for sessile drop experiments.

Sample†	Composition*													
	C	Si	Mn	P	S	Cr	Al	V	Ni	Sn	Mo	Cu	Ti	Other
76 Plain C-2	0.76	0.57	0.72	0.023	0.017	0.08	0.04	0.003	0.03	0.003	0.006	0.050	0.002	
76 Plain C-4	0.76	0.63	0.73	0.023	0.016	0.08	0.05	0.003	0.03	0.002	0.005	0.050	0.002	0.001 B
High Mn	1.08	0.78	13.23	0.340		0.31	0.26							
Stainless Steel	0.08 max	2.0 max	1.5 max	0.04 max	0.04 max	18 - 21			9 - 12		2 - 3			
0.1 Plain C	0.10	0.40	0.46	0.018	0.011	0.06	0.04	0.003	0.03		0.004	0.029	0.004	0.001 Zr
0.27 Plain C-2	0.27	0.38	0.77	0.015	0.021	0.14	0.07	0.001	0.06	0.006	0.030	0.080	0.004	

* Balance Fe

† Sample-# indicates more than one sample of this type was received.

Table 3-2. Substrates used in sessile drop experiments.

	Monolithic Quartz	Zircon Flour	Zircon Sand	Magnesite Flour	Olivine Sand	Chromite Sand
Average Particle Diameter (µm)	-	18.9	133	14.6	292	272
GFN*	-	-	115	-	52	56

*American Foundrymen's Society Grain Fineness Number (Ref. 3).

3.3. Results and Discussion

The measured contact angles for the various experiments performed are given in Table 3-3. Two numbers indicate that the experiments were repeated. Generally the

contact angles of the carbon steels were the highest, followed by stainless steel and high manganese steel, respectively.

Table 3-3. Array of experiments for sessile drop experiments.

Substrate	Alloy				
	A	B	C	D	E
1	100, 101	99, 100	102, 104	18, 16	83, 90
2	113, 112	109, 106	108, 115	96	109
3	103, 100	106, 103	105, 110	87	85
4	-	-	121	109	104
5	-	-	substrate melted	81	substrate melted
6	-	-	79	46	80

Fig. 3-1. Sessile drop for a steel showing non-wetting behavior.

3.3.1. Influence of type of steel and substrate

As one can see in Table 3-3 most experiments result in a non-wetting contact angle. However, steels D and E display a wetting behavior on a number of substrates. The sample shown in Fig. 3-1, exhibited an average contact angle of approximately 100° . This angle is slightly non-wetting, which implies that this alloy may be susceptible to mechanical penetration.

Another steel sample, shown in Fig. 3-2, had an average contact angle of 83° . This is slightly wetting which implies that this alloy would be susceptible to chemical penetration; however, this is just slightly below the distinction between chemical and mechanical penetration, and the reaction zone would not be very noticeable in a sample. This value is slightly less than that of 90° obtained for a previous experiment; however, this is a different sample of same alloy, and spectral analysis was not supplied with the samples. The value of 90° was obtained from a sample taken from penetration sample 4. At 90° this is right on the division between mechanical and chemical penetration, and little, if any, reaction zone would be shown which agrees with the penetration samples submitted by industrial sponsors.

Fig. 3-2. Sessile drop for another steel showing slightly wetting behavior.

Fig. 3-4. Sessile drop for a third steel exhibiting extremely wetting behavior.

One steel, shown in Fig. 3-3, had an average contact angle of 18° . This is an extremely wetting alloy on the substrate. The angle became wetting immediately after melting (at approximately 1 minute after melting the contact angle was 51°). Penetration will certainly occur when pouring this alloy into molds with no coating

Fig. 3-4. Contact angle as a function of time for the five steels on a substrate.

Fig. 3-5. Variation of contact angle with substrate three steels.

Fig. 3-6. Variation of contact angle with grain diameter for zircon sand.

All contact angles decreased with time, as shown in Fig 3-4, for all steels on substrate A. This indicates that the alloys are dissolving the substrate. This trend is also reflected for the other substrates tested. The decrease in contact angle suggests that the alloys are more susceptible to penetration in castings which have a long solidification time.

