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CLEAN FERROUS CASTING TECHNOLOGY RESEARCH

Final Technical Report

September 29, 1993 - December 31, 1995

T. S. Piwonka, editor

January 1996

Work Performed Under Contract No. FC07-93ID13232

**For
U.S. Department of Energy
Assistant Secretary for
Energy Efficiency and Renewable Energy
Washington, DC**

MASTER

**By
The University of Alabama
Tuscaloosa, AL**

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EXECUTIVE SUMMARY

This report details the result of a thirty-month program to develop methods of making clean ferrous castings, i.e., castings free of inclusions and surface defects. The program was divided into three tasks: 1. Techniques for the Production of Clean Steel Castings, 2. Electromagnetic Removal of Inclusions from Ferrous Melts, and 3. A Study of the Causes of Metal Penetration in Sand Molds in Cast Iron.

The primary objective of the Clean Steel Castings program was to develop technology for delivering steel free from oxide macroinclusions to mold cavities. The overall objective is to improve the quality of cast steel by developing and demonstrating the technology for substantially reducing surface and sub-surface oxide defects.

Air entrainment rates from physical modeling of pouring steel were found to correlate well with the cleanliness ratings of casting poured at a participating foundry. Keeping the lip close to the pouring cup is important in reducing air entrainment with teapot and lip pour ladles. A quadrant ladle with a short round lip in combination with a slanted produced low air entrainment rates.

The use of reticulated filters on a 41-lb. carbon steel casting was found to reduce weld repair time by about 90% and saved the foundry about \$16 per casting. Gas shrouding of the pouring stream from a bottom pour ladle produced no improvement in casting quality. Modification of the shrouding system should reduce the likelihood of entrapping gas in the casting. A combination of mechanical shrouding of the pouring stream and a filter riser produced higher quality castings compared to standard practice.

The use of reticulated filters on a 900 lb. stainless castings reduced the weld repair and cleaning room time by about 65% and saved the foundry about \$985 per casting. Metal chemistry at block was found to be an important factor relating heat-to-heat quality with casting cleanliness.

The primary objective of the Electromagnetic Removal of Inclusions from Ferrous Melts program was to demonstrate the commercial feasibility of using electromagnetic fields to remove inclusions from flowing streams of liquid steel. The feasibility of the process was successfully demonstrated on the laboratory scale. However, the non-Federal sponsor of the program was unable to continue funding the project, and the project was terminated prior to the commercial demonstration.

The primary objective of the Metal Penetration in Cast Iron project was to determine the causes and cures of penetration defects occurring in cast iron poured in sand molds. The program consisted of a number of tasks, including developing an analytical model of penetration, measuring the composition of the atmosphere at the mold/metal interface, determining the contact angle between cast irons of varying compositions and various mold

aggregates, and finally writing a spread sheet program which predicts whether a given casting, mold, and metal composition is likely to suffer from penetration defects.

The program found that the atmosphere at the mold/metal interface is always reducing, and is not affected by addition of carbonaceous materials (such as seacoal and cellulose). This is because the high carbon content of cast iron provides sufficient carbon to the surface of the casting that free oxygen cannot exist in the mold (the carbon combines with any oxygen at the mold surface to form carbon monoxide). This finding verified that chemical penetration (the formation of fayalite, a mixture of iron oxide and silica, often found on steel castings) cannot exist in cast iron.

Another finding from this program was that seacoal acts to protect castings from penetration by expanding when heated, and filling up the spaces between the sand grains, so that molten metal cannot penetrate. This indicates that seacoal substitutes which are unable to expand on heating must use another mechanism to stop penetration.

A further finding was that most penetration defects in cast iron are caused by poor casting design. This occurs in internal corners, which concentrate heat and freeze after the rest of the casting. Because graphite expands on solidification, if these corners become isolated from the rest of the casting (i.e., if they freeze after the rest of the casting), the expansion of the graphite will force the metal into the sand. The cure for this is to practice directional solidification in cast iron.

Finally, a "Penetration Prognosticator" was developed and tested in commercial foundries. It is now being distributed by the American Foundrymen's Society.

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I. CLEAN CAST STEEL TECHNOLOGY

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1.0 Introduction

This report documents the results from the Clean Cast Steel Technology Program financially supported by the DOE Metal Casting Competitiveness Research Program. The primary objective of this program is to develop technology for delivering clean steel free of oxide macroinclusions to mold cavities. The overall objective is to improve the quality of cast steel by developing and demonstrating the technology for substantially reducing surface and sub-surface oxide defects.

Steel is reactive with moisture and oxygen in the atmosphere and with oxidizing slags on the metal surface. Aluminum and silicon in carbon steel react with oxygen to form oxides in the metal. Chromium and deoxidizers in stainless steel similarly react with oxygen in air. The turbulence associated with ladling and pouring mixes these oxides with the metal and exposes new surfaces to air for oxidation. These oxide macroinclusions are abrasive, refractory, detrimental to properties, and detrimental to machining operations.

These oxides can often be removed and weld repaired, but repairs and reinspection add about 25% to the direct cost of producing castings. If these defects could be substantially reduced by improved metal handling procedures, production cost savings could be realized while improving product quality.

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 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 project was 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.

2.0 Modeling of Steel Pouring Practices

Water modeling experiments were conducted to explore methods for minimizing air entrainment during pouring of steel. The use of water to model the amount of air entrainment in the pouring of steel has a solid theoretical foundation. Water is a good liquid for modeling steel flow because of the similarity in kinematic viscosity of the two liquids. Air entrainment

when pouring molten steel is expected to be similar to that observed in a full scale water model. In a limited number of casting trials, air entrainment rates from water modeling correlated well with casting cleanliness ratings from castings poured under similar conditions.

Water modeling provides a quick, inexpensive, and effective means by which the effect of various pouring techniques and conditions can be compared in their effect on air entrainment. Although the use of a full scale model of a large bottom pour or teapot ladle is often not practical, a relative comparison of different techniques and conditions can be made using smaller ladles. This can eliminate considerable guesswork and expensive casting trials.

The objective of the water modeling was to explore techniques for reducing air entrainment during pouring of metal. The principles found in the modeling literature study were used in developing the water modeling apparatus, designing the experimental matrices, and conducting trials using bottom pour, teapot, lip, and quadrant pour ladles.

