METAL CASTING TECHNOLOGY CENTER

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CLEAN FERROUS CASTING TECHNOLOGY RESEARCH

TECHNICAL PROGRESS REPORT
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CLEAN FERROUS CASTING TECHNOLOGY
RESEARCH

Annual Report for Period
September 29, 1993 — September 28, 1994

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ABSTRACT

This annual report covers work performed in the first year of research on Clean Ferrous Casting Technology Research. During this year the causes of penetration of cast iron in sand molds were defined and a program which predicts the occurrence of penetration was written and verified in commercial foundries. Calculations were made to size a reaction chamber to remove inclusions from liquid steel using electromagnetic force and the chamber was built. Finally, significant progress was made in establishing pouring practices which avoid re-oxidation of steel during pouring; application of revised pouring practices have led to reduced inclusion levels in commercially poured steel castings.

CLEAN CAST STEEL TECHNOLOGY

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October, 1994

EXECUTIVE SUMMARY

In 1981, the Steel Founders' Society Quality Task Force identified oxide macroinclusions as the number one customer complaint when machining steel castings. In 1991, SFSA technical committees again identified clean steel as a major competitive need for the steel casting industry.

In response to customer needs for more machinable castings, the Steel Founders' Society established a program to determine if some practical approaches could be devised to improve metal cleanliness.

The overall objective of this program is to enhance the competitiveness of the U.S. metal casting industry by performing research that leads to production of higher quality castings at a commercially competitive price, while at the same time meeting all of the environmental and safety regulations.

The objective of this project is to demonstrate technologies that can deliver clean steel from the furnace to the casting cavity. A number of candidate technologies will be evaluated.

The tasks in the project are outlined as follows:

1. Modeling pouring of steel to understand turbulence, fluid flow, and reoxidation during pouring.
2. Conducting casting trials with the casting weights up to 250 pounds using conventional lip pour ladles.
3. Conducting casting trials with casting weights over 500 lbs using stream shrouding.
4. Conducting casting trials using special techniques, such as vacuum-assisted pouring.
5. Developing a data base on cleanliness and defects in steel castings using samples provided by participating steel foundries.
6. Transferring the technology being developed to the U.S. steel casting industry through meetings, seminars, and technical papers.

The focus of research and process evaluation in the past year has been on water modeling of different methods of pouring metal to find methods that minimize air entrainment, conducting plant trials to evaluate commercially available filters for their ability to minimize debris in castings and organizing additional plant trials to evaluate shrouded pouring and heat-to-heat effects on metal cleanliness.

The significant accomplishments of the past year are summarized as follows:

Water Modeling Laboratory Results

1. Ladle lip design was found to significantly influence air entrainment.
2. A quadrant ladle was found to entrain significantly less air compared to the two commercial ladle liners.
3. Water modeling of two gating systems produced results which paralleled the results in casting trials with the same gating systems. Air entrainment in the water model increased from 0.16 cubic feet to 0.30 cubic feet when the runner system was changed. The amount of oxide debris in commercial castings increased from 16.2 to 34.9 inches when the runner system was changed on the same casting. These results indicate that when properly conducted, water modeling can be a predictor of oxidation during pouring.

Steel Foundry Casting Results

1. A series of experiments have been completed on filtration of stainless steel. Filtration reduced the cleaning room time by about 60% and the weld repair time by about 65%.
2. The use of filters saved the foundry about \$985 per casting.
3. Approximately thirty defects from eight foundries have been submitted for analysis. The defects are being examined and the results provided to sponsor companies. A summary of the results obtained was given at a recent meeting of steel foundrymen and will be provided in the next annual report.

A more descriptive summary of the results obtained in the past year is provided in the following sections of this report.

WATER MODELING OF STEEL POURING PRACTICES

Water modeling experiments were conducted to explore methods for minimizing air entrainment during pouring of steel. Water modeling studies at both the University of Toronto and the University of Alabama at Birmingham have shown clear differences in air entrainment when pouring from bottom pour and lip pour ladles.(1-3) The results obtained in bottom pour water modeling trials conducted at Southern Research correlated well with casting results obtained in a commercial steel foundry using standard and cruciform nozzles.(4)

A careful search and analysis of the water modeling literature was presented at the 1992 SFSA T & O Conference.(5) This analysis provided a thorough review of water modeling literature and a theoretical foundation for analog modeling. The study showed that water is a useable fluid for modeling the flow of steel because of a close similarity in kinematic viscosities of the two liquids. This similarity permits Reynolds number matching in one-to-one scale models. In simple terms, a full-scale water model will have flow conditions similar to those of liquid steel.

The largest uncertainty in water modeling lies in surface tension effects which are described by the Weber Number. By converting the Weber Number to the "Z" parameter, the inertial effects found in specific velocity and length terms are replaced entirely with fluid properties, independent of flow conditions. Using the best published data available, the Z parameter for room temperature water is approximately equal (within a factor of two) to that of steel, assuming that a thin film of FeO exists at the air-liquid steel interface.(5)

Air entrainment rates are a function of boundary geometries, fluid flow characteristics, fluid properties, and the availability of air. Similitude permits air entrainment rates to be expressed as a function of the Reynolds, Froude, Weber, and Euler numbers when there are constant geometric ratios. Since these ratios can be approximately maintained, the literature indicates that air entrainment rates during steel flow can be modeled with reasonable accuracy using water under similar pouring conditions.

Experimental Investigation

The objective of the analog water modeling is to measure the amount of air entrained during pouring from different types of ladles. The principles found in the modeling literature were used in developing the water model apparatus, designing the experimental matrices, and conducting trials using bottom pour, teapot, and quadrant pour ladles.

Potential Air Entrainment Factors

Most potential factors affecting air entrainment are related to:

- (1) The way metal is delivered to the mold (pouring system), and
- (2) the way metal is received by and fills the mold (the sprue/runner/gating system).

The velocity and flow characteristics of liquid metal influence aspiration of air down the sprue, mixing of air and liquid in the runner, the jetting action of metal as it enters the mold cavity, and mixing of the metal with air as the mold cavity fills. Air entrainment increases the amount of metal exposed to atmospheric oxygen.

Some factors influencing the amount of air entrained during bottom pouring are illustrated in Figure 1. The liquid height in the ladle and the distance between the ladle and the mold affect the liquid velocity and stream impingement velocity in the sprue. The nozzle opening in a bottom pour ladle has a significant effect because it controls the stream surface area and pouring time. Stopper opening affects stream fragmentation. Nozzle and stopper shape affect the surface roughness of the metal stream.

The size, shape, and orientation of the pouring basin may affect the amount of entrainment that occurs as the flow impacts the basin and is directed into the downsprue. Sprue length, shape, and orientation affect the flow characteristics of the liquid from the pouring basin to the mold. The gating ratio and ingate velocity may have an effect by influencing the stream jetting behavior as the stream leaves the runner and enters the mold cavity. Other factors listed in Figure 1 may also contribute to air entrainment and surface oxidation.

Similar variables influence the amount of air entrained when pouring from other types of ladles. The distance of the ladle lip from the pouring basin, geometry of the ladle lip, pouring basin geometry, sprue height and geometry, and the runner and ingate geometry may have significant effects. The rate of ladle tilt may have an effect because it influences flow volume and stream shape as the metal leaves the ladle spout.

In general, pouring with low metal head pressures, pouring through unflared bottom pour nozzles, and pouring with compact, smooth-flowing streams with minimum impingement velocities are thought to minimize air entrainment and the reoxidation which results from entrainment.

Ladle and Mold Box

An experimental 20 inch square by 26 inch deep bottom pour ladle was constructed in which commercial or experimental nozzles could be mounted. A nozzle could be replaced by removing the mounting ring, replacing the sealing compound, and inserting a new nozzle with its mounting ring. The effective volume of water above the stopper and nozzle contact line was approximately 4 cubic feet providing an equivalent steel capacity of about 2000 lbs.

The mold into which water was poured consisted of an acrylic box cavity with inside dimensions of 18" x 18" x 36". The mold box was drained by a ball valve located on the bottom, and air was vented from the cope surface of the mold box into a gas collection system.

The mold box had a removable top plate through which various sprues could be inserted either vertically or at an angle (tilted). Commercial sand sprues were obtained and sealed with a thin layer of wax to prevent water degradation. Each sprue was then seated in a support ring, and the ring filled with wax to form an airtight seal. A mounting plate surrounded each supporting ring enabling the entire sprue assembly to be mounted on the mold box using screws. An O-ring seal between the mold box top and the mounting plate prevented air leakage from the mold during pouring.

Collection and Measurement of Entrained Air

During pouring, water from the ladle and air entrained by the water entered the mold box. The water collected in the mold box and caused an equal volume of air to be displaced from the box. The entrained air and the air displaced exited the box through a vent and was collected in a sealed bag. After a pouring experiment was completed, the mold was isolated and the total volume of air in the collection bag was determined by pumping the air from the bag through a precision wet test meter. The total volume of air collected minus the displaced air volume (determined from the volume of water poured) provided a direct measure of the volume of entrained air.

To correct for slight variations in the volume of water poured in different experiments, the volume of entrained air was divided by the volume of water poured. This calculation provided an air entrainment ratio defined as the cubic feet (cf) of air entrained per cf of liquid poured.

Experimental Variables

Experiments were conducted with bottom, teapot, and quadrant pour ladles to evaluate the effect of specific variables on the volume of air entrained during pouring. The primary thrust of the effort was to determine the effect of normal foundry pouring variations on air entrainment.

Transmission Case Water Modeling Experiment

Casting trials were conducted earlier at a commercial steel foundry to evaluate pouring techniques and their relation to casting cleanliness.(4) In these trial, cleanliness data was collected on 39 transmission case castings poured from 16 heats. During the trial, the gating system was redesigned, and the runner diameter was increased from 2.5 inches to 3.5 inches to reduce stream velocity in the runner. The original 2.5 inch diameter runner and new 3.5 inch diameter gating systems are illustrated in Figures 2 and 3, respectively.

All castings were bottom-poured through a 2½ inch diameter downsprue. Nine castings were poured using the original gating system and thirty castings were poured with the new gating design.

Casting cleanliness was determined by measuring the total linear inches of dirt on the casting surface after cleaning. A statistical summary of the linear dirt data for the transmission case is presented in Table I. The left data block contains casting statistics on the original runner design. The middle data block contains similar data on the new runner design, and the right block contains the summary statistics on all 39 castings from 16 heats. The dirt length mean was 30.6 inches with a standard deviation of 14.7 inches in the entire transmission case data.

A striking difference in dirt occurrence appeared in the gating system design statistics. The original gating system design resulted in an average of 16.2 inches of dirt, while the new design resulted in an average of 34.9 inches of dirt. The spread in the data for the old design was also lower with a sample standard deviation of 5.2 inches, compared to 18.9 inches with the new design.

Water modeling trials were conducted to determine if a simulation of the gating systems would produce air entrainment volumes that would correlate to casting cleanliness. These trials might also provide confirmation of the correlation between air entrainment and casting cleanliness and the ability of laboratory water model experiments to predict reactions on the casting floor.

The original casting gating system had a 2½ inch diameter downsprue with two 2½ inch diameter horizontal runners. The new gating system had a 2½ inch downsprue with two 3½ inch runners plus an additional 90° turn.

The simulated gating system designs for the water modeling trials are illustrated in Figures 4 and 5 for the original and "new" gating systems, respectively. The gating systems were made with commercial PVC pipe. A 2 inch diameter nozzle and stopper head from the foundry was mounted in the laboratory bottom pour ladle for the water modeling experiments.

The controlled variables in this trial were gating system design (original vs new) and stopper opening (fully open vs throttled). The test matrix was a full factorial orthogonal L4 with triplicate experiments for each condition. The bottom pour ladle was filled to capacity and about one cubic foot of water poured during each test.

The results obtained are presented in Table II. This table lists the trial number, nozzle design, gating design, stopper opening, air

entrainment (corrected for one cubic foot of water), mean entrained air volume in triplicate experiments, standard deviation, and pouring times (corrected for one cubic foot of water).

The analysis of variance (ANOVA) of the data is presented in Table III. This table lists the variation source, sum of squares, degrees of freedom, variance, F-ratio, significance, and contribution. The Fisher ratio or F-ratio is a measure of the response of the factor compared to the error. The higher the F-ratio, the greater the probability that the factor is significant. The significance is a measure of the probability that the measured effect is a random event. The lower the significance number, the higher the probability that the variable really does influence air entrainment. The contribution is the percentage of the air entrainment variation accounted for by the particular variable.

Stopper opening was the largest contributor to air entrainment and accounted for about 73% of the variation. Gating design was also important and accounted for about 22% of the air entrainment. Both variables had statistically significant effects. Interactions between stopper opening and gating design was not significant. Error or residual accounted for about 5% of the variance.

The effect of stopper opening on air entrainment is illustrated in Figure 6. Air entrainment approximately doubled when the stopper was throttled compared to the fully opened nozzle. The effect of gating design on air entrainment is illustrated in Figure 7. The "new" gating system increased air entrainment by about 50%, from 0.285 to 0.415 cubic feet of air per cubic foot of water poured (cfa/cfw), compared to the original gating design.

The volume of air entrained with the new sprue and runner system with a fully open nozzle gave an increase of about 100%, from 0.16 to 0.30 cfa/cfw. This correlates well with the casting cleanliness data where the amount of dirt in the casting increased from 16.2 to 34.9 inches after changing to the new system. The increase in runner diameter from 2.5 inches to 3.5 inches and the geometry changes made to reduce stream velocity caused a considerable increase in entrained air.

MODELING LIP POURING OF CASTINGS WEIGHING UP TO 250 LBS

A set of water modeling experiments were conducted on several commercially available teapot and lip pour ladle liners. The purpose of these experiments was to identify designs or pouring techniques that can be used to reduce reoxidation during pouring of small castings (≤ 250 lbs). The variables examined included sprue length, ladle design, lip shape, and sprue angle.

The apparatus is schematically illustrated in Figure 8. Water was poured from experimental ladles through sprues that were 5.25 and 10.25 inches long. The initial ladle was a commercially available 500 lb teapot ladle liner with an extended lip. The slag dam was removed from the liner to allow a comparison of teapot and lip pour ladles while holding a constant lip geometry. The ladle lip was kept approximately $3\frac{1}{2}$ inches from the cup during pouring. The ladle was full at the start of all experiments and approximately one cubic foot of water was poured during each test. The experimental matrix had a full factorial orthogonal design with triplicate experiments in each condition. The experimental matrix and the results obtained are summarized in Table IV and the ANOVA results are presented in Table V. Changes in the ladle from a teapot to lip pour design had no effect on air entrainment. Sprue length was significant, however, and accounted for about 80% of the variation in air entrainment. Interactions between ladle design and sprue length were not significant. Error accounted for about 20% of the variation.

The effect of sprue length on air entrainment is illustrated in Figure 9. The 10.25 inch sprue length increased air entrainment to 0.20 cfa/cfw compared to a value of 0.16 cf with a 5.25 inch long sprue. The increased drop height associated with the longer sprue increased stream impingement velocity in the sprue well which, in turn, increased air entrainment.

Casting trials are now being planned to evaluate the results on the foundry floor. This foundry has participated in similar foundry trials in the past and has developed a method of rating casting cleanliness. Variables to be examined include a teapot/lip ladle design comparison, vertical vs slanted sprue and ladle lip design.

FILTRATION OF CASTINGS WEIGHING OVER 500 LBS

A trial was conducted at a participating foundry to evaluate the effect of filtration on the cleanliness and repair time associated with the production of stainless steel manifold. Cleaning room and weld repair time were used as indicators of casting cleanliness. The purpose of this trial was to determine the filter performance, the cleanliness of the resulting castings, and the potential economic benefits of a large steel casting. The castings poured are near the upper limit weight range of steel parts that can be successfully poured through filters.

Experimental Procedure

All of the parts were cast from 17-4 PH stainless poured at 2900-2950°F. The steel was melted in a MgO/Al₂O₃ lined induction furnace, and the molds were formed with furan-bonded silica sand. The pouring ladle was a 1000 lb bottom pour and the casting weight was approximately 900 lbs. A schematic of the gating system for the filtered casting is illustrated in Figure 10. Four ceramic 3" x 3" x 1", 15 ppi, foam filters were used on each casting. A tile downsprue with sand runners formed the gating system. The gating system for the unfiltered castings was similar except that no filters were placed in the filter prints.

The castings were cleaned, examined, and given a first stage weld repair after shakeout. The castings were then liquid penetrant tested and radiographed and then given a second stage weld repair.

The effectiveness of filtration was measured by reductions in both the cleaning room and weld repair time. In this report, the first and second stage times associated with both cleaning and weld repair were added together.

The cleaning room and weld repair times for the unfiltered and filtered castings is presented in Tables VI and VII, respectively. The total time was summed, and the results are presented in the third column.

A one way ANOVA analysis was performed to determine if there was a significant difference in cleanliness between the unfiltered and filtered castings. There was a high probability that filtration did affect cleaning room time. The cleaning room time associated with both unfiltered and filtered castings are illustrated in Figure 11. Filtration reduced cleaning room time from about 26 hours for unfiltered castings to 10 hours for filtered castings. Assuming a cleaning room cost of \$33/hour and subtracting the cost of the filters, filtration results in a savings of approximately \$530 per casting.

The effect of filtration on weld repair time was also very significant as illustrated in Figure 12. Filtration reduced the average weld repair time from 11 hours to 4 hours for a 65% reduction. Using a cost of \$37 per hour for weld repair, this translates into a savings of about \$260 per casting.

Filtration had a very significant effect on cleaning room and weld repair time as illustrated in Figure 13. Filtration reduced total cleaning room and weld repair time by about 62% which translates to a savings of about \$790 per casting. The cost of filters used with each casting was about \$24.

STREAM SHROUDING DURING POURING OF
CASTINGS WEIGHING OVER 250 LB

Casting trials using stream shrouding are being finalized. A higher metal velocity produced by a higher metallostatic head pressure is one of the drawbacks of shrouding. The high metal velocities increase metal turbulence and sand erosion during pouring. Ceramic filters in the shroud will be tested to determine if they will reduce metal velocity to produce a less turbulent mold fill. We are awaiting these shrouds from the manufacturer at this time.

SPECIAL POURING ARRANGEMENTS

A series of modeling experiments were conducted with a quadrant pour ladle and the results compared with those obtained using commercial teapot and lip pour ladles. The quadrant pour ladle has the potential advantage that it tilts around the ladle spout, and the spout can be kept close to the mold if the sprue is near the edge of the mold.