From all the substrates tested it is apparent that the highest contact angle is given by D, followed by C, as shown in Fig. 3-5. This makes substrate D the most effective substrate for the prevention of penetration of any substrate tested. The higher contact angle of C and D as compared to A demonstrates that it is advantageous to use C and D in areas where penetration is a concern.

The contact angles for monolithic substrates are given in Fig. 3-6 and Table 3-4. Fine and coarse substrates are needed to determine the contact angle for a particulate substrate.²

Table 3-4. Contact angle for steels on monolithic substrates.

Steel/Refractory	Carbon steel	Stainless steel	Manganese steel
Silica	101	83	17
Zircon	111	113	98

3.3.2. Influence of carbon content in carbon steel

The contact angles for the plain carbon steels do not vary significantly with carbon content as can be seen in Fig. 3-7.

3.4. Conclusions

The contact angle for the carbon steels do not vary significantly with carbon content.

Fig. 3-9. Influence of carbon content in plain carbon steel on the contact angle on quartz and zircon sand substrates.

4. Simplified Model to Predict Chemical Reaction at the Interface

Penetration can exist as a result of mechanical forces, such as metallostatic head, which force the liquid metal into the sand at the interface, or as a result of oxidation of the iron at the interface. To gain a fundamental understanding of whether it is possible to have conditions in the mold which encourage the formation of iron oxide at the interface, a simple one-dimensional model of reactions at the interface was developed. The model had two parts. The first estimated the amount of oxygen which was generated at the mold/metal interface by the dissociation of water present as moisture in the mold. The second estimated the ability of carbon to diffuse to the interface to react preferentially with carbon instead of iron, as long as there is sufficient carbon at the interface, no chemical penetration can occur.

4.1. *Oxygen Generation from Water Vapor in the Mold*

4.1.1. Introduction

When molten metal is pouring into a green sand mold, moisture in the sand is vaporized. The water vapor reacts with the carbon dissolved in the metal to form carbon monoxide and molecular hydrogen. This reaction proceeds at a rapid rate until the sand is dried at the interface. After this period, moisture continues to be drawn to the interface at a slower rate, because of diffusion and capillary forces, and the reaction will continue at a reduced rate. However, as carbon monoxide and hydrogen are generated at the interface, they move away from the interface, impeding the transport of water vapor to the interface. The problem, then is to calculate the net flux of water vapor to the interface.

To solve this problem, a computer program developed by Preuss⁴ to simulate heat transfer and fluid flow of two phase water and gas in a porous medium was modified by including the effect of a chemical reaction at the interface.

4.1.2. Computational details

The assumptions made were:

1. The rate constant for the reaction is infinite (any water vapor which reaches the interface is immediately converted to gas at the rate of two moles of gas (one of CO and one of H₂) for each mole of water vapor.)
2. The reaction is limited by the amount of water vapor which reaches the interface. (For this part of the model it is assumed that there is sufficient carbon in steel to react with the water. Later, this assumption will be relaxed, and we will calculate the ability of carbon to diffuse to the surface to react with the vapor.)
3. The reaction

is the only one to occur at the interface.

4. The surface is at a constant temperature of 1400° C.
5. Only flow at right angles to the interface is considered (i.e., the model is one-dimensional).

The simulation was run using the following parameters:

sand density, 2600 kg/m³
 sand porosity, 0.38
 sand permeability, 1.0×10^{-12} Darcy
 sand heat conductivity (fully saturated), 1.13 W/(m·°C)
 sand specific heat, 700 J/(kg·°C)

Initial conditions were a mold temperature of 20 °C, pressure of 1 atmosphere, and liquid saturation in the sand of 0.132 cubic meters of water vapor per cubic meter of void volume. At the interface, the temperature is 1400 °C, and the steel is impermeable.

Relative permeability was modeled using the functions of Fatt and Klikoff⁵ and capillary pressure function (which draws liquid water to the dry region of the mold) was modeled using Leverett's function.⁶

4.1.3. Results and discussion

Results of the calculations showed that at a very short time after pouring (10^{-7} seconds), water vapor rises (actually spikes) to the extremely high value of 1700 kg/(m²·s). As the vapor is taken up at the interface, more vapor is pulled to the interface to replace it. The flux of vapor rapidly reaches its peak value of 1.7×10^{-4} kg/(m²·s). After the spike, the vigorous vaporization of the water blows the water vapor away from the interface until an equilibrium is reached. The maximum flux is 0.009 kg/(m²·s), which occurs 0.05 seconds after pouring. From there the flux of water vapor falls to 0.003 kg/(m²·s), and at approximately 0.32 s the flux drops to 0.0018 kg/(m²·s). This is the steady state value that continues until the a solidified skin forms on the casting. These values are used in the model of carbon diffusion to the interface for the reaction.