2.1 Theoretical Background

Air is entrained in liquids by vortices which develop by different mechanisms. One of the mechanisms of formation of air-entraining vortices is the impingement of a fast moving liquid on a slow moving liquid, or on a solid surface. The vortices are formed by the shearing action between layers of different velocities. If the vortices are sufficiently strong, they entrain air in the vortex cores that are perpendicular to the flow. A certain minimum flow velocity of the fast moving liquid is needed to form air-entraining vortices. This is the mechanism by which air entrainment occurs in the molten steel during pouring. Air entrainment during steel pouring occurs at two locations: one, where the molten steel jet from the ladle impinges on the solid surface of the pouring basin; and the other, where the molten steel flow from the pouring basin impinges on the surface of the liquid steel column in the sprue.

2.2 Experimental Procedures

The box 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 top surface of the box into a gas collection system. This box was used to simulate the cavity of a typical sand mold.

The top of the box had several holes machined through it to allow various sprues and gating systems to extend through the top and keep an air tight seal. In all cases, commercial sprues were used in trials.

Water was poured directly from a ladle into the pouring cup and downsprue. The gating systems examined were unpressurized systems. Pressurized systems cannot be evaluated with the system because any air entrained in the pouring cup is not collected by the gas collection

system. With unpressurized systems, the water seal at the end of the down sprue traps the entrained air for collection.

During pouring, water from the ladle and air entrained with the water entered the mold box. The water collected in the mold box and caused some air displacement from the box. The entrained air and the displaced air exited the box through vents and was collected in a sealed bag. After a pouring experiment was completed, the mold was isolated from the gas collection system by a ball valve.

The total volume of air in the sealed bag was determined by pumping the air from the bag through a volumetric gas flowmeter. One rotation of the meter was equal to 0.25 cubic feet (cf) with increment marks of 0.001 cf. The total volume of air collected minus the displaced air (determined from the volume (weight) of water poured) provided a direct measurement of the volume of entrained air.

A precision strain gauge load cell was used in the ladle sling assembly so that the ladle weight could be measured and recorded throughout the pour. The difference in gross ladle weights at the beginning and end of each pour was used to calculate the total volume of water poured.

A 20 inch square by 26 inch deep acrylic bottom pour ladle was used for all of the bottom pour trials. The effective volume of the ladle above the stopper and nozzle contact line was about 4 cubic feet providing an equivalent steel capacity of about 2000 pounds. The ladle was constructed to allow various nozzle and stopper combinations to be easily interchanged for testing.

A teapot ladle shell and rotating mechanism were borrowed from a participating foundry. The steel pour weight of this lined teapot ladle was about 700 pounds. The teapot shell allowed various lip shapes and preformed ladle liners to be formed or inserted into the shell for evaluation. Manually formed teapot lips were formed using an oil based modeling clay.

A quadrant ladle was fabricated from 3/16 inch steel sheet. The ladle had a back radius of 36 inches and covered a 60 degree arc. It had a capacity of about 4 cubic feet, equivalent to a capacity of about 2000 lbs. of steel. The ladle pivoted around a steel rod under the lip that was supported on two stands over the pouring box. The before and after pour weights were determined by suspending the quadrant ladle on a load cell, using a rope sling, immediately before and after the pour. The quadrant ladle was designed to allow various lip shapes to be formed and evaluated.

2.3 Design and Analysis of Experiments

All of the water modeling trials were setup to be analyzed using ANalysis of Variance Analysis (ANOVA).¹ All of the data arrays were orthogonal (balanced), full factorial, and

triplicate runs were made for each condition. The data was statistically analyzed using commercial statistical software.

2.4 Results and Discussion

2.4.1 Bottom Pour Water Modeling Experiments

A series of casting trials was conducted at a sponsor's foundry to evaluate various pouring techniques and their relation to casting cleanliness. In one of the trials, a 4530 lb. casting was poured using the original gating design and new gating design. All other variables were held constant.

A water modeling trial was conducted to determine if a facsimile of the gating systems would produce air entrainment volumes that would correlate to the cleanliness ratings observe in the castings. This trial would provide confirmation on the connection between air entrainment and casting cleanliness and on the ability of lab scale water models to truly predict reactions on the casting floor.

The original gating system had a 2 1/2" dia. downsprue with two 2 1/2" dia. runners. The "new" system had a 2 1/2" dia. downsprue with two 3 1/2" dia. runners. It also had another 90° elbow. The gating systems for the water modeling trial were made with commercial PVC pipe and standard ells.

The variables for the water modeling trial was gating system design ("original" vs "new") and stopper opening (fully open vs throttled). The data matrix was a orthogonal full factorial L4. The water level in the bottom pour ladle was full for all tests. Approximately one cubic foot of water was poured for each test. A 2" dia. nozzle and stopper head was supplied by the foundry and used for the trial.

The ANOVA table for the L4 is listed in Table 1. This table lists the variation source, sum of squares, degrees of freedom, variance, F-ratio, significance, and contribution.

The variation sources are the main variables and any two level interactions. The sum of squares determines the influence of a particular factor on the dependent variable being measured. The degrees of freedom for a particular factor are the number of levels minus one. In almost all of the trials, only two levels of a particular factor were examined. The mean square or variance is the sum of squares divided by the degrees of freedom and is indicative of the amount of influence of the factor on the dependent variable. The F-ratio or Fisher ratio is the mean square divided by the mean square of the error or residual. The F-ratio compares the variation caused by the factor to the variation caused by the error or noise. A high F-ratio gives confidence that the factor does significantly influence the dependent variable. A significance of 0.05 or less is considered to be a good indication that the influence is not a random event. While a factor may be significant, its actual contribution to the amount of air entrainment may not be important

Table 1.
Transmission Case Gating Trial
ANOVA Table

Variation Source	Sum of Squares (SS)	Degrees of Freedom	Mean Square (Variance) (V)	F-Ratio	Significance	Contribution (%)
<hr/>						
(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
<hr/>						
(interactions)						
SO * GD	0.0014986	1	0.0014986	1.41	0.2692	----
<hr/>						
Error (residual)	0.008505	8	0.0010631			5
<hr/>						
TOTAL	0.2260812	11				100

compared to other factors. The percent contribution is calculated by subtracting the mean square of the error times the DF of the factor from SS_{factor} and dividing by the SS_{total} and multiplying by 100.