All of the experiments were conducted using a 2 inch diameter vertical sprue with full ladles. The variable factors were ladle design (lip vs teapot vs quadrant) and sprue length.

A quadrant pour ladle had a 60° arc and a back radius of 36 inches. This provided a ladle with a capacity of approximately 4 cubic feet (cf), equivalent to about 2000 lbs of steel. The lip shape was semicircular with a two inch radius. The ladle pivoted around a steel rod under the lip which was supported on two stands. The conditions considered in the quadrant ladle pouring experiments are schematically illustrated in Figure 14, and the results are presented in Table VIII.

A summary analysis of the data is presented in Table IX. Variations in lip and ladle design from teapot to lip to quadrant accounted for 58% of the variance in air entrainment and sprue length accounted for 30%. Interactions of lip design with sprue length accounted for 10% of the variance in entrained air.

The effect of ladle/lip design on the volume of air entrained is illustrated in Figure 15. The quadrant ladle produced the lowest air entrainment with 0.125 cfa/cfw, followed by the 300 lb teapot ladle liner (0.16 cfa/cfw) and 500 lb lip pour ladle liner (0.18 cfa/cfw). The effect of sprue length on air entrainment is illustrated in Figure 16. As seen in previous experimental data, the longer sprue increased the volume of air entrained from 0.133 to 0.174 cfa/cfw. The interactions of sprue length and ladle design is illustrated in Figure 17. The increase in sprue length had a more dramatic effect on air entrained from the quadrant ladle than on the lip or teapot ladles.

These trials show that lip design can have a significant effect on air entrainment. The semicircular lip on the quadrant ladle produced less air entrainment than the commercial lip designs. Experiments to optimize the lip design for teapot, lip, and quadrant ladles are needed in the future. A series of casting trials are being

developed at a participating foundry to compare the effect of a quadrant ladle to a teapot/lip ladle on casting cleanliness.

DATA BASE ON CASTING DEFECTS

Approximately 30 production casting defects have been received from eight different foundries. These defects are analyzed and are being provided to suppliers foundries. The results will be compiled into a written document in the next year of the project.

TECHNOLOGY TRANSFER

Three sponsor meetings have been held in Chicago and Birmingham during the last year to present the results and receive guidance from the industrial sponsors. Three presentations were also made at the November 1994 SFSA T & O held in Chicago, Illinois. The presentations dealt with water modeling, high alloy filtration, and defect analysis.

CONCLUSIONS

In 1981, the Steel Founders' Society Quality Task Force identified oxide macroinclusions as the number one customer complaint when machining steel castings. In 1991, SFSA technical committees again identified clean steel as a major competitive need for the steel casting industry.

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The significant accomplishments of the past year are summarized as follows:

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ACKNOWLEDGEMENTS

This project is being cooperatively supported by several U.S. companies, The Steel Founders' Society of America, and the U.S. Department of Energy, Office of Industrial Technologies under contract #DE-FG07-931D 1232 with the University of Alabama and the University of Alabama at Birmingham. Dr. Charles Bates, Research Professor, at UAB was the principal investigator on the project. He was assisted by Mr. John Griffin, Research Engineer. We wish to express our deep appreciation to Mr. Bob Trimberger of DoE and Dr. Manohar Sohal for their support and enthusiasm for the project.

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Figure 1. Schematic of Possible Bottom Pouring Air Entrainment Factors.

616-158b

Figure 2. Original Transmission Case Runner Design.

RISER INGATE DESIGN

INGATE CONTACT

RISER CONTACT

2½" DIA. DOWN GATE

3½" DIA. RUNNERS

616-158c

Figure 3. Revised New Transmission Case Runner Design..

TABLE I

MACROINCLUSION STATISTICS FOR 4530# TRANSMISSION CASE

Sampling statistics for total linear inches of macroinclusions per casting.			
	Original Runner Design	New Runner Design	Overall Statistics
Standard Nozzle	$n = 9$ $h = 4$ $\bar{x} = 16.2$ $\hat{s} = 5.2$ $SS = 2,582$	$n = 30$ $h = 12$ $\bar{x} = 34.9$ $\hat{s} = 13.9$ $SS = 42,226$	$n = 39$ $h = 16$ $\bar{x} = 30.6$ $\hat{s} = 14.7$ $SS = 44,808$

Legend:

- n = number of castings per configuration
- h = number of heats per configuration
- $\bar{x}$ = mean linear inches of macroinclusions for configuration
- $\hat{s}$ = sample standard deviation for configuration
- SS = sum of squares of macroinclusion linear inches, for configuration

Figure 4. Water Model Simulation of Original Transmission Case Runner Design.

Figure 5. Water Model Simulation of Revised Transmission Case Runner Design.

TABLE II

**EXPERIMENTAL MATRIX AND AIR ENTRAINMENT DATA
WITH ORIGINAL AND REVISED COATING RUNNER SYSTEMS**

Trial	Nozzle Design	Gate Design	Stopper Opening (inches)	Air Entrainment (corrected) (ft ³)	Mean (ft ³)	Standard Deviation (ft ³)	Pour Time (corrected) (sec)
1	2" ID Nozzle	Original Gating	Throttled 1/4	0.4207 0.376 0.4436	0.4134	0.0344	8.00 8.00 8.75
2	2" ID Nozzle	Original Gating	Full 2 1/2	0.1305 0.194 0.1537	0.1594	0.0321	3.50 3.25 3.25
3	2" ID Nozzle	"New" Gating	Throttled 1/4	0.5626 0.5232 0.4773	0.5210	0.0427	7.75 8.00 8.25
4	2" ID Nozzle	"New" Gating	Full 2 1/2	0.2938 0.3154 0.3165	0.3086	0.0128	3.50 3.50 3.50

TABLE III

ANALYSIS OF VARIANCE FOR ENTRAINED AIR WITH
ORIGINAL AND REVISED CASTING RUNNER SYSTEMS

Variation Source	Sum of Squares (SS)	Degrees of Freedom	Mean Square (Variance) (V)	F-Ratio	Significance	Contribution (%)
(main effects)						
Stopper Opening (SO)	0.1654166	1	0.1654166	155.595	0	73
Gate Design (GD)	0.050661	1	0.050661	47.653	0.0001	22
(interactions)						
SO * GD	0.0014986	1	0.0014986	1.41	0.2692	—
Error (residual)	0.008505	8	0.0010631			5
TOTAL	0.2260812	11				100

0 missing values have been excluded.

All F-ratios are based on the residual mean square error.

table3.xls

Figure 6. Air Entrained with Fully Opened and Throttled Nozzle Pouring through Transmission Case Runner Systems. The Bar Length Represents the 95% Confidence Interval on the Data.

Figure 7. Air Entrained with Original and Revised Transmission Case Runner Systems. The Bar Length Represents the 95% Confidence Interval on the Data.

Figure 8. Schematic of the Apparatus Used in Teapot and Lip Pouring Water Model Experiments.

TABLE IV

EXPERIMENTAL MATRIX AND AIR ENTRAINMENT DATA OBTAINED
WITH LIP AND TEAPOT POURING LADLES

Trial	Ladle Design	Ladle Depth	Sprue Length (inches)	Air Entrainment (corrected) (ft ³)	Mean (ft ³)	Standard Deviation (ft ³)	Pour Time (corrected) (sec)
1	Lip	Full	5.25	0.1648	0.1688	0.0100	33.75
			5.25	0.1801			32.00
			5.25	0.1614			31.50
2	Lip	Full	10.25	0.2047	0.2051	0.0047	28.00
			10.25	0.2100			28.00
			10.25	0.2007			27.75
3	Teapot	Full	5.25	0.1612	0.1647	0.0113	28.50
			5.25	0.1556			30.00
			5.25	0.1773			31.50
4	Teapot	Full	10.25	0.1906	0.2094	0.0165	28.50
			10.25	0.2214			29.25
			10.25	0.2163			29.50

TABLE V

ANALYSIS OF VARIANCE FOR ENTRAINED AIR WITH LIP AND TEAPOT LADLES

Variation Source	Sum of Squares (SS)	Degrees of Freedom	Mean Square (Variance) (V)	F-Ratio	Significance	Contribution (%)
(main effects)						
Ladle Design (LD)	0	1	0	0	0.9865	—
Sprue Length (SL)	0.0049329	1	0.0049329	37.915	0.0003	80
(interactions)						
SL * LD	5.25E-05	1	5.25E-05	0.404	0.5496	—
Error (residual)	0.0010408	8	1.30E-04			20
TOTAL	0.0060263	11				100

0 missing values have been excluded.

All F-ratios are based on the residual mean square error.

Figure 9. Air Entrained Using Two Sprue Lengths When Pouring From Teapot and Lip Pouring Ladles. The Bar on Each Data Set Represents the 95% Confidence Interval.

Figure 10. Schematic of Manifold Sprue and Filter Placement.

TABLE VI

CLEANING AND WELD REPAIR TIME FOR UNFILTERED HIGH ALLOY STEEL MANIFOLD CASTINGS

Casting Number	Filter	Total Cleaning Time (hrs)	Total Weld Time (hrs)	Total Time (hrs)
1	No	23.03	9.60	32.63
2	No	23.50	11.00	34.50
3	No	28.90	13.40	42.30
4	No	21.50	13.20	34.70
5	No	23.20	11.40	34.60
6	No	17.40	11.75	29.15
7	No	30.57	10.20	40.77
8	No	24.60	8.70	33.30
9	No	17.50	8.10	25.60
10	No	20.60	8.42	29.02
11	No	32.60	15.90	48.50
12	No	35.35	13.60	48.95
13	No	19.02	6.40	25.42
14	No	27.10	15.70	42.80
15	No	23.20	9.30	32.50
16	No	28.71	10.40	39.11
17	No	29.18	12.00	41.18
18	No	25.15	7.30	32.45
19	No	21.77	5.80	27.57
20	No	28.48	11.10	39.58
21	No	22.87	10.60	33.47
22	No	27.54	9.10	36.64
23	No	28.60	14.90	43.50
24	No	14.02	5.70	19.72
25	No	33.02	15.60	48.62
26	No	26.99	13.70	40.69
Number =		26	26	26
Average =		25.17	10.88	36.05
SD =		5.20	3.02	7.55
Minimum =		14.02	5.70	19.72
Maximum =		35.35	15.90	48.95

TABLE VII

CLEANING AND WELD REPAIR TIME FOR FILTERED
HIGH ALLOY STEEL MANIFOLD CASTINGS

Casting Number	Filter	Total Cleaning Time (hrs)	Total Weld Time (hrs)	Total Time (hrs)
27	Yes	10.82	2.52	13.34
28	Yes	10.03	2.92	12.95
29	Yes	7.10	2.00	9.10
30	Yes	8.13	2.48	10.61
31	Yes	10.09	13.54	23.63
32	Yes	8.73	11.23	19.96
33	Yes	11.09	4.68	15.77
34	Yes	8.71	1.90	10.61
35	Yes	8.94	2.02	10.96
36	Yes	8.93	2.53	11.46
37	Yes	7.77	1.94	9.71
38	Yes	9.58	4.16	13.74
39	Yes	11.15	3.66	14.81
40	Yes	11.70	2.49	14.19
41	Yes	9.04	2.25	11.29
42	Yes	7.52	1.86	9.38
43	Yes	8.77	4.62	13.39
44	Yes	15.75	3.66	19.41
45	Yes	11.42	3.86	15.28
46	Yes	17.87	6.87	24.74
47	Yes	9.46	2.58	12.04
48	Yes	11.55	1.67	13.22
49	Yes	8.54	1.14	9.68
Number =		23	23	23
Average =		10.12	3.76	13.88
SD =		2.51	3.03	4.33
Minimum =		7.10	1.14	9.10
Maximum =		17.87	13.54	24.74

Figure 11. Effect of Filtration on Cleaning Room Time. The Bar Length on Each Data Set Represents the 95% Confidence Interval.

Figure 12. Effect of Filtration on Weld Repair Time. The Bar Length on Each Data Set Represents the 95% Confidence Interval.

Figure 13. Effect of Filtration on Total Cleaning Room and Weld Repair Time. The Bar on Each Data Set Represents the 95% Confidence Interval.

Figure 14. Schematic of the Apparatus Used in the Quadrant Pour and Teapot Pour Water Model Experiments.

TABLE VIII

EXPERIMENTAL MATRIX AND ENTRAINMENT DATA OBTAINED WITH
QUADRANT AND TEAPOT LADLES

Trial	Ladle Type	Sprue Length (inches)	Air Entrainment (corrected) (ft ³)	Mean (ft ³)	Standard Deviation (ft ³)	Pour Time (corrected) (sec)
1	300 lb. Teapot	10.25	0.1599	0.1616	0.0027	38.00
		10.25	0.1647			38.75
		10.25	0.1603			38.75
2	300 lb. Teapot	5.25	0.1475	0.1473	0.0017	36.75
		5.25	0.1489			34.50
		5.25	0.1456			41.00
3	500 lb. Lip	10.25	0.2047	0.2051	0.0047	28.00
		10.25	0.2100			28.00
		10.25	0.2007			27.75
4	500 lb. Lip	5.25	0.1648	0.1688	0.0100	33.75
		5.25	0.1801			32.00
		5.25	0.1614			31.50
5	2000 lb. Quadrant	5.25	0.0847	0.0830	0.0026	38.00
		5.25	0.0844			38.75
		5.25	0.0800			38.75
6	2000 lb. Quadrant	10.25	0.1498	0.1536	0.0086	36.75
		10.25	0.1476			34.50
		10.25	0.1635			41.00

TABLE IX

ANALYSIS OF VARIANCE FOR ENTRAINED AIR USING QUADRANT AND TEAPOT LADLES

Variation Source	Sum of Squares (SS)	Degrees of Freedom	Mean Square (Variance) (V)	F-Ratio	Significance	Contribution (%)
(main effects)						
Lip Design (LD)	0.0141453	2	0.0070726	201.131	0.0000	58
Sprue Length (SL)	0.0073488	1	0.0073488	208.983	0.0000	30
(interactions)						
SL * LD	0.0024113	2	0.0012056	34.285	0	10
Error (residual)	0.000421973	12	0.0000352			2
Total	0.0243273	17				100

0 missing values have been excluded.

All F-ratios are based on the residual mean square error.

Lip Shape

Figure 15. Air Entrained when Pouring From Two Teapot Ladle Designs and Experimental Quadrant Pour Ladle. The Bar on Each Data Set Represents the 95% Confidence Interval.

Figure 16. Air Entrained Using Teapot and Quadrant Pour Ladle When Pouring through 5.25 and 10.25 Inch Long Vertical Sprues.

Figure 17. Interactive Effects of Ladle Type and Vertical Sprue Length on Air Entrainment. The Bar on Each Data Set Represents the 95% Confidence Interval.

ELECTROMAGNETIC SEPARATION OF INCLUSIONS FROM FERROUS METALS

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ELECTROMAGNETIC SEPARATION OF INCLUSIONS FROM FERROUS METALS

First Annual Report
December 1994

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1- INTRODUCTION:

It is well recognized that inclusions in steel have an adverse effect on the mechanical properties and quality of steel castings. Although molten steel is treated prior to casting to improve melt cleanliness, still, the cleanliness levels in the final cast products are far below specifications for quality steel casting. Most of the inclusions found in the final products are small ones, less than 100 microns. This reflects the limitations of current purification technologies, such as filtration, degassing, and stirring systems, in removing small inclusions, which are generally difficult to remove within the time scale of the treatment process.

Recently, there has been a surge of research on alternative purification methods for the production of clean castings. Electromagnetic separation offers an attractive approach for cleaning molten metals from all types of non-metallic inclusions, liquid and solid. Although this approach is being used for separation of minerals, the application of this concept to molten metals is not straight forward one, mainly because of difficulties in developing a practical electromagnetic separation system for conducting materials.

Recently, the principal investigator has proposed an inductively coupled electromagnetic separation system /1/, for purification of molten metals. The

feasibility of this process has already been proven for molten aluminum, both in the lab and in industry. The results of laboratory experiments show that inclusions larger than 10 μ m can be effectively removed from molten aluminum using relatively small field strength, around 0.04 tesla. Dynamic tests trials at ALCOA research center were very encouraging. All inclusions above 40 μ m were removed from the melt flowing at a rate of 30 lb/min using an applied field of 0.08 tesla.

However, there are many unanswered questions regarding the application of this magnetic filtration process to molten steel. Because the electrical conductivity of steel is relatively small (three times smaller than aluminum) the force exerted on the particle by the applied magnetic field is expected to be somewhat small. As a result, the removal efficiency for any given inclusion size range will be less than that for aluminum. In principle, it is possible to overcome this problem by using higher magnetic fields; however, it must be accomplished within constraints of hardware availability of induction technology and of the range of flow rates of interest to steel industry. The objective of the current research project is to demonstrate the feasibility of using electromagnetic forces to separate inclusions from molten steel. Towards this goal the work is divided into three principal tasks:

1. Design of a laboratory electromagnetic separator for molten steel
2. Fabrication and installation of the system.
3. Evaluation of the system performance.

During the first year of the project significant progress has been made in the first two areas. In the following, we shall summarize the work done in these two areas.

2- DESIGN OF THE EMS LABORATORY SYSTEM

Design of the electromagnetic separation element basically involves the design of the induction coil and the EM filter element. Design of these two components cannot be achieved by trial and error; without a computer-aided design tool, it is impossible to obtain the required electromagnetic forces for inclusion separation. Using the previously developed mathematical model of the

process/2/, extensive calculations have been carried out for the design of laboratory system. The design criteria are:

1. Uniform force field distribution in the separation system
2. The migration velocity of the inclusion is larger than 5 mm/s.
3. The maximum melt velocity in the separation chamber must be three times less than the velocity of inclusion particles.