Water vapor is driven away from the interface as the temperature of the sand rises. As the water vapor reaches cooler portions of the sand farther away from the interface, it condenses and saturates the sand (the "mud layer"). In this simulation, the mud layer was calculated to form 0.015 mm from the interface after 0.01 second. As the sand continues to heat, the mud layer is driven farther from the interface. This model correctly predicts the formation and movement of the mud layer.

4.2. Carbon Diffusion to the Interface

4.2.1. Introduction

A decarburized zone has been observed on the metal/core interface of interior cores of gray iron castings, as shown in Fig. 4-1. A drawing of the casting on which this decarburized zone is observed is presented in Fig. 4-2. As the carbon is depleted in the exterior layers of the casting, oxidation of iron will occur. This could lead to chemical penetration through the formation of fayalite.

The problem is to calculate the diffusion of carbon through a solidifying layer of cast iron or steel into the core region in order to predict the occurrence of this decarburized zone. This will be accomplished by a 1-D finite difference model in rectangular coordinates. This assumes symmetry around the core.

Fig. 4-1 Photomicrograph of the decarburized zone around the core of a gray iron casting (100X).

Fig. 4-2 Schematic of casting on which the decarburized zone was observed.

4.2.2. Computational details

The governing equations for heat transfer and diffusivity are both partial differential equations (PDE). The PDE for heat transfer is:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2} + \frac{\Delta H_f}{C_p} \frac{\partial f_s}{\partial t} \quad (4.1)$$

where, T is the temperature in $^{\circ}\text{C}$, t is the time in seconds, α is the thermal diffusivity in m^2/s , x is the distance in m , ΔH_f is the heat of fusion in J/kg , C_p is the specific heat in $\text{J/kg}\cdot\text{K}$, and f_s is the fraction of solid.

The PDE for diffusion is very similar to Equation 4.1 except that solutal diffusivity replaces thermal diffusivity, and there is no source term; the equation is:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (4.2)$$

where, C is the composition in weight percent and D is the solutal diffusivity in m²/s.

The fraction of solid is assumed to be determined by the Scheil Equation

$$f_s = 1 - \left(\frac{T - T_s}{T_L - T_s} \right)^{\frac{1}{1-k}} \quad (4.3)$$

where, T_s is the solidus temperature, T_L is the liquidus temperature, and k is the partition coefficient.

The discretized form of Equation 4.1 with no latent heat for an interior node or an exterior node with a constant boundary condition and an exterior node with a flux boundary condition are given below. A schematic of the grid is given in Figure 4-3.

Fig. 4-3. Drawing of grid system and boundary conditions used in the program.

Constant boundary condition

$$T_i^{n+1} = F_0 (T_{i-1}^n + T_{i+1}^n) + (1 - 2 \cdot F_0) T_i^n \quad (4.4)$$

where, i is a subscript for x-space, n is a superscript for time, F₀ is the Fourier number (α·Δt/Δx²).

Flux boundary condition

$$T_i^{n+1} = 2 \cdot F_0 \left(T_{i+1}^n + \frac{h \cdot \Delta x}{k} T_\infty \right) + \left(1 - 2 \cdot F_0 \left(\frac{h \cdot \Delta x}{k} + 1 \right) \right) T_i^n \quad (4.5)$$

where, h is the heat transfer coefficient in W/(m²·K), k is the thermal conductivity in W/(m·K), Δt is the time step in s, and Δx is the grid spacing in m..

An interior node with latent heat is as follows:

$$T_i^{n+1} = F_0(T_{i-1}^n + T_{i+1}^n) + (1 - 2 \cdot F_0)T_i^n + \frac{\Delta H_f}{C_p} \cdot df_s \quad (4.6)$$

where, df_s is the change in the fraction of solid.