The ANOVA analysis in Table 1 indicates stopper opening as the most important factor contributing about 73% of the air entrainment. Gating design contributed about 22% to the air entrainment total. The interaction between stopper opening and gating design was not a significant factor on air entrainment. Error or residual accounted for about 5%. Figure 1 illustrates the effect of stopper opening on air entrainment. A throttled stopper opening increased the amount of air entrainment by about 100% compared to a fully open stopper. Figure 2 illustrates the effect of gating design on air entrainment. The "new" gating design resulted in about 46% increase in air entrainment compared to the original design.

Statistical analysis of the water modeling data indicates that the new gating design increased the air entrainment rate by about 46%. An increase of 115% in dirt inclusions were observed by the foundry when the new gating system was used in pouring steel castings. However, the overwhelming influence of throttling may have skewed the analysis. On a large casting, throttling may not have been necessary. Comparing the air entrainment data for the fully open nozzle position shows an increase of about 94% for the new gating design compared to the original gating design. This is more in line with the cleanliness ratings of the castings.

The water modeling air entrainment data followed the same trend as observed in the foundry casting cleanliness measurements. The foundry observed a sharp increase (about 115%) in casting inclusions with the "new" gating system compared to the original gating system. The water model showed an increase in air entrainment of about 50% when using the 2" diameter. The fully open stopper condition (a more realistic condition) shows an increase of about 100% from the original gating to the new gating system. This is close to the increase in casting inclusions observed at the foundry.

2.4.2 Teapot/Lip Pour Water Modeling Experiments

A 500 lb. ladle liner was purchased to conduct water modeling studies on a commercial ladle liner. This ladle design was being used by a participating foundry pouring high alloy castings. In the water modeling trials conducted in the previous year of this study, the lip position was varied during the pour. That is, the ladle height was initially set so that a pour could be made without adjusting the ladle height. This is not common foundry practice so lip position was fixed near (about 3.5") the pouring cup during the pour. The sprue length was varied from 5 1/4" to 10 1/4". In previous work, a few trials were conducted with 30° slanted sprues using a lip pour quadrant ladle. These trials indicated that slanted sprues reduced air entrainment. This trial considered the effect of slanted sprues on air entrainment.

The ANOVA table is listed in Table 2. Sprue length was an important factor accounting for 38% of the air entrainment. The effect of sprue length is illustrated in Figure 3. The longer sprue length increased air entrainment about 18% compared to the 5" sprue length. The longer

sprue increased the drop height and hence the velocity of the stream before impact with the pool at the bottom of the sprue. This has a direct effect on air entrainment.

Sprue angle was an important factor accounting for 35% of the air entrainment. The angled sprue increased air entrainment by about 17% compared to the straight sprue. The angled sprue also reduced the pour time by about 33% compared to the straight sprue. The pour rate was constricted only by the ability to pour the water out of the ladle. The higher pour rate with the slanted sprue produced increase turbulent flow in the ladle throat during pouring. This produced a more ragged stream impacting the pool and more air entrainment. Interaction between sprue length and sprue angle only contributed 7% to the air entrainment rate.

This trial indicates that the stream turbulence in a top pour ladle has a strong effect on air entrainment. The higher pouring rate with the slanted sprue produced much higher stream turbulence with the teapot ladle so that any benefit of the slanted sprue was negated. A teapot ladle apparently has a fixed pouring rate, as determined by the throat geometry, for smooth stream flow. A higher pouring rate produced an increasingly more turbulent stream which increases air entrainment.

2.4.3 Quadrant Ladle Water Modeling Experiments

Pouring with low metal head pressures, smooth-flowing streams with minimum impingement angles and velocities are thought to minimize air entrainment, and the reoxidation which results from entrainment.

A quadrant pour ladle was constructed and a limited series of water modeling trials were conducted. The quadrant ladle design did show some improvement in air entrainment rates compared to a teapot and bottom pour ladles used in these trials. The potential benefits of a quadrant pour ladle are that a constant rate of ladle tilt produces a constant volume of metal poured per unit of time, and the ladle lip can be maintained at a constant height above the mold throughout the pouring operation. Quadrant pour ladles usually rotate around a point near the lip, and if the tilt point can be located over the sprue, the drop height of metal into the sprue can be minimized.

A series of water modeling trials were conducted to evaluate the effect of lip shape and channel length on air entrainment. According to theory, lip shape and channel length shape should have an effect on stream shape and turbulence which in turn affects air entrainment.

Three different lip shapes were used in these trials: square, trapezoidal, and round. For open channel flow, the turbulence of water flow is directly proportional to the wetted surface of the channel. The lip shapes were selected to provide a range of wetted perimeters, round being the smallest, square being the largest, and trapezoidal falling in between. Aluminum forms were machined so that a consistent lip/channel could be formed. The cross sectional area of each form was kept constant about 6 inches square. Three different channel lengths were also examined; short, angled, and long.

Figure 1. Effect of Stopper Opening on Air Entrainment.

Figure 2. Effect of Gating Design on Air Entrainment.

Table 2.
Universal Ladle Pouring Trial
ANOVA Table

Variation Source	Sum of Squares (SS)	Degrees of Freedom	Mean Square (Variance) (V)	F-Ratio	Significance	Contribution (%)
<hr/>						
(main effects)						
Sprue Length (SL)	0.0022605	1	0.0022605	22.505	0.0015	38.1
Sprue Angle (SA)	0.0020882	1	0.0020882	20.79	0.0019	35.1
<hr/>						
(interactions)						
SL * SA	5.19E-04	1	5.19E-04	5.165	0.0527	7.4
<hr/>						
Error (residual)	8.04E-04	8	1.00E-04			19.4
TOTAL	1.0056711	11				100

Figure 3. Effect of Sprue Length on Air Entrainment.

The ANOVA analysis of the data is listed in Table 3. Sprue length was the largest contributor accounting for 40% of the air entrainment, followed by sprue angle with 17%, and channel length with 6%. The interaction of sprue angle and sprue length contributed 13% to the air entrainment rate. Error accounted for 25%.

The effect of sprue length was similar to previous trials with the longer sprue entraining more air compared to the shorter sprue as illustrated in Figure 4. A slanted sprue reduced air entrainment by about 20% compared to the straight sprue as illustrated in Figure 5. This trend is similar to other trials with lip pour ladles with a slanted sprues. The effect of channel length on air entrainment is illustrated in Figure 6. The short channel length produced an entrainment rate of about 20% less than the rate for the long channel. The longer channel length will produce more entrainment due to increased turbulence of the pouring stream.