Because the coil current and frequency are not known *a priori*, additional analysis was carried out. In essence, it involves the solution of the electromagnetic field around a single particle in an infinite medium /3/. From the solution of the electric field around the particle, the electric current expressed in terms of current stream function is

$$\xi = \frac{J_0}{2} r^{1/2} R^{3/2} \sin^2 \theta \left\{ \frac{N_{3/2} \left(\frac{\sqrt{R\omega_p}}{R} r \right)}{N_{3/2}(\sqrt{R\omega_p})} e^{-i \left[\Theta_m \left(\frac{\sqrt{R\omega_p}}{R} r \right) - \Theta_m(\sqrt{R\omega_p}) \right]} \right\} \quad (1)$$

where $\delta = \sqrt{\frac{2}{\sigma \mu \omega}}$, $R\omega_p = 2 \left[\frac{R}{\delta} \right]^2$, $N_v(x) = \sqrt{\ker_v^2(x) + \text{kei}_v^2(x)}$, and $\Theta_v(x) = \arctan \left[\frac{\text{kei}_v(x)}{\ker_v(x)} \right]$ are the modules and phase of the $\ker$ and kei Kelvin functions, respectively.

From Ampere's law, the magnetic field around the particle is

$$\vec{B} = B_{a_x} + \left(-\frac{\mu}{r \sin \theta} \xi \right) \hat{a}_\phi \quad (2)$$

From equations (1) and (2) it is possible to express the electromagnetic separation force in terms of the applied magnetic field. This equation was used as a basis for estimating the coil current and frequency of the inductor.

$$\vec{F} = \frac{1}{2} J_0 B_0 \cos(\alpha_0) \left\{ 1 - \frac{g(R, \sqrt{R\omega_p})}{4 \cos(\alpha_0)} \right\} V_p \hat{a}_y \quad (3)$$

where $g(r, \sqrt{R\omega_p}) = R \int \{|J'_\theta| \cos(\alpha' + \alpha_0)\} dr$, and $|J'_\theta|$ and $\alpha'(r, \sqrt{R\omega_p})$ are the amplitude and phase angle of $|J'_\theta|$.

Based on the above analysis and the numerical calculations, the optimal configuration of the inductor and the separation were devised.

Figures 1 and 2 show the configuration of the coil devised for these experiments. In essence it is a water-cooled 20 turn two parallel plate inductor. Each plate is 10 inches long and 11 3/16 inches wide. The distance between the two plates is 10 inches, slightly larger than the width of the separation chamber. The calculated resistance and inductance of the coil are 0.04 Ohm and 78 μ Henry respectively. The water flow rate through the coil at 60 psi was estimated to be 100 l/min. Based on the electrical data and the water flow rate, the coil can carry electric current up to 1000 Amps per turn, which is three times the current needed for removal of inclusions larger than 20 microns.

Figure 1. Sketch of coil

Figure 2. Sktck of the coil Configuration

Figures 3 to 4 show the design of the electromagnetic separation system. The size of the EM filter element, Figure 3, is relatively small, 8 X 7 X 3 inches. The filter elements comprised of four separation channels, with rectangular cross sectional area. The dimensions of the outer and inner channels are 1X 1/4 and 1/2 X 1/4, respectively.

Figure 3. Sketch of the EM filter element

Figure 4. Sketch of the separation system

3- FABRICATION AND INSTALLATION OF THE SYSTEM

This task is almost completed. The EM filter element chamber was fabricated by HI-TECH Ceramics Inc. It is made of zirconia reticulated ceramic filter. Processing of the baffle block involves depositing a ceramic slurry of zirconia and additives on a polyurethane foam precursor. The foam for the baffle block has a pore size of 65 ppi. After slurry deposition, the coated foam is dried. This is followed by intricate machining of the grooves and channels. The filter is then fired to over 1500°C to form a fully sintered ceramic product.

The Induction coil was fabricated at the University of Alabama. Because of the poor matching between the coil and the available 60Hz power supply assigned for the project, a new transformer was ordered and installed.

4. EVALUATION OF THE SYSTEM PERFORMANCE.

The work on this task was initiated in mid November. At present we are exploring various techniques for incorporating non-metallic particles with uniform size particles in molten steel -- which is critical if quantitative data is to be produced.

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CAST IRON METAL PENETRATION DEFECTS

Performed by

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October, 1994

CAST IRON METAL PENETRATION DEFECTS

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1.0 EXECUTIVE SUMMARY

Metal penetration defects in cast iron have accounted for a noticeable percentage of scrapped castings. Many of the theories and solutions proposed for prevention of metal penetration defects have been derived from research work on steel castings. The cast iron foundry industry has assumed that the fundamental principles for steel penetration defects are equally applicable for cast iron castings. However, this study has conclusively shown that steel and cast iron should be considered separately.

In this study, the interfacial mold atmosphere was continuously monitored to determine the gas composition and rate of generation during gray iron casting. The major constituents of the mold atmosphere found were hydrogen and carbon monoxide. Additions of seacoal to the molding aggregate did not significantly alter the gas composition. Because of the high carbon content of cast iron, any oxidizing gases (H_2O , CO_2 , O_2) preferentially react with the dissolved carbon to form a reducing atmosphere at the casting interface. The reducing atmosphere produced blankets the liquid metal and protects it from further oxidation. Therefore, oxidation of liquid iron, the fayalite reaction, and chemical penetration is impossible in cast iron.

Since cast iron naturally provides a reducing atmosphere at the mold-metal interface, the effect of seacoal in decreasing the propensity of metal penetration is not due to formation of a reducing atmosphere. Instead, seacoal fills the void space between the sand grains by expanding and plastically deforming at high temperature. This obstructs any movement of liquid metal into the mold.

The primary mechanism for metal penetration in cast iron castings is purely mechanical. Mechanical penetration can be subcategorized into three types, each operating at different stages of the mold filling-casting solidification cycle. The most prominent type is metallostatic penetration. It occurs after the mold is filled and stops when a thick solidified skin has formed. Metallostatic penetration is a function of the surface tension, contact angle, and ferrostatic height. The second mechanism is expansion penetration. This type of defect occurs during the late stages of eutectic solidification from the volumetric expansion of graphite if liquid is in contact with the mold wall. Progressive solidification is necessary for the prevention of type of defect. The final mechanism, dynamic penetration, occurs only during pouring. Excessive liquid metal velocity from the gates to the mold wall can cause the initial liquid to be forced into void space of the sand grains.

The physics of liquid metal penetration can be described as a pressure balance between the dynamic pressure, metallostatic pressure, frictional pressure and capillary pressure at the mold-metal interface. It was established from the mechanical penetration model that penetration defects are a direct function of the surface energy properties between the metal and sand, the ferrostatic height, the density and packing of the molding aggregate, and the liquid metal velocity entering the casting cavity. A penetration index was derived from the pressure balance that can be used to assess the tendency for mechanical penetration. The penetration index is a ratio of the liquid metal processing conditions and the processing parameters of the mold. Two castings of equal chemical composition but of different casting heights were used to verify the model. The penetration index accurately predicted the critical ferrostatic height required to cause mechanical penetration. This ratio can be used to assist and direct foundrymen in the necessary course of action to prevent liquid metal penetration.

Metal penetration defects from the expansion of graphite during solidification can occur. Expansion penetration is possible if a small pool of liquid is isolated in a hot spot region. If the feeding channels are blocked to this area, eutectic expansion of the graphite during solidification forces liquid into the void space between the sand grains. This type of defect can only be avoided if the casting design promotes progressive solidification.

Metallostatic penetration is a function of the contact angle between the liquid metal and the mold. If the contact angle is less than 90° , then spontaneous penetration will occur. However, metallostatic penetration can still occur when the contact angle is greater than 90° . This happens when the ferrostatic height exceeds the capillary pressure at the mold-metal interface. All foundry variables investigated in this study using the sessile drop method exhibited contact angles greater than 90° . The following significant foundry variables for cast iron were identified:

- An increase in the average grain diameter raises the propensity for liquid metal penetration.
- Lower superheat and pouring temperature reduces the tendency for metallostatic penetration.
- Additions of phosphorus and silicon have a positive effect in preventing metallostatic penetration while carbon, manganese, and sulfur showed a negative effect.
- Sand composition has little effect on metal penetration.

2.0 INTRODUCTION

The production of quality castings requires the casting surface to be smooth and free from defects. One type of defect is caused by metal penetration into the sand-mold. Although metal penetration has been extensively studied for over fifty years, it still accounts for \$65,000,000 in scrap and rework costs in the cast metals industry. In 1989 the Mold/Metal Interface Committee (4-F) of the American Foundrymen's Society (AFS) began a new research project with The University of Alabama to determine definitively the causes of metal penetration in sand molds in ferrous castings. This program has in recent years been supported by AFS, the Department of Energy, and a consortium of foundries. This report summarizes the findings of this study.

An extensive review of past research on the subject was published by AFS in 1989.¹ A brief overview of the significant findings from this review is presented in Appendix A. Most research work on penetration has been performed on steel, and very little has been focused exclusively on cast iron. It has been assumed that the findings for steel apply equally to cast iron. As our research program progressed, it became clear to us that this assumption may not be necessarily true. For this reason, we have concentrated on cast iron in this investigation. The results which we present describe the fundamentals of penetration which we believe to be valid for all materials. However, they have been verified only for cast iron. Their extension to steel is the subject of ongoing research.

3.0 FUNDAMENTALS OF LIQUID METAL PENETRATION IN SAND MOLDS.

The fundamental conclusion from our work is that metal penetration can be analyzed and predicted by a simple pressure balance. In other words, liquid metal will flow into the sand grains when the pressure on it is greater than the pressure which resists the flow. The pressure balance *at the interface* is:

$$P_{st} + P_{dyn} + P_{exp} + P_{\gamma} \geq P_f + P_{gas} \quad \text{Eq. 3.1}$$

P_{st} = the pressure from the metallostatic head.

P_{dyn} = the pressure resulting from dynamic forces exerted during pouring

P_{exp} = the pressure exerted by the expansion of eutectic graphite

P_{γ} = the capillary pressure in the interstices between the sand grains

P_f = the pressure drop experienced by metal when it attempts to flow between sand grains

P_g = the pressure which expanding gas in the mold exerts on metal attempting to penetrate the grains.

This can be seen in Figure 3.1

Figure 3.1. Pressure balance during metal penetration in the molding aggregate.

We examined each of these terms separately, experimentally as well as analytically. The influence of each will be described below.

It will be noticed that we do not mention chemical penetration. Actually, as will be discussed later, chemical penetration is included in the frictional term. The important point is that this simple pressure balance appears to be all that is needed to describe the penetration process.

3.1 P_{st} , Metallostatic Head

The metallostatic head term is very simply the pressure exerted by the weight of the metal in the mold:

$$P_{st} = \rho gh$$

where ρ = the density of the alloy

g = the acceleration due to gravity

h = the height of the metal in the mold above the area where penetration is occurring.

Experimental verification of this was simple: we poured castings of different heights and looked to see whether penetration consistently occurred above a critical height. It did, as will be discussed in a subsequent section.

This term goes to zero the instant that the casting forms a solid skin, because liquid is no longer in contact with the mold.

What this means is that tall castings will tend to penetrate more than short castings. Tall risers also can contribute to penetration, because the total metallostatic head includes the casting height plus the riser height. Orienting castings in the mold so that their vertical dimension is less than their horizontal dimensions is therefore one method which helps reduce the probability of penetration.

3.2. P_{dyn} , Dynamic Pressure

This is the pressure exerted from the velocity of the metal as it enters the mold during pouring.

$$P_{\text{dyn}} = \rho V^2 / 2$$

The velocity of the metal is found from Bernoulli's theorem, and depends on the pouring rate, the height of the sprue, the height of the metal above the sprue, the runner and gate diameters and design. P_{dyn} goes to zero as soon as the mold is filled.

What this means is that lower metal velocities during pouring are better than higher metal velocities. This is consistent with good pouring and gating practice. One way to reduce the tendency for localized burn-in which is opposite a gate is to reduce the velocity of the metal entering the gate, which can be done by altering gating system dimensions.

3.3 P_{exp} Expansion Pressure

When cast iron solidifies, the graphite which forms at the end of solidification expands. The amount of expansion depends on the carbon content, as shown in Figure 3.2.² This expansion is the reason that many iron castings can be made without risers: the shrinkage of the austenite phase is compensated for by the expansion of the graphite, and the resulting casting is sound. However, as pointed out by Levelink and Julian³ the expansion of graphite can also cause penetration.

To see how this could occur, consider a casting with an L-shaped section, as shown below:

Because the internal corner holds heat, it solidifies last. In this case, when the casting is well over half solid, there is still an area at the corner which is liquid. In castings that shrink on solidification, porosity would be expected to be found in this region if the casting were not properly risered. Proper riser design means that the casting solidifies progressively, towards a source of liquid metal.

Figure 3.2. Volumetric Expansion of iron as a function of carbon concentration. For alloys containing greater than 2.1%C shows a decrease in volume contraction until 3.6%C is reached in which higher carbon concentrations exhibit volumetric expansion (Campell, 1990).

However, if the alloy expands on solidification, as cast iron does, a different situation occurs. Now the expansion of the graphite squeezes metal out into the sand at the corner, producing penetration. Figure 3.3 shows the appearance of metal which is found at such a corner. Careful examination of the microstructure shows that the metal which has penetrated has the same graphite shape and distribution as that which remains in the casting. This shows that it solidified at the same time, not before. The penetrated metal was found in a corner of a casting produced by one of the program sponsors (see Figure 3.4). Note that the highlighted region of the casting shown in Figure 3.4 is the area with the highest modulus, and it corresponds to the area where penetration was found. A thermal analysis shows that there is no progressive solidification from the corner to a riser, and that the last metal to freeze will be in this corner.

What this means is that the lack of progressive or directional solidification is the cause of penetration in many iron castings. When this type of penetration is found, it is important to provide directional solidification — i.e., a path of liquid metal connecting the area of penetration to a riser — so that the expanding graphite can squeeze liquid metal to the riser instead of into the sand, thus avoiding penetration. In other words, isolated areas of unfed liquid in cast iron are just as dangerous to casting quality as they are in steel, except that in steel they cause shrinkage defects, and in cast iron they cause penetration defects. This also explains why phosphorus additions decrease penetration. As the phosphorus content increases, graphite expansion decreases. Adding phosphorus can thus cause shrinkage, but stop penetration.

This fact has not been sufficiently recognized before. Penetration in cast iron should be understood in this case to be caused by the same mechanism as shrinkage in steel: lack of a path for liquid metal to flow from the last area to solidify to a riser. These areas are easy to identify using any of the solidification software on the market today, or simply by comparing casting section moduli from the area of penetration to a riser. If this comparison, or the software indicates an isolated area of liquid near a casting surface, the chances of penetration are high. The cure for penetration caused by expansion is to change the gating or (if necessary) the casting design so that there is a liquid path to a riser or gate and the casting solidifies directionally.

Figure 3.3. Metal penetration defect of a class 30 cast iron casting located in a concave zone. For this case, metal penetration was caused by expansion of graphite during eutectic growth.

Figure 3.4. Photograph of a class 30 gray iron casting where metal penetration was observed on most castings produced. The penetrated zone was located in a concave area and in the largest modulus area in the casting. This casting was unique in that the total ferrostatic height for this casting was 7". With this small metallostatic height, mechanical penetration was not the cause for this defect. The chemical analysis of this casting is 3.59%C-2.31%Si-0.499%Mn-0.068%P-0.124%S.

The value of the P_{exp} at the mold/metal interface is zero until the eutectic temperature is reached. It remains zero if there is a liquid metal path to the riser.

3.4 P_g , Gas Pressure

When cast iron is poured into a green sand mold or a resin-bonded sand mold, the moisture or the resin decompose forming water vapor (in the case of green sand), or volatile organic compounds (in the case of resin-bonded molds). It has been suggested that, because the gas is immediately heated by the hot metal, it will expand and exert a pressure in the mold which will oppose the pressure on the liquid metal. If this pressure is large enough, penetration should be avoided.

To determine the magnitude of the pressure generated by the expanding gas during pouring, we placed a pressure probe in green sand molds and resin bonded sand molds, and recorded the pressure rise during pouring. The details are given in Appendices (C and D), which also describe the determination of the gas composition at the mold/metal interface.

We found that the pressure rise in green sand molds is only 0.01 psig, and only 0.02 psig in resin-bonded sands. This pressure is not enough to resist penetration. This means that additions to the mold which decompose into gas phases are not of themselves sufficient to prevent penetration through the pressure exerted by the gas.

3.5 P_f , Frictional Resistance to Fluid Flow between the Grains, and P_γ , Capillary Resistance

These two terms are combined, because they describe the ease or difficulty with which the metal can actually move through the sand.

The interstices between sand grains in a mold are irregular, and hard to model. However, a sensible way to estimate the difficulty that the sand poses to metal flow is to recognize that compacted sand is a porous medium. A great deal of research has been done on the flow of liquids through porous media, and it has been found that P_f can be expressed as

$$P_f = \frac{\mu}{K} L_p V_p$$

Here μ is the viscosity of the liquid metal, K is the permeability of the molding sand, L_p is the length through which the liquid flows (in this case it is equal to the depth of penetration, as shown in Figure 3.1), and V_p is the speed with which the metal moves through the sand during penetration.

The permeability is often measured experimentally. However, it may also be estimated by using the Blake-Kozeny equation:

$$K = \frac{(1-f_d)^3}{180f_d^2} d^2$$

In this equation f_d is the fractional density of the molding sand, and d is the average grain diameter. The velocity of penetration is simply the distance the metal travels during penetration divided by the time it takes for the metal to freeze off in the sand.

This shows that as the permeability increases, the frictional resistance to penetration decreases. Increasing the sand grain size increases the permeability and the chance for burn-in, decreasing the sand grain size and packing it very tightly decreases the permeability of the mold, and reduces the chance for penetration (this is why a facing sand is used in hand molding

operations). Increasing the fractional density of the sand mold (i.e., ramming a harder mold) decreases the permeability of the sand, and increases its resistance to the flow of penetrating metal.

P_γ describes the pressure needed to overcome the attraction or repulsion of the metal and the sand. A brief discussion on the fundamentals of surface chemistry pertaining to cast iron and the sessile drop method is presented in Appendix E. P_γ is evaluated by the following equation:

$$P_\gamma = \frac{4}{d_e} \gamma_L \cos \theta$$

Here d_e is the diameter of an "equivalent capillary tube" which is substituted mathematically for the irregular shape of the interstices between the sand grains, and θ is the contact angle between the metal and the sand mold.

The contact angle can be determined experimentally. Its importance can be judged by the fact that if it is greater than 90° P_γ resists penetration (in other words, P_γ now moves to the right hand side of equation 3.1). If, on the other hand, θ is less than 90° , P_γ encourages penetration. In this latter case, the metal is said to "wet" the mold.