The discretization of Equation 4.2 is:

for interior nodes

$$C_i^{n+1} = F_0(C_{i-1}^n + C_{i+1}^n) + (1 - 2 \cdot F_0)C_i^n \quad (4.7)$$

for exterior nodes

$$C_i^{n+1} = 2 \cdot F_0(C_{i+1}^n) + (1 - 2 \cdot F_0)C_i^n \quad (4.8)$$

Table 4-1. Boundary conditions used for model.

Variable	Variable value	X position
$\partial T / \partial t$	0	0
$\partial T / \partial t$	flux based on heat transfer coefficient	core/metal interface
$\partial T / \partial t$	flux based on heat transfer coefficient	L
C	0	core/metal interface
C	0	L

The boundary conditions to be used are shown in Fig. 4-3 and listed in Table 4-1. The boundary conditions for the heat flow are a zero heat flux at $x=0$ and a heat flux at $x=L$. There is also an air gap at the interface which uses the same heat transfer coefficient as that for the outside boundary. The initial conditions are that all temperatures equal the pouring temperature for the casting, and temperatures in the core are at the ambient temperature. The boundary conditions for the diffusion are at $x=\text{interface}$: $C=0$ and at $x=L$: C is also equal to zero. The initial condition for the diffusion is that all compositions are equal to the initial composition. The assumption that for the maximum composition for the solutal carbon in solid and semi-solid metal is that it will follow the maximum carbon content in austenite or ferrite as a function of temperature which assumes that no graphite or Fe_3C decomposes. These values are determined by the iron-carbon phase diagram. Both silicon and manganese have an appreciable solubility in iron so that no solubility limit is necessary for cast steels.

For the explicit scheme used to be stable the Fourier number must be less than 0.5; however, this is without the latent heat term which necessitates a much smaller time step. The scheme used is explicit forward in time and central in space differencing. This scheme is first order accurate in time and second order accurate in space.

Fig. 4-4. Temperature profiles for 0.1% C steel at 50 s, 150 s, and 250 s.

Fig. 4-5. Silicon profiles for the three steels at 50 s, 150 s, and 250 s.

4.2.3. Results

The temperature profiles for 0.1% C steel are shown in Fig. 4-4. The reason that only one set of profiles is shown is because the temperature profiles do not vary significantly between the three steels. From the values obtained from the model, at approximately 100 s, the sample is completely solid. At 50 s the sample is mostly liquid, and although at 150 s the sample is completely solid, significant diffusion still takes place because the casting is still at a high temperature. It is also shown that the core heats (The vertical line indicates the core/metal interface at 25.4 mm.) up as time goes on which is to be expected.

The assumption to use the Scheil equation for fraction of solid is not the most appropriate for solidification modeling because no recalescence can occur; however, for modeling the diffusion of elements it is adequate because the small differences in temperature between this method and reality will not significantly affect the diffusion of elements.

Fig. 4-6. Manganese profiles for the three steels at 50 s, 150 s, and 250 s.

Fig. 4-7. Carbon profiles of a 0.1% C steel at 50s, 150s, and 250s.

Fig. 4-8. Carbon profiles of a 0.27% C steel at 50s, 150s, and 250s.

Fig. 4-9. Carbon profiles of a 0.76% C steel at 50s, 150s, and 250s.

As shown in Fig. 4-5 the silicon content does not vary significantly with time. This is because the diffusivity coefficient for silicon is small in the liquid and extremely small for the solid. Additionally, the silicon content is not greater than the solubility limit in iron; therefore, all of the silicon which does not react stays in solution. However, it is shown that the silicon is depleted close to the interface.

Manganese also does not vary significantly with time (Fig. 4-6). This is due to the same reasons as for silicon. Although there is variation in the manganese profiles with carbon content, it is not significant, and Fig. 4-6 is representative of all three steels.

Fig. 4-7 to Fig. 4-9 display the carbon profiles for the three steels. There is significant difference between the times of 50 s, 150 s, and 250 s for all three carbon levels. This is due to phase changes that introduce solubility limits and more diffusivity coefficients when compared to silicon and manganese.

The flux for the three steels are shown in Fig. 4-10 to Fig. 4-12. The oxygen consumption is determined from stoichiometric reactions of the three elements checked (C forms CO , Si forms SiO_2 , and Mn forms MnO). $1.6 \times 10^{-3} \text{ kg}/(\text{m}^2 \cdot \text{s})$ is approximately

Fig. 4-10. Flux as a function of time for the 0.1% C steel.