The angled channel length was dropped from the matrix and only the two extremes (short and long) were examined. The ANOVA analysis of the data is listed in Table 4. Lip shape was the largest contributor accounting for 37% of the air entrainment, followed by sprue length with 24% sprue angle with 8%, and channel length with 1%. The interaction of sprue angle and sprue length contributed 10% to the air entrainment rate. Error accounted for 13%.

The effect of lip shape on air entrainment is illustrated in Figure 7. The square lip, which should have the greatest stream turbulence, has the highest entrainment rate, followed by the trapezoidal shape, and the round lip shape. The rounded lip shape reduced air entrainment by 38% compared to the square lip. The slanted sprue reduced entrainment compared to the straight sprue, as illustrated in Figure 8.

3.0 Lip Pour Casting Trials to Produce Castings Weighing Up To 250 lbs.

A casting trial was conducted to determine the effectiveness of filtration of reducing weld repair and machine shop time on a carbon steel transmission casting. This particular casting required a considerable amount of inclusion removal and weld repair time. It was thought that the use of ceramic filters would remove the inclusion material from the metal stream in the gating system.

The pour weight of the casting was 41 lbs. The pouring ladle was a 500 lb. teapot with a 70% alumina breastplate and spout. The molds were green sand with bonded sand cores and a shell downsprue. There was one casting per mold. All castings were poured from the same heat. Filters from two manufacturers were used in the trial and were identified as Filter #1 and Filter #2. Both filters were three inches in diameter by one inch thick reticulated partially stabilized with Filter #1, and twenty with Filter #2.

The filters were mounted in the bottom of a riser and the filtered molds were poured using the riser as a gating system. Pouring time for the standard gating system ranged from 3-5 seconds, to 4-7 seconds for both Filter #1 and Filter #2. The effectiveness of the filters was rated by the amount of time needed to weld repair the castings.

Filtered molds poured with a metal temperature of less than 2920°F typically had problems with filter priming and mold filling. For this reason minimum of 2920°F was needed to ensure that the mold filled. After the castings were weld repaired and sent through the machine shop, it was calculated that the filtered castings had a weld repair time about 90% less compared to the unfiltered castings. This resulted in a net savings of \$16 per casting. The foundry is currently incorporating the filter system into the gating system for use on a production basis.

4.0 Stream Shrouding During Pouring of Castings Weighing Over 250 lbs.

Pouring metal from a ladle, especially a bottom pour ladle, will expose the metal to atmospheric oxygen. Oxygen will react with steel to form reoxidation products which have been shown to compose a large portion of the defects observed in carbon and low alloy steel castings. Bottom pour ladles have the disadvantage of a high metallostatic head pressure compared to teapot/lip ladles. This head pressure produces a high metal stream velocity exiting the ladle which can entrain large amounts of air. Steel mills have for years shrouded their pouring streams to protect the metal from oxygen for this very reason.

The purpose of these trials was to evaluate the effectiveness of two techniques in protecting the pouring stream in a foundry environment and improving casting quality. The technique in the first trial used either an inert gas to blanket the metal stream or to purge the mold of oxygen before pouring or a combination of the two. The technique in the second trial used a mechanical shroud attached to the bottom of the ladle similar to the pouring practice in steel mills.

4.1 Procedure

4.1.1 Gas Shrouding and Mold Inerting Trial

The gas shrouding and mold inerting trial was conducted at a participating foundry. The 8630 steel was melted in a six ton acid electric arc furnace and the ladle was a 1700 lb. bottom pour lined with zircon sand. The casting used in the trial was a bracket with a pour weight of about 338 lbs. The shroud was eight inches in diameter and the metal skirt extended approximately seven inches. Two diffusers were used to disperse liquid argon inside the skirt. Two 1/2" wide viewing slits were machined in the skirt to allow observation of the stream during pouring. Mold inerting was also conducted as a part of this trial. About 150 cc of liquid argon was poured down the downsprue approximately 45 - 60 seconds before the mold was poured.

Prior to conducting the trial, a test was performed to determine the effectiveness of the argon purge. An oxygen sensor was placed in a mold, and 150 cc of liquid argon poured in the

Table 3.
Quadrant Ladle Square Lip Pour Data.
ANOVA Table

Variation Source	Sum of Squares (SS)	Degrees of Freedom	Mean Square (Variance) (V)	F-Ratio	Significance	Contribution (%)
<hr/>						
(main effects)						
Channel Length (CL)	0.0044091	2	0.0022045	11.733	0.0002	5.5
Sprue Angle (SA)	0.0064695	1	0.0064695	34.433	0	17.2
Sprue Length (SL)	0.0149084	1	0.014984	79.347	0	40.2
<hr/>						
(interactions)						
CL * SA	0.0010984	2	0.0005492	2.923	0.0716	1
CL * SL	0.0000836	2	0.0000418	0.222	0.8021	----
SA * SL	0.0047426	1	0.0047426	25.242	0	12.5
<hr/>						
Error (residual)	0.0048851	26	1.88E-04			24.6
TOTAL	0.0365967	35				100

Figure 4. Effect of Sprue Length on Air Entrainment.

Figure 5. Effect of Sprue Angle on Air Entrainment.

Figure 6. Effect of Channel Length on Air Entrainment.

Table 4.
Quadrant Pour Data.
ANOVA Table

Variation Source	Sum of Squares (SS)	Degrees of Freedom	Mean Square (Variance) (V)	F-Ratio	Significance	Contribution (%)
(main effects)						
Sprue Length (SL)	0.01645	1	0.01645	130.215	0	23.6
Sprue Angle (SA)	0.0057156	1	0.0057156	45.244	0	8
Lip Shape (LS)	0.0258309	2	0.0129155	102.237	0	37
Channel Length (CL)	0.0007521	1	0.0007521	5.953	0.0178	0.9
(interactions)						
SL * SA	0.007178	1	0.007178	56.82	0	10.2
SL * LS	0.0001527	2	0.0000764	0.604	0.5498	----
SL * CL	0.0013048	1	0.0013048	10.328	0.0022	1.7
SA * LS	0.0004402	2	0.0002201	1.742	0.1843	----
SA * CL	0.0008114	1	0.0008114	6.423	0.014	1
LS * CL	0.0033669	2	0.0016835	13.326	0	4.5
Error (residual)	1.0072008	57	0.0001263			13.10
TOTAL	0.0692033	71				100

Figure 7. Effect of Lip Shape on Air Entrainment.