Because of the importance of this term, much of the experimental effort in this program was devoted to measuring contact angle for various combinations of mold and metal composition. The details of the techniques used for the measurement are given in Appendix F. The results of these experiments are summarized below (in reading these results, remember that *increasing* the contact angle is desirable, and that *decreasing* the contact angle should be avoided):

3.5.1 Sand Grain Size

Measurements show that the contact angle between molten cast iron and silica sand increases as finer sand is used, as shown in Figure 3.5. As the grain diameter increases (i.e., as coarser sand is used), the surface roughness of the casting increases. The dependence of θ on grain size expressed as the average grain diameter of the sand is:

$$\theta = K_d - A_d d + B_d d^2$$

where A_d , B_d , and K_d are constants.

3.5.2 Type of Sand

Sands other than silica sand are often used in steel casting to avoid penetration problems. However, they are not often used for cast iron. The effect of the type of sand used on the contact angle is shown in Figure 3.6, plotted against carbon equivalent. It is clear that while the type of sand has a major effect on the contact angle in steel, there is little effect in cast iron.

Figure 3.5. Influence of grain size on contact angle

Figure 3.6. Influence of the carbon equivalent of Fe-C alloys on their contact angles on various molding aggregates at 150°C superheat temperature.

It should be pointed out that zircon and chromite sand have higher thermal diffusivities than silica, and therefore will freeze a surface skin on the casting faster than silica. If the faster freezing time prevents penetration without causing chill or mottled iron, then their use to fight penetration might be beneficial. The use of these materials when they are finely divided (as they are in coatings) is also beneficial, because the very fine particles effectively make the average

sand grain size at the surface of the casting much finer (they fill in the spaces between the larger sand grains). As discussed above, this will increase the contact angle. However, switching to a more refractory (and more expensive) sand such as zircon or chromite will not generally solve a penetration problem in cast iron.

3.5.3 Effect of Bentonite

Because bentonite has a different chemical composition from that of silica sand, its effect on the contact angle was also investigated. The results are shown in Figure 3.7, in which the results were obtained at constant superheat. As the bentonite content of the sand is increased, the contact angle also increased. The increase is not large, however, and bentonite additions should not be made merely to attack a penetration problem. It is believed that bentonite fills in the spaces between the sand: as more bentonite is added, more spaces are filled. Its chemical composition does not appear to be a factor.

Figure 3.7. Influence of temperature and bentonite content of the silica sand on the contact angle of three types of Fe-C alloys.

3.5.4 Effect of Pouring Temperature

It is well established that the surface tension of liquid metal depends on its temperature. This is shown for cast iron in Figure 3.8. Higher pouring temperatures lower the contact angle, increasing the opportunity for penetration (they also increase the fluidity of the iron, which also encourages penetration). The effect of pouring temperature on the contact angle was found to be

$$\theta = K_T - A_T T - B_T T^2$$

where K_T , A_T , and B_T are constants.

The proper pouring temperature is, of course, the lowest temperature which fills the casting without causing chill or mottled iron. As the research results show, this also minimizes penetration.

Figure 3.8. Contact angle of synthetic Fe-C-Si alloy on silica sand (AFS GFN 71) in argon atmosphere as a function of temperature.

3.5.6 Effect of Metal Composition and Temperature

The chemical composition of the iron also affects the contact angle. Because cast iron contains a number of alloying additions, the effect is complex. The most efficient way to determine a quantitative relationship between contact angle and metal composition was to conduct a designed experiment, in which the contact angle was measured on heats having different compositions. Because temperature also affects contact angle, as shown above, it was included in the experimental design.

Details of the design and the analysis are given in Appendix (G). The results obtained showed that the contact angle depends on composition and temperature as follows:

$$\theta = K - A_1 * [\%C] - A_2 * [\%Si] - A_3 * [\%S] - A_4 * [\%Mn] - A_5 * [\%P] + A_6 * T + B_1 * [\%C * \%Si] - B_2 * [\%C * T] + B_3 * [\%Si * \%S] + B_4 * [\%S * T] + B_5 * [\%Mn * \%P]$$

where $[\%C]$ = weight percent carbon

$[\%Si]$ = weight percent silicon

$[\%S]$ = weight percent sulfur

$[\%Mn]$ = weight percent manganese

$[\%P]$ = weight percent phosphorus

T = superheat temperature

and K is constant, A_1 - A_6 are the constants for the main effects, and B_1 - B_5 are the constants for the interaction effects determined from the multiple regression model. In this case, $R^2 = 0.87$, and $RMS = 2.893$. The model is thus considered to be a satisfactory representation of the relationship.

3.5.7 Effect of Atmosphere at the Mold/Metal Interface

All of the contact angle measurements gave contact angles greater than 90° , indicating that liquid iron will not penetrate sand by itself. In other words, some sort of pressure (such as

metallostatic head or graphite expansion) must be applied to the liquid metal to make it flow into the sand and cause penetration defects. However, all of the contact angle measurements were made in argon, so the results are strictly valid only if castings are poured in argon. Since it has been shown⁴ that iron oxide easily penetrates sand, and iron castings are almost always poured in air, the obvious question is whether or not iron oxide is formed during the pouring of castings on the foundry floor. If it is, then P_γ becomes positive, and now penetration is aided. In addition, chemical reactions may occur, which accelerate penetration.

An oxidizing atmosphere can react with the mold and metal, changing their composition and properties. Chemical penetration occurs when the reaction products have a lower contact angle or enlarge the pore diameter. An oxidizing atmosphere is difficult to imagine when one looks at a freshly poured casting and sees flames shooting from every seam. Still, much of the previous research on penetration in steel castings implicated fayalite formation and we often mistakenly extrapolate this result to cast iron.

The interfacial atmosphere was investigated to see if oxidizing conditions or high pressures could exist and how they might correlate to mold conditions and observation of penetration defects. The major differences between this and previous investigations are the focus on gray iron castings in green sand molds and the use of a statistically designed experiment. Also, the composition was measured with a mass spectrometer which allowed a virtually continuous measurement.

The effect of several important foundry variables on the gas atmosphere was investigated to determine if the conditions for chemical penetration can exist. The AFS Mold-Metal Interface Committee recommended that the variables be pouring temperature and amounts of moisture, seacoal and cellulose in the sand. Their effect on the interfacial gas composition, temperature and pressure was measured in a two-level full factorial designed experiment. Design and discussion of the statistically designed experiments is given in Appendix D and the experimental method is presented in Appendix C. The casting surface was also inspected for penetration defects.

Large volumes of gas are generated at the interface which could affect the pressure balance. Previous investigators reported little or no increase of gas pressure after pouring. However, it is commonly thought that large pressures can be generated. The pressure never rose higher than 0.01 psig in any experiment, in agreement with previous investigators.

Figure 3.9 and 3.10 shows the gas composition in a green sand mold without and with seacoal additions. Both figures represent the mold atmosphere composition generally encountered during the experiments. In Figure 3.9, the atmosphere was oxidizing enough for the first four minutes to react with pure iron when no carbon was added to the mold. In Figure 3.10, the interfacial atmosphere was never oxidizing in experiments where carbon was added to the mold. However, no evidence of chemical penetration was found in any experiment. The main interfacial gases for all experiments were CO and H₂. N₂ and O₂ originally at the interface were pushed out of the mold by large volumes of steam within two minutes of pouring. CO₂ and CH₄ were also formed in much smaller quantities. Some of the O₂ may have also been removed by the reaction with the dissolved carbon in cast iron.

The carbon in the gray iron protects the iron by oxidizing first. Ghorpade et al (1975) experimentally and theoretically demonstrated that the oxygen solubility concentration in cast iron ranges from 4-10 ppm for cast iron alloys. Clearly, at the casting interface, the oxygen saturation in cast iron is achieved rapidly from the diffusive dissolution of oxygen. The oxidation of carbon and reduction of silica in the liquid iron alloy at the casting interface can occur by the following reaction:

Figure 3.9. Gas composition in a mold without seacoal additions.

Figure 3.10. Gas composition in a mold with 4.9% seacoal additions.

Once the silica reduction stabilizes, oxygen will continue to diffuse into the surface and supersaturate the liquid iron. Dissolved oxygen and carbon will then react by the following reaction in the melt:

resulting in the release of CO from the casting interface. The reaction rate of carbon monoxide is dependent on the temperature of the interface, the diffusion of oxygen to the liquid metal

interface, the diffusion of carbon to the casting interface, and the consumption of oxygen at the mold interface.

To assess the influence of the oxygen potential in the atmosphere, an experiment was run using synthetic Fe-3.68%C-1.25%Si sessile drop on a silica sand 108 + 9% sodium bentonite substrate in a 5% O₂/95% Ar gas mixture. The furnace temperature was raised to 1320°C under an argon atmosphere for the duration of the heating cycle of the experiment. A photograph was taken when the temperature was stabilized to record the initial shape of the sessile drop. Then, oxygen was introduced into the argon stream and flushed into the reaction chamber for 2 minutes to stabilize the gas atmosphere at 5% O₂, after which the furnace was sealed. Figure 3.11 shows the variation of the contact angle and oxygen concentration versus time.

Figure 3.11. Contact angle of synthetic Fe-3.68%C-1.25%Si alloy on silica sand 108+ 9% sodium bentonite in 95% argon + 5% oxygen atmosphere.

The sessile droplet experiment clearly indicates from monitoring the changes in the contact angle that the sacrificial removal of dissolved carbon from the liquid iron by oxygen does indeed occur. The contact angle decreased from the solutal reduction of dissolved carbon and an increase in the oxygen concentration as indicated during the first four minutes of Figure 3.11. After this time period, significant carbon monoxide boiling was observed in addition to a decrease in the oxygen concentration. The reaction ceased by the solidification of the droplet after 50 minutes. Solidification commenced when the solidus temperature of the droplet from the depletion of dissolved carbon reached the same temperature as that in the furnace chamber. This experiment conclusively supports the theory that carbon monoxide will form at the liquid cast iron interface when oxygen is present. Therefore, it is impossible for chemical penetration to occur for cast iron castings.

3.5.7.1 Model of Transport and Reaction

A model of transport and reaction of chemicals in the interfacial region is developed here to answer the fundamental question of the mold-metal atmosphere tests: can there be chemical penetration in green sand molds in casting gray iron?

The designed experiments demonstrated that:

- a. Air was not detected after a few minutes.
- b. The major gases were always CO and H₂ and usually in a 1:1 ratio.

- c. CH_4 was produced in small quantities but in a larger amount when using the resin-bonded sand.
- d. CO_2 was also produced in small quantities but in a larger, transient amount when no carbon was added to the mold.
- e. The interfacial gas composition was fairly insensitive to the design variables.
- f. At higher temperatures the gas composition was close to that predicted by chemical equilibrium as shown in Appendix D.6.
- g. No metal penetration defects could be produced in these experiments.

3.5.7.2 Proposed Sequence of Events

Based on these facts, a sequence of events can be hypothesized.

- a. The mold is initially a mixture of sand, clay, and water with some carbon additives. Water should be adsorbed on the sand surface and condensed in the sand voids. The gas in the voids consists of humid air.
- b. After the molten metal is introduced, the water in the sand (near the interface) immediately vaporizes. This can cause a thousand-fold increase of the gas volume.
- c. The vaporizing water effectively flushes the air out from the interface. For moist molds the initial gas composition should have absolutely no effect on the resulting atmosphere.
- d. The only gas present immediately after pouring is water vapor. It can react with carbon or metal according to these reactions:

The equilibrium for both reactions is very far to the right, but the equilibrium for the oxidation of carbon is several orders of magnitude greater than that for iron. As long as carbon is present, iron will not oxidize. Since there is a lot of carbon in the metal and that is where the temperature and catalytic effects are greatest, the majority of the reactive carbon is from the metal.

- e. Initially, the amount of water compared to carbon is very large (even larger when no carbon is added to the sand). This allows a competing reaction to form CO_2 :

After the water is diluted with reaction products the equilibrium no longer favors CO_2 and its concentration should decrease.

- f. A layer of CO and H_2 builds up at the interface. This was produced by an equilibrium reaction so they will be effectively inert at the metal surface. A concentration gradient exists so these gases will diffuse away from the interface. Also, reaction continues at the interface producing 2 moles of product for every mole of water that arrives. This causes a convective flux of products from the interface.

- g. The reaction depletes the carbon in the first molecular layer of the metal. This produces a concentration gradient and the reaction becomes limited by diffusion of carbon through the molten metal to the interface rather than by chemical reaction.
- h. As soon as water reaches the interface it reacts with carbon. This produces a concentration gradient through the product layer. The reaction rate also becomes limited by this diffusion rather than by chemical reaction.
- i. As the metal cools down the situation gets more complicated. The reactions may not be at chemical equilibrium. Also, the metal surface forms a skin which prevents carbon from diffusing through the molten metal to replace the reacted carbon. Whatever happens, the experiments show that during the time frame of interest the interfacial gas composition does not change much.

3.5.7.3 Discussion

The objective of the mold-metal atmosphere experiments was not only to measure the effect on composition of several variables, but to understand how it is related to chemical penetration. However, to date there has been no compelling evidence that chemical penetration has ever been seen for gray iron in green sand molds. Could it be a myth?

Oxidizing atmospheres could not be produced in the laboratory experiments even with high moisture and no carbon additives. Surfaces of laboratory castings showed no evidence of penetration. Thermodynamic analysis confirms that oxidation of iron under these conditions should be impossible. In fact, industrial practitioners could not provide samples or convincing accounts that chemical penetration had ever occurred. All penetration defects seem likely to result from mechanical or expansion penetration.

Why doesn't chemical penetration occur? The first step requires oxidation of iron to FeO. The equilibrium conversion for oxidation of carbon is much higher than that of iron. As long as carbon is available it will act as a sacrificial element and react with water. More than enough carbon is dissolved in the metal to prevent any iron oxidation.

This means that chemical penetration cannot occur with gray iron in green sand molds. The carbon in the metal is oxidized by steam before the iron or other metals. The reducing atmosphere (CO and H₂) produced by this reaction blankets the casting and protects it from further oxidation. A small amount of carbon addition to the mold prevents even a temporary oxidizing atmosphere, but large amounts of carbon do not significantly change the gas composition. The mold atmosphere measured in The University of Alabama casting laboratory were verified in trials at The University of Northern Iowa, Ashland Chemicals, Dalton Foundries, and Rochester Metal Products.

3.5.8 The Effect of Seacoal

Seacoal is added to the sand mix to prevent penetration. A number of explanations have been given for its effectiveness, the most popular one in the United States being that seacoal burns and produces a reducing atmosphere which prevents oxidation of the metal. However, as the experiments described above clearly show, the effect of seacoal on the composition of the mold atmosphere is minimal, and, for cast iron, of little importance, since the carbon in the metal is high enough to produce its own reducing atmosphere. But seacoal clearly is effective in reducing penetration defects. Why?

Coal is a mixture of carbon and volatile organic compounds. As it is heated, the compounds begin to expand. In so doing, they deform the coal. Coal is actually plastic when it is heated. If a block of coal is placed in an oven so that it completely fills the space in the oven, and only a small hole is left in the top of the oven, as the coal is heated a coal "worm" will be noticed growing out of the hole in the oven. In other words, coal heated to the temperatures of

molten iron can deform and ooze into the spaces between the sand grains, filling them up, and mechanically blocking the movement of penetrating iron.

That this actually occurs can be seen in Figure 3.12. Deformed seacoal (which, because the gaseous impurities have been liberated from it now appears as vitreous carbon) is found dispersed between the sand grains. In this case, taken from a casting poured in a commercial foundry, the plastic deformation of the seacoal and its movement between the sand grains was not enough to counteract the pressure of the metal (which was being squeezed into the sand by the expansion of eutectic graphite). However, the appearance of the seacoal clearly shows that it operates by flowing between sand grains at the interface.

Figure 3.12. Enlarged area of metal penetration shown in Figure 3.1. The large dark areas on the photograph are silica sand grains surround with bentonite. The lighter gray areas between the metal and sand grains are vitreous carbon. Magnification 250x.

4.0 Prediction of Penetration

4.1 The Penetration Index

Section 3 (above) discussed the basic equation which governs penetration of cast iron in sand molds, and evaluated analytically and experimentally each of its terms. With this information, it should be possible to evaluate equation 3.1 and predict the conditions under which penetration will occur.

We have shown that P_g is negligible for cast iron in sand, so this term can be dropped. P_{exp} has been shown to depend on the design of the casting and/or the gating system, and, as such must be evaluated (as discussed) separately for each casting. For this reason, it will be dropped from the general analysis. And, we also have shown that there is no chemical penetration, so that P_γ is always negative.

With this in mind, we can substitute into equation 3.1 and solve for the length of penetration L_p . When this is done, the result is:

$$L_p = \left[\frac{d^2 t_p (1 - f_d)^3}{180 \mu f_d^2} (\rho g h + \rho V^2 + \frac{4}{d_e} \gamma_{LV} \cos \theta) \right]^{1/2}$$

When there is no penetration, $L_p = 0$. We can solve the equation for any of the variables, such as f_d or θ , to determine the minimum value they should have if all other variables are held constant so that penetration is just avoided (i.e., so that the length of penetration is 0). However, of all the variables, the one which is easiest to control by the foundryman is the contact angle, θ , because it depends on composition and temperature. When we do this, we find that:

$$\theta_{cr} = \cos^{-1} \left[-\frac{d_e}{4\gamma_{LV}} (\rho g h + \rho v^2) \right]$$

θ_{cr} is the *critical contact angle* at which penetration is expected to occur, based on the processing variables which the foundry uses for the mold, the mold hardness, and the height of the casting. In other words, fixing the mold variables, which are determined by the casting height and the molding system used, establishes the critical contact angle for penetration. If these are changed, a different value for the critical contact angle is found.

Depending on the composition and pouring temperature of the metal, however, the *actual contact angle*, θ_A the metal makes with the mold will usually be different from the critical contact angle. If the actual contact angle is greater than the critical contact angle needed for penetration, no penetration is expected. This can be expressed as a *Penetration Index*:

$$P = \frac{\theta_A}{\theta_{Cr}}$$

When P is less than 1, penetration is likely. P is an indicator of whether or not penetration is likely to occur, assuming that the casting and gating system are designed so that expansion penetration does not occur.

4.2 Validation of the Penetration Index

The Penetration Index was validated in the foundry laboratory at The University of Alabama and at four other foundry sites, and found to be valid. Details of the casting validation trial at The University are given below:

Two castings were poured, one 12 inches high, and one 22" (0.56 m) high. Data was entered into the Penetration Index equation for both castings as shown in Table 4.1.