Fig. 4-11. Flux as a function of time for the 0.27% C steel.

Fig. 4-12. Flux as a function of time for the 0.76% C steel.

Fig. 4-13. Traces of carbon composition at approximately 0.5 mm from the interface for all three steels.

the steady state value obtained for oxygen movement to the interface by the model in section 4.1. Only the 0.76% C steel has a consumption value that approaches the value predicted by this model. This implies that additional oxidation of other elements, i.e. iron, will occur in the 0.1% C and 0.27% C steel.

The sharp drops in the flux curves for carbon indicate phase changes in the metal. These occur because only solutal carbon is evaluated by the program. The program assumes that none of the graphite or Fe_3C dissolves; however, in reality a small amount of both phases dissolve.

Fig. 4-13 shows the traces of carbon composition at a node approximately 0.5 mm from the interface. The composition begins at the initial composition and rapidly drops off as time progresses. The composition then stabilizes when solidification occurs. Sharp drops occur as the austenite transforms to ferrite and pearlite.

When compared with the results of the case study of penetration this would indicate that castings with long solidification times would be more susceptible to chemical penetration as the elements other than iron would become depleted.

Fig. 4-14 shows the manganese and silicon traces at 0.5 mm. As with the carbon it decreases rapidly initially and levels off when solidification occurs. If chromium was also included in this study, this would indicate why no oxidized region was found in the stainless steel samples in the case study of penetration samples. With the large amounts of chromium present in stainless steels (11.5%-21%) this would prevent the iron from oxidizing.

Fig. 4-14. Traces of manganese and silicon composition at approximately 0.5 mm from the interface for all three steels.

4.2.4. Conclusions

The program uses a 1-D finite difference model to calculate carbon diffusion for a cored casting using the stated boundary conditions. This model when used in conjunction with oxygen movement model in section 4.1 predicts that the reaction will be limited for possibly 0.76% C steel, and that the diffusing elements will react fully for the 0.1% C and 0.27% C steel. This implies that oxidation of iron will be more prevalent in the 0.1% C and 0.27% C steel.

4.2.5. Data Used in Calculations

All steels

Ambient Temperature 30 °C

Pouring Temperature 1600 °C

Heat of Fusion 246 kJ

Heat Transfer Coefficient $1/(4.81E-4 - 1E-6 \cdot T + 6.23E-10 \cdot T^2)$ W/(m²·K)

Density of Solid Metal 7100 kg/m³

Density of Liquid Metal 7000 kg/m³

Density of Silica Sand 1500 kg/m³

Specific Heat of Solid Metal 846 J/(kg·K)

Specific Heat of Liquid Metal 917 J/(kg·K)

Specific Heat of Silica Sand 800 J/(kg·K)

Thermal Conductivity of Solid Metal 48 W/(m·K)

Thermal Conductivity of Liquid Metal 20 W/(m·K)

Thermal Conductivity of Silica Sand 0.3 W/(m·K)

Solutal Diffusivity of Carbon in Liquid Metal 2E-8 m²/s

Solutal Diffusivity of Carbon Solid Metal $7E-6 \cdot \exp(-31350 \text{ cal/mole}/(R \cdot T))$ m²/s

Solutal Diffusivity of Silicon in Liquid Metal 5E-9 m²/s

Solutal Diffusivity of Silicon Solid Metal $1.6E-3 \cdot \exp(-70000 \text{ cal/mole}/(R \cdot T))$ m²/s

Solutal Diffusivity of Manganese in Liquid Metal $2E+9 \cdot \exp(-64000^\circ \text{ C}/T)$ m²/s

Solutal Diffusivity of Manganese in Solid Metal $4.9E-5 \cdot \exp(-66000 \text{ cal/mole}/(R \cdot T))$ m²

5. Atmosphere at the Mold/Metal Interface

A more in depth explanation of the modifications to the analytical equipment follows in the Appendix in Section 8.

5.1. MS Modifications

Previous MS analyses have quantitated nitrogen by making the assumption that it is always present in a ratio of 79/21 to oxygen even though this may not always be a valid assumption. The analysis was performed in this manner because it is impossible to distinguish between the mass of nitrogen and carbon monoxide molecules. Experiments have shown that it is possible to determine nitrogen indirectly by measuring fragments of nitrogen molecules. These fragments have a mass different from that of carbon monoxide and are naturally produced during the process of ionization.