Figure 8. Effect of Sprue Angle on Air Entrainment.

downsprue. After approximately 30 seconds, the oxygen level in the mold dropped to less than 1% and remained less than 1% for at least three minutes.

A full factorial experimental matrix was designed to evaluate both gas shrouding of the stream and inerting of the mold. Two heats were poured due to the number of molds needed to complete the matrix. The pouring order for each heat was randomized to eliminate any bias caused by head height variation in the ladle. There were four different conditions: standard practice, mold inerting only, gas shrouding only, and a combination of mold inerting and gas shrouding. Six molds were poured from each heat for each condition. A total of forty-eight castings was poured in the trial. Metal cleanliness was rated by weld repair time at the foundry. Historical weld repair data was also available for this casting to allow comparison to the trial data.

4.1.2 Mechanical Shrouding Trial

The mechanical shrouding trial was conducted at a participating foundry. The 1025 steel was melted in a five ton acid electric arc furnace. Green sand molds were made using the SFSA test plate pattern used in previous casting trials. The ladle was a 2500 lb. bottom pour. A fused silica shroud was attached to the bottom pour ladle with clamps and a pliable gasket was used to make a seal with the bottom of the ladle. The SFSA test plate riser was modified to allow the shroud to be lowered to the bottom of the mold.

Two problems have been associated with mechanical shrouding in past experiments. One problem involves making the shroud removable and still obtaining a good seal with the bottom of the ladle. Any leak will aspirate air during the pour. A combination of a pliable gasket to seal the shroud and an inert gas cover around the seal appears to have worked in a previous trial at the foundry. The second problem involves dealing with the additional metal velocity caused by the shroud. Two different methods were used to reduce the metal velocity as it entered the mold. The first method placed a ceramic filter at the bottom of the riser to absorb the impact of the metal at the start of pour. The second method was to use a filter/riser combination to reduce the velocity of the metal.

Ten molds were poured under three different conditions: standard gating, shrouding with a filter placed in the bottom of the riser to reduce the impact of the metal, and shrouding and pouring the metal into the riser/filter. Casting quality was determined by radiograph as well as by a visual rating of the surface of the casting.

4.2 Results

4.2.1 Gas Shrouding/Mold Inerting

An Analysis of Variance was run on the data to determine the effect of gas shrouding/mold inerting on casting quality. Figure 9 illustrates the effect of mold condition on

welding time. Weld times on castings from the shrouded or purged molds were not statistically different from the weld times for the castings poured using conventional methods. In two cases, weld repair times for castings poured in the shrouded or purged molds were considerably worse. The historical weld time for these casting was about 18 minutes which is lower than the average weld time for the conventional castings from this heat. This is an indication that another factor overwhelmed any beneficial effect of shrouding. The effect of mold condition on weld repair time for the second heat is illustrated in Figure 10. Again, there was no statistical difference between the four groups. There was uniformly less weld repair time for all of the castings from this heat. The wider variation in casting quality for the purged or shrouded molds may indicate a loss of process control.

A plot of the weld repair times for the conventionally poured castings from both heats is illustrated in Figure 11. There was clearly a reduction of variation in casting quality in Heat 2 compared to Heat 1.

Liquid argon was observed dripping into the mold during pouring in the shrouding trial. Possibly argon gas was being trapped in the castings and increasing the weld repair times. The foundry observed that some of the worst defects in the castings appeared to be gas holes. Three castings were selected and a section of defect removed for examination. The defects appeared to be caused by gas trapped in the casting. Little or no indication of solid inclusion material was observed in these castings.

No benefit in casting quality from shrouding or purging was seen in this trial. However, this may have been caused by argon being entrapped in the casting. Too much argon could have been used to shroud the mold and produced gas defects in the shrouded castings and resulted in higher weld repair times. A change in diffusers to produce more gas instead of liquid argon may eliminate the gas defects. There were no oxide macroinclusions observed in the castings examined which indicates that the metal was protected from atmospheric oxygen.

4.2.2 Mechanical Shrouding Trial

ANOVA results on the x-ray rating and the two surface visual ratings are given in Table 5. A statistical difference was observed between the three pouring conditions. The effect of pouring condition on casting quality as measured by X-ray rating is illustrated in Figure 12. The castings poured with the shroud with the filter/riser combination had the best casting quality with an average x-ray rating of about 2. The conventionally poured castings and the shroud with filter splash plate casting were statistically similar. However, the shrouded castings obtained ratings which were as good as the shroud/filter in some cases and in some cases worse than the conventionally poured castings. Figures 13 and 14 illustrate the effect of pouring condition on casting quality as measured by a visual rating of the casting surface. The results were similar to the x-ray results with the shroud/filter combination producing the best castings followed by the shroud and conventionally poured castings.

A steel buildup was observed to form on the shroud during pouring. This buildup in conjunction with the difficulty in holding the ladle steady when lowering into the riser caused the shroud to contact the side of the riser. Sand may have been dropped into the mold during pouring. Examination of the castings did not reveal any erosion.

Three conventionally poured castings and three shrouded castings were selected and sample defects were removed from the plates. Defects removed from the shrouded test plates were primarily composed of silica sand grains. This supports the theory that molding sand was introduced into the mold upon pouring and was washed into the casting. Typical sample defects from the conventionally poured test plates were composed of a mixture of reoxidation products and silica sand grains.

The decrease in pouring time for the shrouded castings indicates that the shroud did in fact seal. The two higher pouring times were either throttled or opened and closed repeatedly. The shroud with the filter/riser combination consistently produced the highest casting quality compared to the shrouded or conventionally poured castings. The combination of the mechanical shroud and the filter which reduced metal velocity and provided filtration improved casting quality. The difficulty in lowering the shroud into a relatively small riser and the steel buildup on the shroud make conclusions on the shrouded castings difficult. The wide variation within the group indicates that the process is not controlled. Defects removed from the shrouded test plates indicate silica sand is the predominate inclusion material. This may have been a result of the shroud contacting the side of the riser and introducing sand into the mold during pouring.