No penetration was found in the shorter casting, as predicted. Penetration was found, however, in the taller casting, at the height predicted (see Figure 4.1).

Table 4.1 Metal and Mold Variables used for Penetration Index Verification Test

Mold Variables	12" Casting	22" Casting
Metallostatic Head (m)	0.31	0.56
Mold Hardness	87	87
AFS GFN	71	71
Metal Velocity (m/sec)	0	0
Metal Variables		
<u>Cast Iron Composition</u>		
%C	3.50	3.50
%Si	1.80	1.80
%Mn	0.70	0.70
%P	0.12	0.12
%S	0.12	0.12
Superheat Temperature (°C)	200	200
PENETRATION INDEX	1.04	0.87

Figure 4.1. Plot of Penetration Index as a function of metallostatic height. The graph shows for the variables used in the experiment (given in Table 4.1) that liquid metal penetration should not be observed over 8" in casting height. The actual casting, had metal penetration at a height of 9".

A major advantage of the penetration index is that it not only indicates when a problem is possible, it can be used to indicate what corrective actions are possible. Figures 4.2 to 4.4 show three graphs to illustrate this point. In Figure 4.2, the conditions selected give a penetration index value of 0.97, indicating that penetration is likely. However, the graph shows that the index would become positive if the carbon content were reduced to 3.2% (holding the silicon content constant) or the silicon content was increased to 2.0% (holding the carbon content constant). The trend lines show that a general increase in silicon and/or decrease in carbon will

be beneficial; by substituting in possible compositions the foundry can determine what metal composition will alleviate the penetration problem. The graph also shows that changing the phosphorous, sulfur or manganese levels will probably not have much effect on the penetration index.

Figure 4.5 shows what can be done with the mold variables to eliminate penetration if changes in composition of the magnitude shown are not possible. The mold hardness can be raised from 87 to 90, or a finer sand can be used, or, if possible, a shorter cope can be used to decrease the height of the casting plus risers.

Figure 4.2. Graph of metal variables used in verification experiment for a metallostatic height of 16". This gives a Penetration Index of 0.97 the variables used in Table 4.1.

Figure 4.3. Since sulfur and phosphorus additions are made in small quantities, another metal graph is provided to identifying the effect of phosphorus and sulfur on the Penetration Index.

Figure 4.4. Graph of the mold variables determined from the Penetration Index equation. The graph used the same inputted variables as shown in Figure 4.2.

5.0 Conclusions

1. Penetration of cast iron into sand molds is caused by the physical movement of liquid metal into the sand. No oxidation of the liquid metal surface takes place, and no reaction between iron and oxygen in the mold atmosphere to form iron oxide is possible under pouring conditions normally encountered in cast iron production. The mechanisms of penetration can be analyzed by a simple pressure balance equation. Use of the Penetration Index clearly shows what the effect of altering casting variables will be on the occurrence of penetration.
2. The three driving forces for penetration are dynamic penetration, metallostatic penetration, and expansion penetration. Each operates over its own distinctive part of the pouring and solidification sequence, as shown in Figure 5.1.

Figure 5.1. Schematic illustration of the three types of mechanical penetration and their occurrence as a function of time.

3. Dynamic penetration occurs only during pouring. It results from excess velocity of the molten metal as it enters the casting cavity. It is corrected by altering the gating system to reduce the gate velocity of the metal.
4. Metallostatic penetration operates from the moment metal enters the casting cavity until a solid skin has formed and liquid is no longer present at the mold/metal interface. Metallostatic penetration is due entirely to the pressure exerted by the weight of the molten metal in the mold. It can be countered by altering mold hardness, sand GFN, metal composition and pouring temperature.
5. Expansion penetration results from the pressure exerted on molten metal at the interface by the expansion of graphite during eutectic solidification. It is caused by incorrect thermal management of the solidification sequence, allowing hot spots to exist where liquid metal is in contact with the mold interface, but cut off from the rest of the casting. Expansion penetration is countered by assuring that the casting freezes progressively from all parts of the casting surface to a riser or gate.
6. Although further confirmation is necessary, it appears that seacoal is effective in countering penetration by plastic deformation into the interstices between the sand grains at the mold/metal interface.

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APPENDIX A - Literature Review

The general term for metal penetration accepted by the foundry industry, as defined by Draper and Gaindar (1975), is the condition in which liquid metal has entered the pore space of the molding material up to and beyond the first layer of sand grains. Before describing the mechanisms of cast iron penetration defects, it is necessary to first clarify the two different types of penetration defects. The penetration defects are classified in order of severity as follows:

1. **Burn-On/In.** In steel, the difference between burn-on and burn-in was the type of fayalite phase formed at the casting interface. The term burn-on will be used since this research has shown that fayalite does not form in cast iron. Burn-on is the condition where the molten metal has penetrated the mold surface up to the midpoint of the first layer of sand grains and does not chemically react with the sand. Occasionally, the sand grains adhere to the casting surface but can be removed easily. The surface of the casting has the appearance of small protrusions as a result of the sand grains and the solidified metal being in contact.
2. **Metal penetration.** This is the condition where the molten metal has penetrated beyond the first layer of sand grains. The resultant mass of metal and sand grains is permanently adhered to the casting surface requiring removal by chipping or grinding. Figure 3.3 shows a photomicrograph of this condition. In some cases, this agglomerated mass is so large or difficult to remove that the casting has to be scrapped.

A.1 Mechanical Penetration

Mechanical penetration is the transport of molten metal into the interstices of the molding aggregate as a result of excessive ferrostatic pressure (Wagner, 1979). Variables that influence mechanical penetration are sand fineness, pouring temperature, metallostatic pressure, surface tension and contact angle between the liquid metal and molding material, and external pressure such as mold gas pressure (Fawley, 1974).

A.1.1 Effect of Molding Media

Early investigators realized that soft ramming of a mold or lower sand fineness lends to an increased tendency for penetration (Goodale, 1930). The average pore size between the sand grains was considered to be the main factor in metal penetration caused by metallostatic pressure. Sand fineness, represented by AFS grain fineness number (GFN), and the degree of compaction determines the average pore size (Thorpe, 1950). Increasing the sand fineness or raising the bulk density of the sand dramatically increases the resistance to metal penetration as shown in Figure A.2 and A.3. Variables that affect the metallostatic pressure are pouring temperature, chemical composition of the liquid metal, and casting height. In the absence of other external variables such as chemical reactions with the metal and molding material, physical penetration can be corrected by a judicious selection of sand fineness and adequate ramming of the mold.

Figure A.2. Experimental linear relationship between the bulk density of a molding aggregate and required casting height to cause mechanical penetration (Thorpe, 1950).

Figure A.3. Experimental logarithmic relationship between the sand fineness and the casting height required for mechanical penetration (Thorpe, 1950).

A.1.2 Melt Chemistry

Alloying additions to cast iron are usually done to enhance the physical and mechanical properties. They also change the surface energy of the liquid metal. Hoar and Atterton (1950) have shown that liquid iron does not wet silica. Because of the non-wetting behavior of iron and silica, iron cannot penetrate into the void space between the sand grains unless sufficient pressure is applied, as by metallostatic pressure (the height of the liquid metal). However, the critical metallostatic pressure required to cause liquid state penetration is a function of the surface tension and contact angle of the iron alloy. Hoar and Atterton showed that the critical pressure is directly proportional to the surface tension of iron. They also found that as the surface tension of iron is reduced by alloy additions, the critical pressure for penetration also decreases.

A.2 Mold-Metal Interface

Several important studies have been made of conditions at the mold-metal interface. These include temperature, pressure and composition of the gas, its rate of evolution, and the chemical reactions that produce the gas.

A.2.1 Interfacial Temperature

Emmons and Bach (1955) were among the first to measure the temperature near the mold-metal interface while making steel castings. The temperature at distances of 1/4", 1/2" and 1" from the interface in sand-silica flour molds was measured using bare and sheathed platinum-platinum 10% rhodium thermocouples and an optical pyrometer. It takes about 15 minutes to reach the melting point of steel at 1/4" from the interface and the temperature gradient with distance reaches a steady state after about the same amount of time.

Sanders (1965) measured the temperature at the mold metal interface in a gray iron-green sand system and reported that penetration was observed two minutes after pouring when the temperature at 1/8" from the interface was only 1000°C. The nature of this penetration is not clear. The temperature at the interface stayed above the melting point of cast iron for about 8 minutes after pouring. Owusu and Draper (1978) and Wagner (1979) reported similar trends in the temperature profile in green sand molds when steel was poured but the actual temperatures were higher. An increase in the moisture content of the green sand mold produced lower interface temperatures. The greater evaporation of the water in the wetter molds and possibly a higher heat transfer rate due to forced convection kept the interfacial temperature lower. Levelink and Julien (1973) measured the temperature, at various distances inside the metal in a gray iron-furan bonded chromite sand system. The metal was solid instantly after it came in contact with the sand but it heated up and became liquid again.

A.2.2 Interfacial Pressure

Owusu and Draper (1978) were the first to measure the pressure at the mold-metal interface using an inclined tube water manometer. The pressure at the interface of their green sand mold-steel system was atmospheric. An initial pressure of about 2.2" of water (1.005 atm) immediately after pouring dropped rapidly to about 0.2" of water. The mold was being purged from the bottom and so the pressure inside the mold might have been slightly higher than in a normal mold. Wagner (1979) repeated these tests and reported similar results. In addition to the water manometer he verified the pressures with a pressure transducer.

Bates and Monroe (1981) measured the pressure in a gray iron-furan core. Their pressure-time profiles show large spikes in the interfacial pressure. The pressure reached a maximum of 1.25 atm absolute which is much higher than in the case of green sand molds. This is not surprising because an increase in the permeability of the mold should reduce the amount of gas accumulation at the mold-metal interface thereby decreasing the pressure at the interface. Also, higher LOI of the sand should produce greater gas evolution rates and higher pressures.

A.2.3 Interfacial Gas Composition

The gas composition measurements conducted by the various investigators can be divided into two categories. The first type of test maintained a controlled gas atmosphere by flushing the mold with a specific gas. These tests revealed the effect of a particular gas atmosphere (and oxidizing potential) on surface defects. The gas atmosphere used in these tests does not reflect the gas atmosphere in normal molds. The second type of test simply collected the total gas evolved or the gas specifically from the interfacial area to analyze for composition.

A.2.3.1 Controlled Atmosphere Tests

The importance of gas atmosphere on the surface quality of steel castings was first demonstrated by Savage and Taylor (1950). Stainless steel and carbon steel pins heated in a reducing and neutral atmosphere did not react with the sand, whereas the same pin lost its metallic luster and produced fayalite in an air atmosphere. Draper and Gaiindhar (1977) altered the gas atmospheres in green sand molds by flushing the mold with an oxidizing, reducing or neutral gas before, during and after pouring a steel casting. Molds poured in reducing and neutral atmospheres had a smoother casting surface whereas castings made in air and carbon dioxide atmosphere showed significant metal penetration. They may have unwittingly reduced the moisture content of the mold while flushing because they could not produce similar results in an oxygen atmosphere. Owusu and Draper (1978) and Wagner (1979) later repeated this same experiment with additional equipment to control the moisture content of the flushing gas and prevent the drying of the mold. Their results confirmed that oxidizing atmospheres produce poorer surface quality and more penetration than reducing atmospheres.

A.2.3.2 Interfacial Gas Measurements

All previous measurements of interfacial gas composition were made with a gas chromatograph. Some investigators pulled samples from the interface with a tube while others collected the gas evolved.

Emmons and Bach (1955) measured the gas atmosphere in a steel casting and found that the predominant gases at the mold metal interface were carbon monoxide and hydrogen. The composition of these two gases rose rapidly and reached a relatively constant value after the first 4 minutes. Carbon dioxide, oxygen and nitrogen accounted for less than 20% of the total gas.

One of the most extensive gas composition analyses to date was done by Scott and Bates (1975, 1976, 1977, 1978) on steel and gray iron poured in various chemically bonded mold systems. A silica tube placed in the middle of a buchner funnel was used to collect the gas samples from the interface. Hydrogen and carbon monoxide were once again the main constituents.

A.2.4 Gas Evolution Rates

Scott, Goodman and Monroe (1978) and Bates and Monroe (1981) measured the gas evolution rates from various chemically bonded molds. A bubble flow meter and tracer gas injections were used to find the flow rate of the gas collected from the interface. The gas evolution trend resembled the pressure trend. There was an initial rapid evolution of gas which caused a higher pressure initially, followed by a decrease in gas evolution and a lower pressure. Different binder systems gave different gas evolution rates and there seemed to be a correlation between the gas evolution rate and the LOI of the mold. The peak gas evolution rate varied between 15 to 35 cc/sec for chemically bonded molds.

A.2.5 Mold-Metal Reactions

Savage and Taylor (1950) found fayalite (iron silicate, Fe_2SiO_4) reaction product in steel pins held molten in an oxidizing atmosphere and in the sand covering foundry castings. It was concluded that fayalite was the end product of mold-metal reactions and its mechanism of formation was by oxidation of the metal followed by reaction with silicon oxide. The oxidation of the iron was believed to be caused by reaction with oxygen, water or carbon dioxide. Fayalite formation in steel castings was found to be unavoidable and independent of mold atmosphere, cereal additives and moisture content (Owusu and Draper, 1978), but the thickness of the fayalite layer formed depended on the above three variables. Savage and Taylor (1950) concluded that fayalite helps the "peelability" of castings and gives good surface finish. Draper and Gaiindhar (1977) reported that crystalline fayalite

can be more easily removed from the surface of the castings than non-crystalline silicates and so fayalite does not always cause surface defects.

Colligan, Van Vlack and Flinn (1958) studied the reaction between iron and pure silica under different oxidizing atmospheres. The reaction depends on the oxidizing potential of the atmosphere, as determined by the ratio of carbon dioxide to carbon monoxide in the gas phase and on the temperature of the system. By repeating some of the experimental points in Darken's Fe-Si-O equilibrium diagram they showed that the reaction products at any temperature and for any atmosphere can be predicted from this diagram. The gas atmosphere for any system is first written as an equivalent CO_2/CO ratio. This value along with the temperature is then used to predict the reaction products. Similar diagrams need to be drawn for Fe-Si-O-C systems to understand the effect of carbon on the reactions. Dissolved carbon gets preferentially oxidized before the metal and, acting as sacrificial element, prevents the oxidation of the metal as indicated by the equilibrium constant for the two oxidation reactions. Savage and Taylor (1950) calculated these values and found that the oxygen partial pressure for carbon oxidation was about six orders of magnitude less than that for iron oxidation. The order of oxidation was $\text{C} > \text{Si} > \text{Mn} > \text{Fe}$. In addition to the fayalite reaction, Sanders (1965) hypothesized that iron carbonyls were being formed by reaction of iron with carbon monoxide at high pressures and low temperatures. This theory was, however, shown to be false on the basis of thermodynamic data by Svoboda and Geiger (1969) as such high pressures are never produced.

A.3 References

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APPENDIX B - Expansion Penetration

Heine (1986) has analytically explained the volumetric expansion during eutectic solidification. This model will be used to demonstrate that metal penetration for cast iron can be a result of graphite expansion. The initial composition of the preeutectic austenite phase can be estimated by the equilibrium phase line between austenite and graphite as function of silicon concentration at 1150°C. The equation of this line is:

$$\%C_{\gamma} = 2.11 - 0.23\%Si$$

Since alloying additions were made to the cast iron, these additions will affect the maximum solubility of carbon in austenite. Using the slope of austenite and graphite phase line from the ternary diagram, the thermodynamic solubility correction factors used to account for alloying additions (Metals Handbook, Vol. 15, 1988), and assuming equilibrium solidification conditions exists, the following equation can be used to estimate the maximum solubility of carbon in austenite:

$$\%C_{\gamma} = 2.11 - 0.23\%Si + 0.006\%Mn - 0.35\%P - 0.08\%S$$

where $\%C_{\gamma}$ = maximum solubility of carbon in austenite

$\%Si$ = silicon concentration of the gray iron alloy

$\%Mn$ = manganese concentration of the gray iron alloy

$\%P$ = phosphorus concentration of the gray iron alloy

$\%S$ = sulfur concentration of the gray iron alloy

The fraction of austenite and graphite in the cast iron can be simply calculated by using the lever rule on the ternary diagram.

Knowing the maximum solubility of carbon in austenite and assuming silicon is completely dissolved in the austenite phase, the specific volume (spv) of the austenite phase can be determined from the following relationship (Heine, 1986):

$$\text{spv } \gamma, 1155^{\circ}\text{C} = 0.1330 + 0.0013 (\%Si - \%C)$$

The specific volume of the poured cast iron is the sum of the specific volume fraction of the austenite and graphite phases. The volume expansion or contraction can then be determined by comparing the specific volume of the solid cast iron to the specific volume of liquid cast iron. This relationship can be written as:

$$\%Vol = \frac{\text{spv(solid)} - \text{spv(liquid)}}{\text{spv(liquid)}} * 100$$

Thus, if the specific volume of solid cast iron is greater than the specific volume of the liquid, there will be volume expansion on eutectic solidification. For expansion penetration, if a solid skin does not form at the mold wall, then the remaining liquid in this region will expand upon solidification and force the liquid into the pore spaces of the mold.

Reference

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APPENDIX C. Evaluation of the Atmosphere at the Mold-Metal Interface

C.1 Apparatus

The equipment consisted of the flask, sampling system and instruments. Figure C.1 is a sketch of the experimental equipment and the flask. More detail can be found in Pattabhi (1995).

The cope measured 2' on each side and 1' deep. The drag was 10" deep. Together they held about 200 lbs of green sand. The casting was a cylinder with a length of 12" and a diameter of 6". It was gated through the bottom.

The sampling system was three stainless steel tubes that ran from the bottom of the drag to within 1/8" of the mold/metal interface. They were held in place by a support bar imbedded in the sand. The mold was rammed with the tubes in place and it was confirmed that their presence did not affect the mold hardness.

Figure C.1. Schematic diagram of experimental equipment to measure the gas composition at 1/8" distance from the mold-metal interface

An 1/8" tube was used to pull gas with a vacuum pump at a rate of 6-10 cc/min. Calculations showed that the sampling rate was much smaller than the gas evolution and so would not perturb the measurement. The gas first passed through a humidity meter (used in only a few experiments) to measure water content. Next was a 2 micron filter to remove particulates and a drierite (CaSO_4) bed to remove water. Finally it entered a 0-100 amu mass spectrometer which could continuously measure the partial pressures of the gases.