5.2. GC Modifications

Analyses have been performed by GC as a means of verifying the MS data and to determine nitrogen independently. Unfortunately it has not previously been possible to measure hydrogen concentrations. A thermal conductivity detector is used to quantitate gases by measuring changes in this property. Because hydrogen has a thermal conductivity very near that of the carrier gas (helium), it is not detected. This problem was eliminated by using a different carrier gas (argon), which has a different thermal conductivity. When argon is used, a similar problem arises with the quantitation of other gases. The solution is to perform the analysis twice, once with each carrier gas. This requires that a portion of the sample be analyzed at the time that the experiment is performed with one carrier gas, and a second portion be saved for later analysis with the second carrier. Previous attempts to store a gas sample for later analysis have resulted in contamination of the sample by air. A method of minimizing this contamination has been developed using sample valves.

6. Conclusions and Future Work

The results of the first year's investigation include the following:

1. Penetration in steel castings were found to be caused by both mechanical penetration and chemical penetration.
2. Contact angles for steel alloys on all mold substrates were lower than those found in cast iron
3. Diffusion models for carbon in steel and oxygen in the mold indicate that carbon may be depleted at the casting interface during solidification, allowing iron oxide to form there, as a precursor step in the formation of chemical penetration.

During the second year of the project, the following will be accomplished:

1. Sessile drop experiments will be extended to cover more alloys and mold aggregates.
2. Gas compositions at the mold/metal interface will be measured for alloy/mold binder system combinations to determine whether certain combinations produce oxidizing conditions.
3. The composition of intermediate phases found in experimental and production samples of penetration will be determined.
4. The possibility that some penetration defects are formed after the casting is solid will be evaluated.

7. References

1. P. Delannoy, D.M. Stefanescu, and T.S. Piwonka, "A Critical Review of Theories for the Formation of Casting Metal Penetration Defects", *AFS Research Reports*, April 1990.
2. D.M. Stefanescu, S.R. Giese, T.S. Piwonka, and A.M. Lane, "Cast iron Penetration in Sand Molds, Part I: Physics of Penetration and Penetration Model," submitted to *AFS Transactions*, vol. 104 (1996), paper 96-206. Also S.R. Giese, D.M. Stefanescu, J. Barlow, and T.S. Piwonka, "Cast iron Penetration in Sand Molds, Part II: Experimental Evaluation of Some of the Main Parameters Responsible for Penetration," *AFS Transactions*, vol. 104 (1996), paper 96-207. Also R. Pattabhi, A.M. Lane and T.S. Piwonka, "Cast iron Penetration in Sand Molds, Part III: Measurement of Mold/Metal Interfacial Gas Compositions," *AFS Transactions*, vol. 104 (1996), paper 96-208.
3. T.S. Piwonka, "Aggregate Molding Materials", *Metals Handbook*, Vol. 15, 9th Ed., ASM International: Metals Park, OH, 1988, pp. 208-211.
4. K. Preuss, "TOUGH User's Guide," prepared for Sandia National Laboratory, 1987.
5. I. Fatt and W. A. Klikoff, "Effect of Fractional Wettability on Multiphase Flow Through Porous Media," *AIME Transactions*, vol. 216 (1959), p. 246.
6. M. C. Leverett, "Capillary Behavior in Porous Solids," *AIME Transactions*, vol. 142 (1941), p. 152.

8. Appendix: Modifications to the GC and MS

8.1. *Rationale for the Experiments*

As shown in Section 4, the simple model of carbon diffusion to the interface indicates that in low carbon steels it is possible for an oxygen-containing atmosphere to react with molten iron at the mold/metal interface, forming FeO. FeO is then capable of reacting with the silica sand to form fayalite (Fe_2SiO_4) which has a lower melting point than low carbon steel and has been implicated in chemical penetration in steel castings. As a result, it is important to measure the atmosphere generated at the interface, to determine under what conditions (mold composition, temperature, time, etc.) it may become oxidizing.