4.2.3 Filtration of High Alloy Steel

A trial was conducted to determine the effect of filtration on cleaning room and weld repair time of a high alloy steel manifold casting. Steel casting filter technology has improved significantly over the past ten years. Filter design and ceramic mechanical properties have improved the ability of the filter to handle the thermal shock and prime easily. The purpose of this trial was to verify the improvements in filter technology and their economic benefits.

The casting selected was a 17-4 PH precipitation hardened stainless steel manifold casting. The mold was produced with Furan bonded silica sand and had a casting weight of about 900 lbs. The gating system consisted of a tile downsprue and sand runner system. Four 3" x 3" x 1" ceramic foam filters were used for each casting.

The stainless steel was melted in an MgO/Al₂O₃ lined induction furnace charged with returns and raw materials. The molds were poured with a 1000 lb. bottom pour ladle and the pouring temperature ranged from 2900 - 2950° F.

After shakeout, the castings were cleaned and weld repaired. The castings were then examined using both liquid dye penetrant and radiography. Any castings flaws uncovered by the

Figure 9. Effect of Mold Condition on Weld Time. (Heat 1)

Figure 10. Effect of Mold Condition on Weld Time. (Heat 2)

Figure 11. Effect of Heat Number on Weld Time.

Table 5.
ANOVA Results for Shrouding Trial.

Source	Sum of Squares	Degrees of Freedom	Significance
X-Ray Rating as Dependent Variable			
Between Groups	70.34	2	99
Within Groups	47.64	21	
Total	118	23	
Visual Rating (jg) as Dependent Variable			
Between Groups	59.8	2	99
Within Groups	83.15	21	
Total	143	23	
Visual Rating (jag) as Dependent Variable			
Between Groups	77.96	2	99
Within Groups	127.18	21	
Total	205.2	23	

Figure 12. Casting Quality Measured By X-ray Rating .

Figure 13. Casting Quality Measured By Visual Rating (jg).

Figure 14. Casting Quality Measured By Visual Rating (jag).

examination of the castings were then recleaned and repaired. The cleaning room and weld repair times for each casting was documented. The high level of casting examination as well as the documentation of cleaning room and weld repair time provided an excellent method to rate casting cleanliness.

A total of 26 castings poured without filters was used in this study. The total cleaning room time averaged 25.17 hours with a standard deviation of 5.2 hours. The total weld repair time averaged 10.88 hours with a standard deviation of 3.02 hours. The total cleaning room and weld repair time averaged 36.05 hours with a standard deviation of 7.56 hours.

A total of 23 castings poured with filtration was used in this study. The total cleaning time averaged 10.12 hours with a standard deviation of 2.51 hours. The total weld repair time averaged 3.76 hours with a standard deviation of 3.03 hours. The total cleaning room and weld repair time averaged 13.88 hours with a standard deviation of 4.33 hours.

The data were analyzed using a one way Analysis of Variance (ANOVA) statistical analysis method. The ANOVA method compares the two populations to determine if there is a statistical difference between groups compared to the variation within the groups. There was greater than 99.9 % confidence that there was a significant difference between the filtered and unfiltered castings in both weld repair and cleaning room time. Cleaning room time was reduced on average by about 60%. Weld repair time was reduced on average by about 65%. Adjusting for the cost of the filters, the use of filters saved the foundry approximately \$985 per casting.

4.2.4 Clean Heat / Dirty Heat Trials

Most foundries experience a wide variation in overall casting quality from heat to heat. In two casting trials examining bottom pour nozzle configuration and filtration of steel castings, heat to heat variation was shown to be significant factor in the overall casting quality.

A long term trial was conducted at three foundries to determine if a correlation could be made between some variable or variables in the melting practice and pouring practice and average heat casting quality. The ultimate goal was to gain a better understanding of the influence of melting and pouring practice on casting quality and, ultimately, to reduce the heat to heat variation.

4.2.4.1 Procedure

There were several requirements that the foundry was required to meet in order to participate in the trial. The foundry was required to have a casting that was being produced for about thirty heats. The thirty heat criteria was selected because it should provide enough data for a good statistical analysis. A minimum of five castings were required to be produced within each heat to provide a basis for predicting the variation within the heat. The method by which

casting quality was to be measured was left up to the foundry. The participating foundries were asked to supply information on these variables along with any other documentation such as the heat sheets that might be available. Samples of the slag from the furnace and the pouring ladle along with samples of metal were taken to further document each heat.

After 25 heats had been submitted for analysis, the variables from each heat were keyed into a statistical analysis program. Since the data was numeric and not categorical, the data was analyzed using linear regression analysis. Due to the large number of variables (in some cases up to 140), a method was needed to reduce the variable set to a manageable number. Two methods were used to reduce the number of possible variables. In the first method, each variable was analyzed individually using simple regression and then ranked according to the highest R^2 and the highest statistical significance. R^2 is the amount of variation that can be explained by a variable or a set of variables. In the second method, the cleanest heats were compared to the dirtiest heats. A t-test was performed to determine which variables were significant different between the two sets of heats.

From this variable list, there were usually 10-15 variables that stood out as having strong correlation with heat quality. Among these 10-15 variables, there were usually some variables that obviously autocorrelated. For example, if a particular element is high or low at meltdown, it will probably be high or low at the block or at tap. In that case, only the variable with the highest R^2 was selected and the others removed from the list. The list was then analyzed using a multi-linear regression using the stepwise process. In this process, all of the variables are initially used in the regression and then variables are removed or added until the fewest number of variables are used to produce the highest R^2 .

4.2.4.2 Results

Two acid foundries and one basic foundry were involved in the trial. The first acid foundry melted 1025 carbon steel in a ten ton acid electric arc furnace. They pour from a ten ton bottom pour ladle and deoxidized at tap with aluminum and Graphidox.™ The molds were green sand with bonded sand cores. The test castings had a pour weight of about 1760 lbs. with a finish weight of 1340 lbs. From seven to ten castings were poured from each heat. Casting quality was measured by counting the number of one inch diameter circles needed to cover the dirt on the casting surface.

The second acid foundry melted 1025 carbon steel in a twenty ton acid electric arc furnace. They poured from a twenty ton silica brick lined bottom pour ladle. The heat was deoxidized at tap with aluminum and then treated with calcium wire. The molds were green sand. Mold pour weight was about 2250 lbs. Four to five castings were poured from each heat. Casting quality was determined by measuring the length of dirt inclusions on each casting surface.