The dried gas was also analyzed with a gas chromatograph. It used a Haysep D column, a thermal conductivity detector (TCD) and Helium as the reference and carrier gas. The gas was either injected with a syringe or an on-line 10 ml sampling loop.

A Chromel-Alumel thermocouple coated with zirconia paste ran through a 1/4" tube to the interface. Temperature was recorded with a data acquisition system at 1 second intervals.

Another 1/4" tube was fitted with a psi to mV transducer to measure pressure. The transducer was calibrated to read in the 0-15 psig range and the pressure was recorded on a strip chart.

C.2 Sand Mulling and Mold preparation

One hundred pounds of washed silica sand of AFS grain fineness number 71 was charged into a Beardsley and Piper muller. Weighed amounts of western bentonite (clay) and cellulose were added to get 6% western bentonite in the dry sand mixture and the appropriate cellulose composition. Measured amounts of water were also added and this mixture was mulled for about 5 min. The muller was kept closed during the mulling operation to minimize evaporation losses. A sand sample was withdrawn to check cellulose content using the loss on ignition (LOI) test. A calculated amount of seacoal was added to the mixture and the mulling was continued for another 5 minutes. Another sample was withdrawn for an LOI test. The difference between the weight losses on ignition from the second test and that from the first gave the seacoal content of the sand. The moisture content in the sand was also determined by finding the weight loss after drying the sand samples at 220°F for 3 hours. These tests ensured that the actual sand composition was close to the targeted sand composition.

The compactability of the sand was found by finding the percentage compaction of the sand when a standard weight was used to ram the sand three times. The gas permeability of a one inch section of the sand after ramming it three times with a standard weight was determined using a gas permeability meter. The mold hardness of the sand was measured with a mold hardness tester. Care was taken to hold these variables constant within controllable limits.

The sand mixture was put in the pattern flask and the molds were hand rammed with the probes in place. The gas composition, pressure and temperature probes were fixed exactly 1/8" from the base of the cylindrical cast. This was the closest they could be positioned without the molten metal plugging the tubes.

C.3 Metal Composition and Pouring

The metal was melted in a 100 kW, high-frequency induction furnace. Commercially pure pig iron was charged and melted in the furnace and chemical adjustments were made to the molten pool. Charcoal was added on top of the molten pool to keep a reducing atmosphere inside the furnace. The metal composition is shown in Table C.1.

Table C.1 Metal composition of gray iron used in experiments.

Element	Percentage
Carbon	3.5%
Silicon	1.8%
Manganese	0.7%
Phosphorus	0.12%
Sulfur	0.12%

The pouring temperature was recorded using a thermocouple. Gas composition data was recorded for about 15 min. from the time of pouring. A sample injection was taken for gas

chromatographic analyses, after the gas compositions reached steady state as measured by the mass spectrometer.

C.4 Statistical Design

The number of experiments N needed to conclusively prove the effect of a particular variable depends on the standard deviation δ and the value of the possible real effect we are looking for, Δ , where $N=16 \delta^2/\Delta^2$. For our purposes using the maximum standard deviation of 1.7% (see next section) and calling effects greater than 2.5% as significant, the number of experiments required is 7.4 without repetitions. Including repetitions at least 16 experiments were required. A two-level factorial design involving four variables and sixteen experiments would be able to detect the effect of all the four variables and their interaction effects. The high and low levels of the four variables were recommended by the Mold-Metal Interface Committee of the American Foundrymen Society.

C.5 Reproducibility of the Experiment

The reproducibility of the results using this experimental setup is illustrated in Figures C.2 and C.3. Tests 1, 2 and 3 in Figure C.2 represent three molds that were prepared using the same sand which contained the same amount of seacoal and cellulose. The moisture level and the pouring temperature were also kept constant so these three molds were identical and should theoretically have had the same gas atmosphere. The difference in gas atmosphere in test 1, 2 and 3, represents the variability of the results due to experimental error and slight changes in some of the variables. The variance in gas compositions in Figure C.3 is summarized in Table C.2. The standard deviations are shown in Table C.3.

Figure C.2 Reproducibility of the Gas Compositions at the Mold-Metal Interface.

Table C.2. Variance in experimental results from tests 1, 2 and 3

Time min.	Variance					
	H ₂	N ₂	CO	O ₂	CH ₄	CO ₂
5	2.14	0.00	1.70	0.03	0.72	0.01
7	3.62	0.00	2.51	0.00	0.51	0.05
8	2.17	0.00	0.74	0.00	0.50	0.05
9	3.26	0.00	0.71	0.00	0.52	0.04
Average Variance	2.80	0.00	1.41	0.01	0.56	0.04

The standard deviation in these three experiments was small. The data points collected in the first five minutes of test 1 were not used for comparison as this test was done with a slightly different gas collection system and had a different time lag. But after the first five minutes the system reached a steady state and this part of the data can still be used for comparison. There was a very small drop in the carbon content caused by burning of the carbon when the sand was used again in tests 2 and 3.

Figure C.3 Reproducibility of the Gas Compositions at the Mold-Metal Interface.

Table C.3. Standard deviation of experimental results from tests 1, 2 and 3

Time min.	Standard Deviation					
	H ₂	N ₂	CO	O ₂	CH ₄	CO ₂
5	1.46	0.06	1.30	0.17	0.85	0.12
7	1.90	0.01	1.58	0.05	0.71	0.22
8	1.47	0.00	0.86	0.03	0.70	0.23
9	1.81	0.00	0.84	0.01	0.72	0.21
Average Deviation	1.66	0.02	1.15	0.06	0.75	0.19

C.6. Free Energy Calculation for a Test Case

A widely-accepted algorithm for calculating chemical equilibrium is the NASA method (Gordon and McBride, 1962) which was modified to include a database management system by Kirkpatrick and Pike (1992). The program is called CHEMQ and was used to calculate the chemical equilibrium compositions for this system. The program was verified with a test case as shown in Pattabhi (1995). A simplified version of the problem studied by Damkohler and Edse (1943) and reviewed by Smith and Missen (1982), was used as a test case to check the NASA method. The system consists of carbon dioxide, nitrogen, water, carbon monoxide, oxygen, nitrogen monoxide and hydrogen at 2200K and 40 atmospheres produced by the combustion of propane in stoichiometric proportion of air. Due to the high temperature the system would behave ideally and the reactions would reach Equilibrium. The results calculated by CHEMQ agree well with those of Smith and Missen as seen in Table C.4.

Table C.4. Comparison of Chemq's Results for the Test Case With Smith and Missens.

<i>Species</i>	<i>Chemq</i>	<i>Smith & Missen</i>
CO	0.003	0.003
CO ₂	0.108	0.108
H	2.00E-05	0
H ₂	0.001	0.001
H ₂ O	0.147	0.147
NO	0.001	0.001
N ₂	0.7388	0.739
O	1.00E-05	0
OH	0.0007	0
O ₂	0.0012	0.001

C.7 References

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APPENDIX D - Experimental Results for Interfacial Atmosphere Measurements

D.1 Statistical Design

The objective was to measure the effect of certain variables on the gas composition at the mold-metal interface. The important variables in this system include metal composition, sand composition, mold properties and pouring temperature. Not all variables were expected to affect gas composition. For instance, AFS grain fineness number certainly impacts mechanical penetration but has no obvious impact on the chemical reactions.

Four variables and their range of values were recommended by the Mold-Metal Interface Committee of the American Foundrymen Society. These were seacoal, cellulose, moisture and pouring temperature. The experimental design is shown in Table D.1. The effects measured were gas composition (CO , H_2 , N_2 , O_2 , CH_4 and CO_2), temperature and pressure.

Table D.1. Statistically designed experimental grid showing the variables with high and low values.

Mold #	MOISTURE %	SEACOAL %	CELLULOSE %	TEMPERATURE °C
Mold 1	3.7	4.9	0.5	1440
Mold 2	3.7	4.9	0.5	1357
Mold 3	3.7	4.9	0.2	1440
Mold 4	3.7	4.9	0.2	1357
Mold 5	3.7	2.1	0.5	1357
Mold 6	3.7	2.1	0.5	1440
Mold 7	3.7	2.1	0.2	1440
Mold 8	3.7	2.1	0.2	1357
Mold 9	2.3	4.9	0.5	1440
Mold 10	2.3	4.9	0.5	1357
Mold 11	2.3	4.9	0.2	1440
Mold 12	2.3	4.9	0.2	1357
Mold 13	2.3	2.1	0.5	1440
Mold 14	2.3	2.1	0.5	1357
Mold 16	2.3	2.1	0.2	1440

Molds 1-16 were the designed experiments. Others were also conducted. Blank 1 and 2 were molds with no carbon addition. Mold 19 used a phenolic resin with pepset as a catalyst. Its purpose was to probe the differences between resin-bonded and clay-bonded molds. Nonvented 1-3 were poured with the casting cavity completely covered up with a block of sand to see if venting the top had a significant effect on composition. Molds 17 and 18 were duplicates of the nonvented molds made for comparison.

D.2 Mold Properties

The mold properties and pouring temperatures of the actual experiments are shown in Table D.2. It was difficult to hit the target values exactly. The cellulose contents were contents were not controlled sufficiently to use them in the analysis.

Table D.2. Properties of the molds made for gas composition analysis.

<i>Mold #</i>	<i>Mold Hardness</i>	<i>Compactability %</i>	<i>AFS Gas Permeability</i>	<i>Moisture %</i>	<i>Seacoal %</i>	<i>Cellulose %</i>	<i>Pouring Temp. °C</i>
<i>Blank 1</i>	85	35	105.4	3.3	-	-	1397
<i>Blank 2</i>	85	30	119.0	2.8	-	-	1400
<i>Mold 1</i>	78	40	112.1	4.4	4.8	1.2	1395
<i>Mold 2</i>	79	30	97.0	4.2	4.9	1.5	1358
<i>Mold 3</i>	82	30	94.0	3.2	5.1	1.3	1443
<i>Mold 4</i>	84	25	103.7	3.4	4.8	1.1	1357
<i>Mold 5</i>	83	35	106.1	4.2	1.7	1.2	1359
<i>Mold 6</i>	88	35	107.4	4.3	2.2	1.1	1415
<i>Mold 7</i>	84	35	89.4	4.1	2.2	1.1	1440
<i>Mold 8</i>	84	30	96.9	4.3	2.1	1.1	1364
<i>Mold 9</i>	77	15	94.0	2.3	5.0	1.5	1452
<i>Mold 10</i>	79	30	89.8	2.9	4.7	1.1	1350
<i>Mold 11</i>	83	25	107.4	2.5	4.8	.9	1436
<i>Mold 12</i>	81	25	79.2	3.2	4.7	1.2	1349
<i>Mold 13</i>	80	25	127.6	2.9	2.1	1.4	1424
<i>Mold 14</i>				2.8	2.2	1.1	1368
<i>Mold 15</i>	88	30	129.6	2.9	2.1	.9	1420
<i>Mold 16</i>	83	35	114.3	3.1	2.1	1.0	1358
<i>Mold 17</i>	90	25	121.7	2.7	4.5	1.3	1393
<i>Mold 18</i>	88	30	99.4	2.9	-	-	1460
<i>Mold 19</i>	-	Pepset	Mold	-	-	-	1352
<i>Non Vented 1</i>	87	25	85.9	3.8	-	-	1440
<i>Non Vented 2</i>	88	35	82.9	4.5	5.0	1.3	1446
<i>Non Vented 3</i>	89	30	95.0	4.1	4.5	1.2	1389

D.3 Interfacial Gas Composition

Representative gas composition profiles are shown in Figure D.1 (Blank 1, no carbon), Figure D.2 (Mold 2, high seacoal) and Figure D.3 (Mold 8, low seacoal). These are real-time compositions where the time lag and mixing effects were eliminated by correcting the raw data. The method for transforming the raw data is described in Pattabhi (1995).

The main interfacial gases were CO and H₂. N₂ and O₂ originally at the interface were pushed out of the mold by large volumes of steam within 2 minutes of pouring. Some of the O₂ may have also been removed by reaction with carbon. CO₂ and CH₄ were also formed in much smaller quantities.

Figure D.1. Gas composition in a mold without seacoal additions (Blank 1).

Figure D.2. Gas composition in a mold with 4.9% seacoal additions (Mold 2).

Figure D.3. Gas composition in a mold with 2.1% seacoal additions (Mold 8).

The gas compositions changed with time so it was necessary to compare at a representative point in time. Seven minutes after pouring was used since an apparent equilibrium was achieved in most experiments by this time. The gas compositions at each design level are shown in Table D.3. The high levels are represented by "+1" and the low levels by "-1". X1; X2, X3 and X4 are the four variables moisture, seacoal, cellulose and pouring temperature. The cellulose content was not controlled well and should show no significant effect.

Table D.3. Mold-metal interface gas composition at different levels.

	Moisture Seacoal Cellulose Temperature				Gas composition at time = 7 minutes.						
	X1	X2	X3	X4	H2	N2	CO	O2	CH4	CO2	Total
Mold 1	1	1	1	1	44.72	0.00	48.19	0.17	1.75	0.69	95.52
Mold 2	1	1	1	-1	50.03	0.00	38.34	0.15	3.68	0.65	92.86
Mold 3	1	1	-1	1	55.15	0.00	35.53	0.00	2.32	0.69	93.68
Mold 4	1	1	-1	-1	51.25	0.00	40.05	0.00	2.77	0.48	94.55
Mold 5	1	-1	1	-1	33.12	0.00	57.86	0.61	2.40	1.23	95.22
Mold 6	1	-1	1	1	46.33	0.00	45.86	0.10	1.79	1.06	95.13
Mold 7	1	-1	-1	1	47.08	0.00	44.61	0.00	1.82	1.38	94.90
Mold 8	1	-1	-1	-1	41.61	0.00	50.91	0.00	2.10	1.15	95.77
Mold 9	-1	1	1	1	44.68	0.00	46.63	0.60	2.30	0.41	94.63
Mold 10	-1	1	1	-1	43.08	0.00	47.75	0.13	3.37	0.59	94.92
Mold 11	-1	1	-1	1	46.76	0.00	44.29	0.26	2.33	0.72	94.35
Mold 12	-1	1	-1	-1	46.19	0.00	46.33	0.00	3.21	0.20	95.93
Mold 13	-1	-1	1	1	42.63	0.59	38.55	2.61	1.87	1.38	87.63
Mold 14	-1	-1	1	-1	42.07	0.00	47.69	0.00	2.61	2.23	94.59
Mold 15	-1	-1	-1	1	48.91	0.00	41.70	0.45	2.09	0.61	93.75
Mold 16	-1	-1	-1	-1	46.50	0.00	45.30	0.03	2.27	0.92	95.02

Table D.4 shows the direct effect of the variables on the gas composition along with the standard deviation of those measurements and the smallest effect that can be called significant. The effect is calculated by comparing the average of a measurement at each level (Hendrix, 1979). For example, to calculate the effect of moisture on the H_2 concentration:

$$\text{Effect} = (\Sigma \% H_2 \text{ at "+1" levels} - \Sigma \% H_2 \text{ at "-1" levels})/8 = 1.06\%$$

This value is not significant. Significant effects are designated with an (s). Even though cellulose shows significant effects for CO and H_2 these are not highlighted because there was little control on cellulose level. Significant effects on O_2 and N_2 are also discounted because the levels at 7 minutes are very low.

Table D.4. Comparison of the effect of variables on gases with significant effects.

Variable	Effects of Variables on Gases					
	H_2	N_2	CO	O_2	CH_4	CO_2
Moisture	1.06	-0.07	0.39	-0.38	-0.18	0.03
Cellulose	-4.60 (s)	0.07	2.77(s)	0.45	0.11	0.26
Seacoal	4.20 (s)	-0.07	-3.17(s)	-0.31	0.60	-0.69(s)
Temperature	2.80 (s)	0.07	-3.61(s)	0.41	-0.77	-0.07
Standard Deviation	1.66	0.02	1.15	0.06	0.75	0.19
Significant Effects	2.34	0.03	1.63	0.08	1.10	0.27

Increases in seacoal and temperature had the effect of increasing the H_2 to CO ratio. Seacoal decreases the amount of CO_2 formed which decreases the oxidizing potential of the atmosphere. Overall, the effects of these variables on the interfacial gas composition was small and probably unimportant in affecting chemical penetration.

While adding carbon to the sand in large amounts is unnecessary to maintain a reducing atmosphere, not adding carbon did produce a transient oxidizing atmosphere. Figure D.4 shows the CO_2 to CO ratio for Blank 1, Mold 2 and Mold 8 with time. These are no-carbon, low-carbon and high-carbon molds. According to Darken's Fe-Si-O equilibrium diagram which was verified by Colligan, Van Vlack and Flinn (1958) no oxidation of iron will occur for CO_2/CO less than 0.1 and a temperature above 1200°C. For molds with carbon additions the ratio never exceeded 0.1. However, for the blank molds, the ratio did exceed 0.1 for a few minutes. Still, no penetration defects were seen on the castings. Presumably, the carbon in gray iron acted as a sacrificial element for oxidation.

Phenolic Urethane Mold:

The interfacial gas composition of the resin-bonded mold (Figure D.5) was similar to the green sand molds in that CO and H_2 were the dominant gases. There was about 7-10% CH_4 and almost no CO_2 formation. This indicates a more reducing atmosphere.

Gas Chromatography Results:

The gas chromatograph showed that no N_2 or O_2 was present after a few minutes. The 28 mass peak could then only be attributed to CO . The chromatograph could not be used to measure overall composition since hydrogen could not be measured accurately.

Figure D.4. Carbon dioxide and carbon monoxide ratio for three molds as a function of time.

Figure D.5. Gas composition in a PEPSET mold (Mold 19).

Water Vapor Content:

Although water is an extremely important component of the gas, it could not be measured with the mass spectrometer since it condensed on the internals and created an excessive background signal. For some experiments an in-line humidity meter was used. Table D.5 shows that the moisture content of the interfacial gas was about 2 mole % after several minutes.

Table D.5. Moisture content of the gas sampled from the mold metal interface.