The experimental procedure has been described in previous reports covering the work in cast iron. (In cast iron it was found that the atmosphere is *never* oxidizing, because of the high carbon content of the metal.) Results for cast iron invariably showed that the atmosphere was approximately 50% H_2 gas and 50% CO, both reducing gases. This confirmed the model predictions, which showed that the carbon in cast iron would preferentially react with any oxygen in the atmosphere before iron would, so that FeO would not be formed on the surface of the casting.

A preliminary experiment with steel showed that the gas was approximately 80% H_2 and 20% CO, in contrast to cast iron results. Because of these results and the fact that the model suggested that it was possible that FeO might form, it was decided to revise the analytical method used in the measurements. Work during the first year has concentrated on this revision.

8.2. *Modification of MS/GC*

Previous studies have used both Mass Spectrometry (MS) and Gas Chromatography (GC) to determine the identities and quantities of gases produced at the interface of molten metal and mold or core material. The use of a quadrupole MS system allows the detection and quantitation of gases based on the mass to charge ratio of ions at intervals of four seconds. This provides the information necessary to determine how the concentrations of the gases at the interface change with time from the first contact of mold and metal until equilibrium conditions are reached. Unfortunately the resolution of this system does not make it possible to distinguish between ions whose masses differ by less than one atomic mass unit. In particular, both nitrogen and carbon monoxide contribute to the signal for ions with a mass to charge ratio of 28.

In previous work assumptions were made to determine the concentrations of nitrogen and carbon monoxide. When the mold is poured the increase in temperature at the interface causes the water present to vaporize. The large quantities of steam produced flush the other gases initially present (air) away from the interface. Any oxygen detected is assumed to originate from this original atmosphere consisting of nitrogen and oxygen in a 79/21 ratio. If oxygen and nitrogen are flushed from the interface at the same rate

the concentration of nitrogen can be found by multiplying the concentration of oxygen by the ratio 79/21.

The introduction of large amounts of water vapor cause an increase in the background signal and internal pressure of the mass spectrometer, both of which decrease the performance of the system. This problem has been eliminated by drying the sample gas before analysis. However, no determination can be made of the water vapor produced after the sample has been dried.

Gas chromatography with thermal conductivity detection has been used for analysis because of its ability to distinguish between nitrogen and carbon monoxide. Unfortunately the GC, as previously outfitted, could not provide accurate quantitation of the hydrogen produced. The thermal conductivity (TC) detector used by the GC measures the difference in TC between the carrier gas and the analyte. Helium is normally used as the carrier gas because it is non-reactive and has a much lower TC than most other gases. However, the thermal conductivities of hydrogen and helium are very close. In addition, the TC of mixtures of hydrogen and helium do not vary linearly with concentration. In fact, a minimum exists where the TC of the mixture is lower than that of either pure gas. It is the combination of these factors that make it difficult to determine hydrogen concentrations.

The analysis of each sample by GC requires approximately 20 minutes. This makes it impossible to perform multiple analysis for each experiment on-line. It is desirable to obtain information about the gas compositions at more than one instant in time for any given experiment, but impossible with on-line analysis. Off-line analysis makes it possible to do this but also introduces some problems. All of the off-line samples have been contaminated with air. Since nitrogen and oxygen are two of the primary gases that need to be quantitated this is a serious problem.

The analytical instrumentation used for interfacial gas studies has been modified both to improve the quality of data obtained and to present a system more suited for use with cast steel rather than cast iron. Specifically that means a system is capable of better quantitation of oxygen and carbon dioxide. Because steel has a lower carbon content than cast iron it is likely that more carbon will be completely oxidized to carbon dioxide. Although less likely, it is possible that small quantities of oxygen may be present as well.

Large quantities of carbon monoxide and hydrogen are produced from the reaction between steam and carbon. Therefore it is desirable to produce a method for the determination water vapor concentrations at the interface. A method for off-line analysis without sample contamination is desirable so that gas concentrations can be determined as a function of time.

The GC has been modified to use either helium or argon as a carrier gas. The thermal conductivity of argon is much less than that of either helium or hydrogen and the thermal conductivities of hydrogen-argon mixtures do vary linearly with concentration. This produces a greater sensitivity for hydrogen. Because the signal obtained for hydrogen with the argon carrier is negative the polarity is reversed before sending to the integrator.