The third foundry melted 1025 carbon steel in a ten ton basic electric arc furnace. The heat was deoxidized with aluminum, manganese, and silicon during tap. The molds were poured

from a ten ton bottom pour ladle. The molds were green sand with a pour weight of about 1650 lbs. and a net weight of 1245 lbs. Ten to twelve castings were poured from each heat. Casting quality was measured by counting the number of one inch diameter circles needed to cover the dirt on the casting surface.

The variables from Acid Foundry #1 that correlated with heat cleanliness were final carbon, final silicon, and final chromium concentration and heats on the bottom pour nozzles. These variables accounted for 66% of the variation in heat quality.

The variables from Acid Foundry #2 that correlated with metal quality were silicon concentration at block, ladle head height, slag modifier, and titanium concentration in the ladle. These variables accounted for 68% of the variation in heat quality.

The variables for Basic Foundry #3 that correlated with heat cleanliness were weight of manganese added to the ladle, final manganese concentration, furnace repair material, and aluminum concentration at block. These variables accounted for 72% of the variation in heat quality.

4.2.4.3 Trends

Metal chemistry of oxidizable elements after block were common for all three foundries. These elements tend to indicate the oxygen level in the heat which may influence metal quality. General housekeeping such as furnace repair or heats on a nozzle were also important to casting quality.

5.0 Castings Produced Using Special Pouring Techniques

A series of modeling experiments was conducted with a quadrant pour ladle and slanted sprues 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. A slanted sprue was shown to reduce air entrainment if used in combination with a lip pour ladle such as a quadrant ladle compared to a standard vertical sprue.

The casting selected for the trial was a WCB valve body. The mold was produced with PepSet™ bonded silica sand coated with zircon mold wash. The casting had a pour weight of 626 lbs. and a casting weight of 305 lbs. The WCB carbon steel was melted in a 9 1/2 ton acid electric arc furnace and deoxidized with Calsibar™ and aluminum upon tapping in the ladle. The molds were poured from either a board lined 700 lb. teapot ladle or a 1500 lb. quadrant pour ladle. Pouring temperature was about 2850 °F.

Casting cleanliness was rated by measuring the surface area of the macroinclusions on the casting surface after shakeout and cleaning.

The location of the downsprue and pouring cup was not optimized for pouring from the quadrant pour ladle. The inability of the quadrant pour ladle to be moved hindered the pouring of the molds. These factors increased the pouring time of the quadrant ladle molds from about 30 seconds to 80 seconds compared to the teapot poured molds. The slower pouring times produced cold metal related defects on the casting surface. This made reliable appraisal of the quadrant ladle impossible.

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II. ELECTROMAGNETIC SEPARATION OF INCLUSIONS FROM FERROUS METALS

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1.0 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 often far below specifications for quality steel casting. Most inclusions found in the final products are small ones, less than 100 microns in diameter. 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 a straight forward one, mainly because of difficulties in developing a practical electromagnetic separation system for conducting materials.

Recently, an inductively coupled electromagnetic separation system was proposed for purification of molten metals.² The feasibility of this process has already been proven for molten aluminum,³ both in the lab and in industry. The results of laboratory experiments show that inclusions larger than 10 μ 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 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 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 the 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.

Significant progress has been made in the first two areas. However, the project was terminated before system performance was evaluated.

2.0 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 trail 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,⁴ 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.⁵ From the solution of the electric field around the particle, the electric current expressed in terms of current stream function is

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

where $\delta = \sqrt{\frac{2}{\sigma\mu\omega}}$, $R\omega_p = 2 \left[\frac{R}{\delta} \right]^2$, $N_v(x) = \sqrt{\ker_v^2(x) + kei_v^2(x)}$, and

$\Theta_v(x) = \arctan \left[\frac{kei_v(x)}{\ker_v(x)} \right]$ are the modules and phase of the $\ker$ and kei Kelvin functions,⁶ respectively.

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

$$\vec{B} = Ba_x + \left(-\frac{\mu}{r \sin \theta} \xi \right) a_\phi \quad (2)$$

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.

$$\vec{F} = \frac{1}{2} J_0 B_0 \cos(a_0) \left\{ 1 - \frac{g(R, \sqrt{R\omega_p})}{4 \cos(a_0)} \right\} V_p \hat{a}_y \quad (3)$$

where

$g(r, \sqrt{R\omega_p}) = R \int \{|J'_0| \cos(a' + a_0)\} dr$, and $|J'_0|$ and $a'(r, \sqrt{R\omega_p})$ are the amplitude and phase angle of $|J'_0|$.

In these equations, the following nomenclature is used:

ξ = current stream function

J = current density

R = radius of the particle

B = magnetic flux density

μ = magnetic permeability

a_0 = phase shift

V_p = volume of the particle

F = expulsion force

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

Figures 15 and 16 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 ⁷11 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.

Figures 17 and 18 show the design of the electromagnetic separation system. The size of the EM filter element, Figure 3, is relatively small, 20 X 18 X 5 cm. The filter elements comprised of four separation channels, with rectangular cross sectional area. The dimensions of the outer and inner channels are 1 X 1/4 and 1/2 X 1/4, respectively.

Figure 15. Sketch of coil

Figure 16. Sketch of the coil Configuration

Figure 17a. Side View of EM Filter Element

Figure 17b. Top View of EM Filter Element

Figure 18. Sketch of the separation system assembly

3.0 Fabrication and Installation of The System

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

The induction coil was fabricated at The University of Alabama, and a special transformer installed for its evaluation. However, industrial support for the project was withdrawn prior to testing the coil, and the project was terminated.

III. CAST IRON PENETRATION IN SAND MOLDS

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Part I: Physics of Penetration Defects and Penetration Model

1.0 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 some \$65,000,000 in scrap and rework costs in the cast metals industry. A more detailed analysis of the annual cost of metal penetration defects is given in Figure 19.⁷ In 1989 the Mold/Metal Interface Committee (4-F) of the American Foundrymen's Society (AFS) initiated a new research project with The University of Alabama to determine definitively the causes and mechanisms of iron penetration in sand molds.

Figure 19. Cost of penetration defects.

An extensive review of past research on the subject was published by AFS in 1989.⁸ A summary of the significant findings from this review is presented in the following paragraphs.