Mold #	Relative Humidity %	Temperature °C	Moisture mole %
Mold 2	76.67	21	2.23
Mold 3	78.84	16	2.23
Mold 4	68.07	17	1.98
Mold 9	62.78	18	1.82

D.4 Interfacial Temperature

The temperature profiles at 1/8" from the mold metal interface of green sand molds are shown in Figure D.6. The temperature dropped below the melting point of cast iron about a minute after pouring. The temperature profiles that are shown here are similar to those reported by other investigators (Wagner, 1979, Emmons and Bach, 1955, Levelink and Julien, 1973, and Owusu and Draper, 1978). No attempt was made to statistically correlate the temperature with design variables.

Figure D.6. Temperature profile at 1/8" from the mold-metal interface.

D.5 Interfacial Pressure

The pressure increase at the mold-metal interface was about 0.01 psig, close to atmospheric pressure. There was no increase in pressure caused as a result of closing the top of the mold. These results suggest that gases generated at the mold-metal interface were removed by flushing of the mold at the rate at which they were generated. Hence there was no accumulation of gases at the mold-metal interface. Owusu and Draper (1978) and Wagner (1979) reported similar pressures at the mold-metal interface.

D.6 - Chemical Equilibrium Calculation by Free Energy Minimization

The mold-metal interface is at an extremely high temperature compared to most chemical reaction processes. In fact, iron is a common catalyst to speed up the rates of the reactions that occur at the interface. It might be assumed that the measured gas compositions are the equilibrium amounts. This can be checked by calculating the compositions at the mold-metal interface based on an assumption of chemical equilibrium, and to compare these compositions to the actual compositions at the mold-metal interface.

D.6.1 Basis for Calculation

In order to calculate the equilibrium compositions at the mold-metal interface it is necessary to know the temperature, pressure and the initial composition of the system. For the purposes of the calculation the following assumptions were made:

- The whole system is at the pouring temperature of the metal and one atmosphere pressure.
- The metal, sand and the air trapped in the pores of the sand are all completely mixed and the system was assumed to be homogenous.
- The composition of the metal and the sand is the same as the original composition before pouring.
- The volume of air trapped in the pores of the sand is equal to the pore volume of the packed sand.
- The system is isolated and there is no inflow or out flow of mass or energy.

The pore volume of the sand was estimated from the particle density of the sand grains and the bulk density of packed sand with a mold hardness of 85. A basis of 1:1 by volume of the metal and the sand was used to calculate the overall composition of the various reactants shown in Table D.6.

D.6.2 Results of the Calculation

Tables D.7 and D.8 compare the equilibrium and experimental compositions at seven minutes after pouring for cereal and non-cereal molds respectively. There is a difference in compositions but the agreement is still fairly good considering the assumptions made. Flushing the mold by steam produced at the interface displaces most of the initial air trapped in the mold. Hence the system no longer behaves like a batch system, which is one of the assumptions made. Also, a major source of carbon is from the metal and the rate of the reactions at the interface are probably diffusion controlled. So for an ideal model the heat and mass transfer effects on the

reactions at the interface have to be considered. In the light of these facts the agreement between the predicted and experimental compositions is good.

Table D.6. Initial composition of reactants at the mold-metal interface.

<i>Reactant</i>	<i>Chemical Formula</i>	<i>Initial Weight %</i>
Metal - Gray Iron (l)	$\text{Fe}_1\text{C}_{0.173}\text{Si}_{0.038}\text{P}_{0.02}\text{S}_{0.02}$	81.155%
Nitrogen(g)	N_2	0.004%
Oxygen (g)	O_2	0.002%
Water (l)	H_2O	0.672%
Seacoal (s)	$\text{C}_1\text{H}_{0.4}\text{O}_{0.1}$	0.89%
Cellulose (s)	$\text{C}_6\text{H}_{10}\text{O}_5$	0.091%
Western Bentonite (s)	SiO_2	1.09%
Sand (s)	SiO_2	16.096%

Table D.7. Comparison of equilibrium composition of cereal molds with experimental data.

<i>Species</i>	<i>Mold 13, 1440°C</i>		<i>Mold 14, 1357°C</i>	
	<i>Chemq</i>	<i>Exp.</i>	<i>Chemq</i>	<i>Exp.</i>
CH_4	0.03	1.87	0.08	2.61
CO	42.26	38.55	14.64	47.69
HCP	0.94	-	0.93	
H_2	54.33	42.63	80.07	42.07
H_2S	0.05	-	0.19	
N_2	0.1	0.59	0.15	0
O_2	-	2.61	-	0
PN	0.13	-	0.15	
PS	1.82	-	3.40	
P_2	0.34	-	0.39	
CO_2	-	1.38	-	2.23

The deviation of the thermodynamic equilibrium compositions from the actual interface composition is a lot more in the case when the calculations are done at 1357°C as compared to 1400°C. The reason for this large difference might be that at 1357°C the metal is a lot closer to its melting point of 1250°C; there might be a solid skin formed at the interface that prevents proper contact of the metal, sand and the gases. The system is farther from equilibrium at 1357°C as compared to 1400°C.

The volume of gas in the mold increases over a thousand times from 0.178 liters initially to 253 liters. This means that the additional gas escapes through the sand and very effectively flushes the mold. There was no carbon dioxide formed at equilibrium. A very small amount of carbon dioxide was found in the experiments. The relatively large carbon dioxide peak that disappears within ten minutes after pouring in the case of non-cereal molds, is not predicted by the equilibrium calculations as it is only a transient effect. There was no oxygen or water left behind at the mold

metal interface as it was completely reacted in the calculations. In conclusion, free energy calculations can help us get useful estimates of the compositions at the mold-metal interface.

Table D.8. Comparison of equilibrium composition of non-cereal molds with experimental data.

Species	Blank Mold, 1440°C		Blank Mold, 1357°C	
	Chemq	Exp.	Chemq	Exp.
CH ₄	0.04	0.62	0.06	0.65
CO	42.58	50.6	14.76	64.7
HCP	1.17	-	1.16	
H ₂	51.58	45.6	76.38	30.9
H ₂ S	0.09	-	0.26	
N ₂	0.17	0	0.13	0
O ₂	-	0.1	-	0
PN	0.26	-	0.19	
PS	3.5	-	6.42	
P ₂	0.61	-	0.64	
CO ₂	-	0.34	-	0.83

D.6.3 Effect of Water to Metal Ratio on Equilibrium Compositions

The main reactants at the mold-metal interface are metal and water. All the other reactants are present only in small quantities. Water is also present in small quantities compared to the metal but it is still important as it is the only oxidizing gas available. The oxygen initially present in the air trapped in the sand is in extremely small quantities and gets flushed out by the steam. Hence an important variable that would determine the reaction products is the water to metal ratio which is also approximately equal to the water to carbon ratio. This ratio is constantly varying at the mold-metal interface. Immediately after pouring, the steam that is generated completely envelops the metal and hence this ratio would be at its maximum. A little later the amount of water at the interface reduces as it is removed by reaction with the metal and is also flushed out. Hence the mold starts drying-out.

An increase in the water to metal ratio makes the gas atmosphere more oxidizing and increases the amount of oxidation products formed. The main oxidation products that are formed are carbon monoxide, carbon dioxide and iron oxide. Carbon monoxide exerts a reducing atmosphere and is not of interest here. However, the formation of carbon dioxide and iron oxide would indicate that there is a severe oxidizing atmosphere and a chance of penetration. Using chemical equilibrium calculations the change in equilibrium composition of carbon dioxide and iron oxide formed with changes in this ratio is shown for a mold with no cereal additions and for a mold with 2.1% cereal additions in Figures D.7 and D.8 respectively.

Clearly more carbon dioxide and iron oxide are formed as the gray iron to water ratio decreases. It is interesting to note that as the water to iron ratio increases, carbon dioxide is first formed which is followed by a region where both the oxides are formed. Thus, if iron oxide is to be formed then carbon dioxide must also be formed simultaneously. From the mold experiments we know that there is very little carbon dioxide produced in molds with cereal additions. In these molds there can be no iron oxide formation and hence there can be no chemical penetration.

Figure D.7. Mole fraction FeO, CO₂ formed versus Fe:H₂O ratio without cereal addition.

Figure D.8. Mole fraction FeO, CO₂ formed versus Fe:H₂O ratio 2.1% seacoal addition.

Comparing Figure D.7 and D.8 it is clear that the water to iron ratio required to form a specific percent of carbon dioxide increases slightly as a result of adding 2.1% of cereal to the sand. In the case of non-cereal molds we know that there is a transient formation of carbon dioxide so we may or may not have iron oxide formation and hence chemical penetration. Since there was no penetration seen in the experiments even in the case of the blank molds, we can safely conclude that there is no chemical penetration in gray iron castings made in green sand molds.

D.7 References

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APPENDIX E - Physical Chemistry of Surfaces

E.1 Contact Angle

Penetration of liquid metal into the void space of the molding aggregate can be described by the phenomenon of capillary rise or depression with the use of Young and Laplace equation (Adamson, 1988). Figure E.1 shows the difference between the behavior of a liquid in contact with a solid capillary tube is marked by the rise or depression of the curved meniscus. As for the case for a concave meniscus, the liquid lies parallel to the capillary wall and is constrained to the wall by its surface tension. For this condition, the liquid wets the solid capillary tube. For a convex meniscus, the liquid is not constrained to the capillary wall and the pressure difference across the liquid surface is such that the pressure in the liquid is greater than in the gas phase. For this case, the liquid is considered non-wetting.

Young and Laplace recognized that the molecular attractive forces in the liquid surface would create a pressure difference across the curved interface (Davies, 1961). To formulate this pressure difference across the curved surface, consider a gas bubble of radius r . If the gas bubble is enlarged by an amount dr , the work required is $8\pi r\gamma dr$. Now, instead of changing the curved surface of the gas bubble by adding or removing particles, the surface is changed by an external pressure P_s . Hence, the work done to change the size of the surface is $P_s dV$. Substituting for the volumetric change of the surface and equating to the work of changing the radius gives:

Figure E.1. Capillary rise (a) and depression (b). (a) shows a liquid that is considered to be wetting while (b) shows the case for a liquid that is non-wetting.

$$P_s = \frac{2\gamma}{r} \quad \text{Eq. E.1}$$

However, the curved surface of the capillary tube is restrained by the internal walls. If one considers the meniscus of the liquid as part of a spherical drop of radius r , the liquid surface is tangential to the solid inner walls of the tube and the contact angle θ is zero. Since the solid material of the inner walls can affect equilibrium conditions, the contact angle may be greater than zero. Assuming that the meniscus is still spherical in shape, one can write:

$$r = r_1 \cos \theta \quad \text{Eq. E.2}$$

Substituting r in equation E.1 with r_1 and γ is the surface energy between the liquid and vapor phase gives:

$$P_s = 2\gamma_{LV} \cos \theta / r \quad \text{Eq. E.3}$$

Mathematical analysis of equation E.3 shows that:

when $\theta < 90^\circ$, $P_s > 0$ indicating wetting behavior of the liquid

when $\theta > 90^\circ$, $P_s < 0$ indicating non-wetting behavior of the liquid

E.2 Sessile Drop Method

Within the bulk of a pure liquid metal, individual atoms are attracted to each other because of an equal intermolecular force balance between the atoms. A surface is defined as a region where there is an asymmetrical force field separating the effect of the metallic atoms in its liquid and vapor state. The net resultant force of the surface atoms is from the balance between the liquid atoms leaving the monolayer of the surface and the intermolecular forces of the bulk that attracts the vapor atoms back to the monolayer surface.

The most accurate technique presently available for measuring surface tension, particularly at high temperature, is the sessile drop method. This method has been successfully used in the evaluation of particulates for composite materials. In the sessile drop method, a metal sample is placed on a higher melting temperature material, referred to as the substrate, and is heated until the sample becomes a molten liquid droplet. The final shape of the static drop, familiarly referred to as a sessile drop, can be determined by the force balance that produces a sphere by minimizing the surface free energy of the liquid and the gravitational force of the droplet on the surface of a substrate that tends to flatten the droplet (Davies, 1961). The force balance between the surface tension and gravity intrinsically gives the sessile drop an elliptical shape in appearance for a non-wetting liquid.

The equilibrium configuration of a non-wetting liquid droplet resting on a flat, chemically inert solid surface is determined by the surface tension relationship between the solid and vapor, liquid and solid, and liquid and vapor, assuming that the system is saturated with the liquid vapor as schematically shown in figure E.2. The equilibrium balance, in terms of surface tension and contact angle, can be expressed by Young's equation:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad \text{Eq. E.4}$$

where γ_{LV} is the liquid/vapor surface tension, γ_{SV} is the solid/vapor surface tension, γ_{SL} is the liquid/solid surface tension, and θ is the contact angle. Though θ can be measured directly and γ_{LV} determined from the shape of the droplet, the values of γ_{SV} and γ_{SL} cannot be easily determined.

Figure E.2. Surface energy balance for the liquid metal -- solid silica system.

The contact angle can be used as a parameter in determining the wetting characteristics of a liquid metal on ceramic substrates. If the contact angle is greater than 90° , the liquid metal is considered non-wetting. On the contrary (i.e. when the contact angle is less than 90°), the liquid metal is considered to be wetting. The degree of wettability is a function of temperature and surface roughness.

E.3 Surface Energy of Cast Iron

When a solute is added to the bulk liquid, the surface tension as well as the contact angle changes as result of the intermolecular forces between the solute atoms and solvent atoms. For the case where $\gamma_{LV}(\text{Bulk}) > \gamma_{LV}(\text{solute})$ and depending on the total free energy of the system, small additions of elements generally decrease the surface energy of the metal. If the change in surface energy is significant, the solute additive is said to be surface active. For binary iron alloys, this is true for metallic and non-metallic additions as shown in Figure E.3 (Allen, 1972).

Alloying elements change the surface tension of cast iron. Extensive research performed by Washchenko and Rudoy (1962) on cast iron showed that carbon, silicon, manganese, sulfur, phosphorus, and magnesium additions have significant effects. Figure E.4 shows the surface tension dependence of carbon and silicon. It can be seen from Figure E.4 that for a 0.1% Si alloy, the minimum surface tension occurs at the eutectic point of 4.3% carbon. As the silicon content increases, the minimum surface tension shifts to the left, corresponding to a lower carbon content. This shift is also observed for the eutectic point of the iron-carbon-silicon phase diagram. Also, Figure E.4 shows that as the carbon content decreases, the surface tension increases.

In Figure E.5, it can be seen that the influence of manganese is significant at contents above 1.5% Mn. Below this level, manganese is neutralized by sulfur because of the formation of MnS, which is insoluble in cast iron. Sulfur, on the other hand, is known to be a surface active element in cast iron. As shown in Figure E.6, the surface tension is strongly dependent on the sulfur content and logarithmically decays with increasing sulfur content. Addition of phosphorus, as shown Figure E.7, has little influence on the surface tension of cast iron. The surface energy effect of manganese, sulfur, and phosphorus is in line with the data for binary iron alloys shown in Figure E.3.

Figure E.3. Effect of various elements on the surface energy of liquid iron at 1550-1570°C (Allen, 1972)

Figure E.4. The effect of silicon on the surface tension for varying carbon concentrations. (Washchenko and Rudoy, 1962)

Figure E.5. The effect of manganese on the surface tension of cast iron. (Washchenko and Rudoy, 1962)

Figure E.6. The effect of sulfur on the surface tension of cast iron. (Washchenko and Rudoy, 1962)

Figure E.7. The effect of phosphorus on the surface tension of cast iron. (Washchenko and Rudoy, 1962)

Figure E.8. The effect of magnesium on the surface tension of cast iron (Washchenko and Rudoy, 1962).

Figure E.9. Critical contact angle and oxygen concentration required for wetting (Kaptay and Stefanescu, 1991).

The effect of magnesium used for the production of spheroidal cast iron has a very characteristic effect of the surface tension as shown in Figure E.8. However, several factors have to be considered in evaluating the influence on magnesium additions. Magnesium is reactive with sulfur and dissolved oxygen. The formation of MgS and MgO , which are both insoluble in cast iron, will increase the surface tension of cast iron by removing the surface active components from the liquid. This occurs up to 0.018% Mg. Beyond this content, the surface tension decreases, presumably from the solution of the remaining free magnesium (Washchenko and Rudoy, 1962).

Liquid metal penetration can be attributed to the increase in wettability due to increasing oxygen content in iron. While data on the influence of oxygen on the surface energy of cast iron could not be found in the literature, oxygen is known to affect the surface tension and contact angle

of pure iron as shown in Figure E.9. In a theoretical study on the effect of oxygen in the iron-silica system by Kaptay and Stefanescu (1991), the contact angle was calculated as a function of temperature and oxygen content in the liquid iron. Shown in Figure E.9, an iron at 1550°C dissolved with 0.006% O has a contact angle of 90°, which is the critical contact angle for wetting, is lowered to 50.7° when the oxygen level is at 0.06%.

E.4 Effect of Temperature

As the temperature of the system is increased, the atoms in the bulk liquid begin to vibrate more and escape the monolayer more frequently. The intermolecular forces holding the bulk atoms decrease allowing the bulk and the monolayer surface to expand. As result, the surface tension decreases with a rise in temperature. This has been demonstrated by several investigators for pure iron, numerous binary alloys, and cast iron alloys (Keene, 1988).

In general, surface tension decreases in a nearly linear fashion with increasing temperature (Keene, 1988), provided there is no phase changes in either bulk phase with increasing temperature. Rhee (1971) has recognized that there is a general linear relationship between the contact angle θ and temperature. The linear relation can be expressed as:

$$\cos \theta = 1 + B(T - T_{CS}) \quad \text{Eq. E.5}$$

or

$$\cos \theta = 1 + b(\gamma_{CS} - \gamma_{LV}) \quad \text{Eq. E.6}$$

where B is the slope of contact angle vs. temperature line, T_{CS} is the critical temperature for spreading, i.e. the temperature at which the contact angle approaches zero, b is the slope of the surface energy vs. temperature line, γ_{LV} is the surface energy of the liquid metal sessile drop, and γ_{CS} is the critical surface energy for spreading at T_{CS} .