As soon as a syringe needle is removed from a septum air begins to diffuse into the needle. In our experiments the amount of air diffusing into the needle alone is enough to cause significant problems. Air can be prevented from entering the needle by applying pressure to the plunger as soon as the needle is removed from the septum and until the

sample is transferred, causing a portion of the sample gas to be expelled. This sample cannot be injected directly through the column septum because it is not possible to determine the exact volume of gas remaining in the syringe. A solution is to use a six port valve with a sample loop, as is done with the on-line analysis. A large quantity of gas (10mL) is forced through a sample loop of much smaller size (10 microliters). When the valve is turned on the flow of carrier gas is directed through the sample loop, injecting an exact volume onto the column. It is no longer necessary to know the exact volume of gas in the syringe as long as it is sufficient to purge all other gases from the sample loop. Because we wanted to maintain our ability to perform on and off-line analysis, two six port valves were connected in series as shown in Fig. 8-1. This allows the sample loop to be filled by syringe injection through a septum or by pulling the sample directly from the system by vacuum.

A procedure to collect, store, and inject samples is as follows. A 20 mL syringe is flushed with helium. The needle of the syringe is pushed through the septum of the sample line just before all of the helium is expelled and then filled with the sample gas. The sample is transferred to a tevlar sample bag while maintaining a positive pressure on the plunger. Later a 10mL sample is transferred to the GC for analysis in a similar manner. The second 10mL portion is used for analysis with the second carrier gas.

Other modifications have been made to the system to improve the reproducibility of results. These include the use of non ambient temperature programs for the injector,

Fig. 8-1. Valve system used for sample injection. The sample loop is filled with valve 1 in the off position (top left). The sample is injected by turning valve 1 on (top right). On line sampling is performed with valve 2 off (bottom left). Off line analysis is performed with valve 2 in the on position (bottom right).

Fig. 8-2. Calibration curve for hydrogen by GC with argon carrier gas.

oven and detector. This will make the chromatography less susceptible to changes caused by daily temperature variations. Restrictions in the gas lines have also been rearranged to maintain the sample loop at a pressure closer to atmospheric pressure without increasing the flow rate from the system. This reduces the variations in the quantity of sample injected.

A system is currently being developed to quantitate the water vapor produced by the system with the GC. Although the GC is capable of detecting water vapor the primary problem is transporting the vapor from the metal interface to the GC without condensation.

The calibration curve for hydrogen by using argon as a carrier gas is linear as shown in Fig. 8-2. The sensitivity for hydrogen is approximately equal to that obtained for other gases with helium carrier gas. However the sensitivities for the other gases are approximately ten times less with argon carrier gas than with a helium carrier. This effect of the carrier gas is demonstrated by the slopes of the calibration curves as shown in Table 8-1. The similar thermal conductivities of argon and carbon dioxide make it impossible to obtain satisfactory quantitation of carbon dioxide with the heavier carrier gas. In order to obtain the information needed for all of the gases of interest it is therefore necessary to run each sample twice, once with each carrier gas.

Table 8-1. Slope of Calibration Curves. Percent Volume Concentration/Peak Area.

	Argon Carrier	Helium Carrier
Methane	1.57×10^{-5}	3.83×10^{-6}
Carbon Monoxide	3.83×10^{-5}	2.82×10^{-6}
Hydrogen	4.38×10^{-6}	-----
Carbon Dioxide	-----	2.57×10^{-6}
Nitrogen	3.94×10^{-5}	3.10×10^{-6}
Oxygen	3.10×10^{-5}	2.90×10^{-6}

In the laboratory gas samples were transferred to the GC without air contamination. However, off-line samples collected from a steel/core interface show the presence of nitrogen. Air contamination is suspected. Additional measures may be taken to avoid

contamination in the future. GC analysis with argon carrier gas do confirm the large quantities of hydrogen produced as determined with the MS.

The MS results show that larger quantities of carbon dioxide are present at the interface of steel than are present for cast iron. This demonstrates that the composition of the metal does play a major role in the interfacial reactions.

8.3. *Conclusions*

The use of argon carrier gas allows the quantitation of hydrogen by GC. However the advantage of using multiple carrier gasses cannot be fully realized until the problem of air contamination has been remedied. The solution chosen is to collect and inject samples under an atmosphere of argon or helium. The analytical equipment has been modified to permit this method of operation.