Before discussing the experimental results, a qualitative analysis of Eq. E.6 is in order to demonstrate how surface tension data can be used to correlate contact angle data. Clearly, the values for the $\cos \theta$ term in either Eq. E.5 or E.6 ranges from -1 to +1. Therefore, the term $b(\gamma_{CS} - \gamma_{LV})$ from Eq. E.6 or $B(T - T_{CS})$ from Eq. E.5 must have a range between 0 and -2. In Eq. E.5, the sign of the slope, B , has to be positive since the difference in the spreading temperature and actual temperature will always be negative. If the same analysis is performed on Eq. E.6, the sign of the slope, b , will be negative since $\gamma_{LV} \leq \gamma_{CS}$. Qualitatively, using Eq. E.5 and E.6 with the data reported by Washchenko and Rudoy, an increase in the surface tension of cast iron from an increase in temperature will result in a decrease in the contact angle. However, when considering the effect of solutal additions to cast iron at constant temperature, a decrease in the surface tension will result in a decrease in the contact angle.

E.5 References

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APPENDIX F - Sessile Drop Experimental Approach

The objective of this study was to evaluate the parameters that influence the contact angle and its relationship to mechanical and chemical penetration using the sessile drop method. The following experimental variables were used to assess the role of the contact angle on metal penetration: chemical composition of the liquid metal (C, Si, Mn, P, S, and Mg), chemical composition of the sand (silica, chromite, zircon, and carbon), sand additives (seacoal, iron oxide, and western bentonite), atmosphere (neutral, oxidizing, and reducing), sand grain fineness, and superheat temperature. All of these variables investigated have been directly correlated to the cause of metal penetration defects.

F.1 Sessile Drop Sample Preparation

At the onset of this investigation, two groups of alloys were prepared. The first group, designated as synthetic grade alloys, were prepared from pure base materials for exploratory experiments to evaluate the role of chemical composition on the contact angle. The second group, labeled as commercial grade alloys, were prepared from commercial high grade pig iron and alloy additions were made with foundry grade alloys. These alloys were used for the majority of the experiments since the results obtained from this study would closely represent the surface energy conditions experienced during actual casting operations.

Both types of sample materials were prepared either in a resistance furnace or in an induction furnace. The synthetic grade alloys prepared were based exclusively on pure elements. The second type, commercial grade alloys, was prepared from high purity pig iron. After melting in either furnace, alloying elements were added to the melt, and then a 5 mm diameter quartz tube with a suction bulb attached to one end was inserted into the melt. A cylindrical rod, approximately 5-8 cm in length, was withdrawn for preparation of the sessile drop sample. After vacuum drawing the cylindrical rods, the remaining melt was poured into a copper mold for chemical analysis performed with a Spectro spectrometer. Chemical compositions for exploratory experiments are given in Table F.1. Discs, 5 mm high and 5 mm in diameter were sectioned from these rods for the sessile drop experiment. Before each experiment the metal sample was polished using fine emery grinding paper with 97% isopropyl alcohol, to remove any oxides on the surface. The sample was then dried in acetone and immediately placed on the substrate.

For the statistical array of experiments, four base alloys were prepared with high purity pig iron in a 50 lb. 100kW high frequency induction furnace. The carbon and silicon contents were adjusted according to the experimental array before tapping the furnace and casting into a cylindrical copper mold. The bars were fractured into 150-225 gram samples. Sixteen samples were then remelted in a 100 ml alumina crucible using a low frequency induction furnace. The chemical composition of each sample was adjusted according to the paired rows of the experimental array. Sessile drop preparation followed the same procedure as previously described.

Several types of sand substrates were used to evaluate the role of molding aggregate on the contact angle of several iron alloys. The sands used are listed in Table F.2 along with sieve analysis. The chemical composition for chromite and silica sand is reported in Table F.3. For experiments using loose granular sand, sand was placed in a 35mm by 6mm circular crucible. For substrates containing no clay binder additives, the crucible was filled with the dry sand, leveled, and then sonically vibrated for 5 minutes. Additional sand was added to the surface, leveled, and vibrated for an additional 5 minutes. This step was repeated two more times.

For the substrates containing clay binders, dry sand and clay binder were added into a bowl and thoroughly mixed. Roughly 5-10% water was added to the bowl and vigorously mixed for 10 minutes. The sand/clay binder mixture was then hand packed, similar to green sand molding, into the circular alumina crucible and leveled. The packed crucible was then dried in a furnace at 100°C for 4 hours to remove the excess water.

Table F.1. Chemical analysis (wt%) of ferrous alloys

Alloy	C	Si	Mn	P	S	Mg
Alloys prepared from high purity pig iron (commercial grade)						
Fe-C	3.67	0.0225	0.0086	0.013	0.0086	0
Fe-C-Si	3.68	1.25	0.0202	0.015	0.0104	0
Fe-C-Si-Mn	3.67	1.25	0.457	0.015	0.0121	0
Fe-C-Si-S	3.74	1.19	0.0189	0.016	0.1650	0
Fe-C-Si-P	3.68	1.25	0.0203	0.111	0.0155	0
Fe-C-Si-Mg	3.61	1.37	0.0213	0.014	0.0131	0.019
Alloys prepared from pure elements (synthetic grade)						
Fe-C	0.50	0.084	0.0032	0.016	0.015	0
Fe-C-Si	3.66	1.30	0.01	0.001	0.04	0
Fe-C-Si-Mn	2.88	1.42	0.42	0.002	0.03	0
Fe-C-Si-S	4.20	1.22	0.02	0.001	0.13	0
Fe-C-Si-P	3.79	1.35	0.02	0.050	0.01	0

Table F.2. Characteristics of Ceramic Materials

Material Analysis	Carbon Sand	Silica sand 108	Silica sand 71	Chromite Sand	Zircon 120
+ 30	0.04	-	0.01	0.63	0.01
- 30 + 40	1.06	0	0.03	8.76	0.02
- 40 + 50	6.79	0.08	7.89	24.70	0.11
- 50 + 70	18.31	1.25	28.60	28.49	2.41
- 70 + 100	33.94	31.76	40.48	21.02	14.98
- 100 + 140	23.70	35.40	17.99	11.10	54.74
- 140 + 200	12.73	24.42	4.71	4.26	27.33
- 200 + 270	2.98	5.96	0.26	0.76	0.38
- 270 + 325	.34	-	-	0.20	-
PAN	0.08	1.13	0.01	0.09	0.0
AFS GFN	107.9	107.7	71.0	55.3	105.5

Table F.3. Chemical composition (wt%) or specification of materials used for substrate preparation

Chromite sand		Iron oxide		Silica sand		Seacoal	
Cr ₂ O ₃	46.5	Fe	76	SiO ₂	99.779	H ₂ O	6.0 max.
SiO ₂	0.85	C	0.05	Fe ₂ O ₃	0.016	S	10.0 max.
FeO	24.5	Mn	0.51	Al ₂ O ₃	0.07	Volatiles	32-38
Al ₂ O ₃	14.87	P	0.009	TiO ₂	0.014	Fixed C	54-56
MgO	10.4	S	0.01	CaO	0.012	Ash	8.0 max.
CaO	0.15	Si	0.04	MgO	0.003		

F.2 Vacuum Furnace Method

Figure F.1 shows a schematic diagram of the Centorr furnace chamber assembly used for sessile drop experiments. The furnace chamber assembly is evacuated using a mechanical pump and diffusion pump capable of maintaining pressure down to 10^{-5} to 10^{-6} Torr (10^{-7} to 10^{-8} atm.). The furnace can operate under vacuum or in an argon atmosphere.

Before placing the sample and substrate into the furnace chamber, the specimen support was leveled using a bull's-eye level. The crucible was placed on top of the support and the chamber was then sealed. The furnace chamber was evacuated to 10^{-5} Torr and then flushed with dried argon gas for 5 minutes. The argon gas was dried by flowing the gas through a heated rare earth based copper oxide column to remove oxygen followed by two columns containing sodium hydroxide to remove carbon monoxide and magnesium perchlorate for water removal. The chamber was reevacuated, filled and flushed with argon for 5 minutes. This step was repeated before heating. After the final flushing, the temperature was rapidly increased to the melting point of the sample. The temperature was then adjusted slowly to the desired experimental condition. As soon as the experimental temperature was controlled, a series of pictures was taken in two minute intervals. The temperature was recorded for each photograph.

Figure F.1. Schematic drawing of the experimental apparatus for the measurement of the wetting angle and of the surface energy.

F.3 Tube Furnace Method

The experimental method used for the oxidizing/reducing atmosphere experiments is similar to that conducted in the vacuum furnace. The ferrous samples and ceramic substrates were prepared in the same manner as those prepared for the vacuum furnace. Figure F.2 shows the experimental setup used for the tube furnace experiments.

Figure F.2. Schematic drawing of the vacuum tube furnace.

1. Gas Cylinders	9. Gas Analyzer Probe
2. Flowmeters	10. Thermometer
3. Drierite Columns	11. Residual Gas Analyzer
4. Inert Gas Purifier	12. Tube Furnace Chamber
5. Gas Inlet Valve	13. Mullite Tube
6. Water Cooled Collar	14. Gas Outlet
7. Water Cooled End Seal	15. Viewing Port
8. Thermocouple Probe	16. Water Cooled End Seal

The sample and ceramic substrate were placed on a ceramic pedestal and carefully pushed to the center of the furnace. The end seals were attached to the water-cooled collar and a high temperature gasket sealant was applied to prevent gas leaks. The furnace was programmed with the following heating schedule: the furnace was heated to 1200°C in four hours and held at that temperature for five minutes to complete the melting of the sample and stabilize the drop. This was done since there is roughly a 50°C difference from the internal ceramic tube temperature and furnace temperature. After holding for five minutes, the temperature was quickly raised to 1350°C and held at this temperature for the duration the experiment. The furnace was then allowed to cool

to room temperature in six hours. Gas analysis of the reaction chamber atmosphere was done with a Quadrex 200 mass spectrometer. The mass spectrometer was calibrated during the heating cycle with flowing argon by measuring the atmosphere of the chamber and then closing the sampling line to record the residual atmosphere in the ionization sensor. The difference between partial pressures of residual atmosphere and the actual atmosphere gives the actual chemical composition of the reaction chamber atmosphere. This was performed several times until the vacuum pressure in the ionization sensor stabilized. During the experiment, sampling of the chamber atmosphere was taken every two minute. A photograph was taken at this time to record the shape of the sessile drop.

F.4 Contact Angle Measurements

Contact angle measurements between the sessile drop and sand substrate were performed by projecting the photograph image onto a screen and transferring that image to an Olympus C-222 Image Analyzer through a television camera. A horizontal line was drawn along the plane where sessile drop and substrate were in contact. The cursor was moved below the horizontal line and a tangent line drawn to determine the contact angle.

F.5 Furnace Validation Experiments

It was important to ensure that results of experiments performed on the Centorr furnace were equivalent to those run in the tube furnace. Consequently, a parallel experiment was conducted in the two furnaces using a synthetic Fe-3.68%C-1.25%Si alloy on a monolithic quartz substrate in an argon atmosphere. The results shown in Figure F.3 are similar, demonstrating that data obtained in the Centorr furnace can be compared with those from the tube furnace.

Figure F.3. Furnace comparison of synthetic Fe-3.68%C-1.25%Si alloy on monolithic quartz in argon atmosphere at 1235°C.

F.6 Effect of Sample Geometry

Some of the experiments performed at the beginning of the research project were run on cubical samples, while most experiments were conducted on cylindrical samples. An additional validation experiment was run in the Centorr furnace using silica sand GFN 71 as the substrate material in an argon atmosphere to compare results obtained with the two types of samples. Data in Figure F.4 show that the results are practically independent of sample geometry for the first minute. Variation in data obtained from the cubical sample could be a result of erroneous measurements since, initially, the contact angle was constant and then increased dramatically in five seconds. This observed deviation in contact angle is not encountered in surface tension work.

Generally, any changes in contact angle will occur gradually as a result of thermodynamic and kinetic effects.

Figure F.4. Comparison of contact angle for a synthetic Fe-3.68%C-1.25%Si alloy on silica sand 71 in argon atmosphere using different sample shapes.

F.7 Evaluation of Experimental Error

During experimentation on the L32 array, six experiments with Alloy 27-28 on monolithic quartz at 150°C superheat temperature were run to evaluate the experimental error in measuring the contact angle. For each experiment 18 contact angle measurements were performed at 2 minute time interval. The average contact angles over the time interval for the six experiments are given in Table F.4. It was calculated that the mean contact angle was of 122.7° with a standard deviation of 1.1°.

Table F.4. Average contact angles for individual experiments

Experiment No.	1	2	3	4	5	6
Contact Angle	125.3°	121.7°	122.5°	122.4°	122.1°	122.2°

APPENDIX G - Statistical Design for Chemical Composition Experiments

The chemical composition of iron dramatically influences the surface tension as discussed in Appendix E. However, most data collected in this area has focused on binary alloys of iron. In cast iron, there exists a variety of alloying elements used for the purpose of microstructural control of the graphite shape and type and the accompanying matrix structure. In this segment of the study, the role of minor alloying additions to cast iron, mainly C, Si, P, Mn, S, and Mg, was evaluated to determine their effect on the surface tension of iron. In the first section, alloys were prepared from high purity elements to explore the effect of the elements on the surface tension. The next section focused on commercial alloys. These alloys were used in a statistically designed experiment to study the main effect of the alloying additions and an equation formulated to predict the contact angle based on the chemical composition and superheat temperature.

G.1 Preliminary Experiments

The experimental results in terms of average contact angle for the different commercial alloys on monolithic quartz and silica sand with western bentonite additions substrate in an argon atmosphere are shown in Figure G.1. It can be seen that silicon addition increases the contact angle of the Fe-3.6%C alloy on monolithic quartz from 119 to 127°. This was an unusual observation since silicon additions reduce the surface tension as shown in Figure E.4. This would then correspond to an expected decrease in the contact angle. Though not measured, it is surmised that the observed increase in the contact angle can be attributed to the lowering of the oxygen content in the Fe-C-Si melt as compared with the Fe-C melt. Theoretical discussion by Kaptay and Stefanescu (1991) on the effect of oxygen showed that as the oxygen content in a Fe-C melt increases the contact angle decreases. Another possible influence is that of the melt superheat. Indeed, while the temperature of the drop was the same (1300°C), the Fe-C-Si alloy has a lower superheat temperature as compared with the Fe-C alloy. Effectively, as was shown in Figure 3.8, a lower superheat temperature corresponds to an increase in contact angle:

Figure G.1. Influence of minor elements on the contact angle at 1300°C for commercial purity Fe-3.68C-1.25Si alloys on monolithic quartz substrate (for comparison the data point of the Fe-3.6C alloy is also shown), and for synthetic purity Fe-C-Si alloys on silica 71 + 9% sodium bentonite.

All the minor elements used in this work, that is Mn, P, S and Mg, decrease the contact angle on monolithic quartz and on silica 71 + bentonite substrates. For discussion, the results obtained on monolithic quartz will be used since it is not well understood what the effect of western bentonite has on the contact angle. Also, the surface roughness of the sand substrate will significantly alter the true contact angle. Manganese and phosphorus showed little if any influence

on the contact angle. Both elements are in line with the findings shown in Figure E.5 and E.6 in Appendix E. Sulfur additions significantly decreased the contact angle. This was expected since sulfur is considered to be a surface active element in cast iron.

Surprisingly, magnesium showed the highest specific influence in decreasing the contact angle. It was expected that an increase in the content angle would result with the addition of magnesium. This unexpected observance in the decrease of the contact angle can be attributed to the preparation of the alloy. Initially, the liquid melt was first deoxidized by the addition of silicon. Magnesium was then added immediately afterwards. Since the melt is already deoxidized and low in sulfur content, the magnesium does not combine with oxygen and sulfur. Thus, magnesium acts as a solutal addition to the melt only and will decrease the contact angle.

G.2 Designed Experiments

An L32 factorial experimental array was used to assess the role of alloying elements on the contact angle of cast iron on monolithic quartz substrates. Preliminary results presented in Section G.1 showed that alloying elements significantly affect the contact angle. It was shown that silicon addition to a base Fe-3.6%C alloy increased the contact angle, though it was unclear if this was the result of the effect of superheat temperature (Fe-C-Si has a lower superheat temperature than Fe-C) or from the deoxidization of the base alloy by silicon. Also from this study, it was determined that magnesium has the highest influence on decreasing the contact angle followed by sulfur, manganese, and phosphorus, respectively. However, the influence of the interactions between other alloying additions in the melt could not be determined from the exploratory study. For this reason, a statistically designed experimental array was developed to determine the role and interactions of alloying additions on the contact angle.

Figure G.2 shows the main effects of the independent variables determined from a multiple regression analysis. As expected, silicon showed a positive response on the contact angle, supporting the theory that silicon controls the dissolved oxygen content of cast iron. Manganese and sulfur have a strong negative effect on the response of the contact angle. However, the contact angle response for manganese addition produced a larger effect than sulfur. This is contrary to the fact that sulfur is a stronger surface active element in cast iron than manganese. One possible explanation is the formation of MnS. At high manganese contents, manganese neutralizes the effect of sulfur, particularly at low sulfur concentrations. Thus, the effect of manganese is magnified at low sulfur levels. Carbon, phosphorus and superheat temperature have a positive but weak effect since the results fall within the standard deviation of the experiment. Phosphorus also exhibited a positive effect; though, it is unknown why phosphorus has this effect since solutal additions reduce the surface tension of cast iron based on data presented by Keene (1988). However, Levenlink and Julian (1973) has shown that the depth of penetration decreases with increasing concentrations of phosphorus. As explained in Section 3, this is because of the effect of phosphorus on the expansion of graphite.

A multiple regression model was run to predict the contact angle for the chemical compositional range used in this study. After constructing several regression models, the following mathematical model was selected based on the best root mean square and regression coefficient:

$$\theta = K - A_1 * [\%C] - A_2 * [\%Si] - A_3 * [\%S] - A_4 * [\%Mn] - A_5 * [\%P] + A_6 * T + B_1 * [\%C * \%Si] - B_2 * [\%C * T] + B_3 * [\%Si * \%S] + B_4 * [\%S * T] + B_5 * [\%Mn * \%P]$$

where [%C] = weight percent carbon

[%Si] = weight percent silicon

[%S] = weight percent sulfur

[%Mn] = weight percent manganese

[%P] = weight percent phosphorus

T = superheat temperature

and K is constant, A_1 - A_6 are the constants for the main effects, and B_1 - B_5 are the constants for the interaction effects determined from the multiple regression model. The coefficient of determination for this model is $R^2 = 0.87$ and $RMS = 2.893$. This model is satisfactory in that all factors are included into the prediction equation. The statistical equation developed in this section can be used to calculate the actual contact angle for the penetration index.

Elemental Effect on Contact Angle

Figure G.2. Plot showing main effect of alloying additions.