The general definition for metal penetration accepted by the foundry industry, as proposed by Draper and Gaindhar,⁹ is the condition in which liquid metal has entered the intergranular space of the molding material, up to and beyond the first layer of sand grains. They classified penetration defects on the basis of appearance, in order of severity, as follows:

1. *Rough Surface*: 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 exhibits small protrusions.

2. *Burn-in*: the molten metal has penetrated the mold surface up to the midpoint of the first layer of sand grains and has chemically reacted with the sand, producing crystalline fayalite ($\text{FeO} \cdot \text{SiO}_2$); the surface of the casting can be easily cleaned by sand blasting.
3. *Burn-on*: similar than burn-on but resulting in formation of vitreous fayalite that cannot be cleaned easily.
4. *Metal penetration*: the molten metal has penetrated beyond the first layer of sand grains; the resultant mass of metal and sand grains strongly adheres to the casting surface requiring removal by chipping or grinding. Figure 20 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.

Figure 20. Micrograph of metal penetration defect of a class 30 gray iron casting.

Although this is a useful classification method, in this paper the preferred terminology will be that based on penetration mechanisms.

1.1 Mechanical Penetration

Some metal penetration mechanisms have been readily recognized by early investigators. Thus, mechanical penetration was defined as the transport of molten metal into the interstices of the molding aggregate because of excessive metallostatic pressure.¹¹ A summary of the factors that influence the tendency to mechanical penetration is given in Table 6.

Table 6. Factors affecting mechanical penetration

Increased penetration	Ref.	Decreased penetration	Ref.
metallostatic pressure	11	surface energy	10
dynamic pressure	10,2	metal/mold contact angle	14
sand grain size (permeability, bulk density)	2	sand coating	11,2
pouring temperature	11	mold density	4,15
	12		16
	13		
	11,2		
	3		

Coatings are helpful in reducing penetration^{14, 15} The average pore size between the sand grains was considered by earlier investigators to be the main factor in mechanical penetration. Sand fineness, represented by the AFS grain fineness number (GFN), and the degree of compaction determines the average pore size.¹⁶ Increasing the *sand fineness* and/or the *bulk density* of the sand dramatically increases the resistance to metal penetration as shown in Figure 21 and Figure 22.

Figure 21. Experimental relationship between the bulk density of a molding aggregate and the required casting height to cause mechanical penetration.¹⁰

Figure 22. Experimental relationship between the sand fineness and the casting height required for mechanical penetration.¹¹

Because liquid iron does not wet silica, iron cannot penetrate into the voids between the sand grains unless sufficient pressure is applied. The critical metallostatic pressure required to cause penetration is a function of the liquid metal/vapor *surface energy*, γ_{LV} , and *contact angle*, θ , between iron and sand, as calculated from:

$$P_{\gamma} = -\frac{2\gamma_{LV}}{d_e} \cos\theta \quad (4)$$

where d_e is the average pore opening between sand grains. Note that when $\theta > 90^\circ$ P_{γ} is positive, which means that the capillary pressure is opposing penetration. Hoar and Atterton¹⁰ found that as the surface energy of iron is reduced by alloy additions, the critical pressure for penetration also decreases.

In general, *chemical composition* of both the metal and the mold is an important factor in controlling penetration, since it affects both the surface energy and the contact angle. However the direct relationship between metal chemistry and penetration is not always easy to understand, because other effects may be involved such as the oxidation tendency of the melt or the expansion during solidification.

The *pressure of gasses* evolved during mold filling and metal solidification may affect mechanical penetration by opposing it. However, measurements of the gas pressure at the

mold/metal interface were in the range of 1 atm for green sand mold/steel,¹⁷ and reached a maximum of 1.25 atm. for a furan core/gray iron system.¹⁸

1.2 Chemical Penetration

Since the pressures required for mechanical penetration were calculated to be rather high, most investigators agreed that some chemical reaction may be involved in facilitating penetration. Indeed, when studying (4) it becomes obvious that, if the contact angle is smaller than 90° the pressure P_g becomes negative. This means that the metal is drawn in between the sand grains by the capillary pressure. This type of metal penetration is called chemical penetration.

Savage and Taylor¹⁹ 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. The basic reaction is:

Indeed, when studying the SiO_2 -FeO phase diagram presented in Figure 23 it is seen that fayalite has a low melting point of about 1200 °C, and thus is liquid even after the solidification of steel. It is then reasonable to assume that it can freely flow in the intergranular spaces and induce penetration.

Figure 23. The silica-wustite (FeO) equilibrium phase diagram.

Fayalite formation in steel castings was found to be unavoidable and independent of mold atmosphere, cereal additives and moisture content,¹⁷ but the thickness of the fayalite layer formed

depended on the above three variables. According to some researchers¹⁹ fayalite helps the "peelability" of castings and gives good surface finish. Apparently, 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.¹⁰

Metal chemistry was found to have a significant influence on chemical penetration. It was found that as the dissolved oxygen in steel increased penetration was also increased.²⁰ This was attributed to a decrease in contact angle. When the oxygen content reached the equilibrium value with FeO, severe penetration occurred. The detrimental effect of manganese on penetration is well known and documented for high-manganese steels, and attributed to the increased susceptibility to oxidation of high manganese melts.²¹

Since to produce fayalite the iron must be oxidized first, it was logical to assume that the *atmosphere at the mold/metal interface* may play a significant role. Colligan *et al.*²² found that the reaction between iron and pure silica 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. They showed that the reaction products at any temperature and for any atmosphere can be predicted from the Fe-O-Si diagram. The gas atmosphere for any system was first written as an equivalent CO₂/CO ratio. This value along with the temperature was then used to predict the reaction products. Similar diagrams need to be produced for the Fe-Si-O-C system to understand the effect of carbon on the reactions. Dissolved carbon is preferentially oxidized before the iron and thus prevents the oxidation of iron as indicated by the equilibrium constant for the two oxidation reactions. Indeed, calculation of these values¹⁹ demonstrated that the oxygen partial pressure for carbon oxidation is about six orders of magnitude less than that for iron oxidation. The order of oxidation was C>Si>Mn>Fe.

The next step was to test directly the influence of atmospheres of various compositions. 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.¹⁹ By intentionally altering the mold/metal interface atmosphere through flushing it was demonstrated that, in the case of steel castings, oxidizing atmospheres produce poorer surface quality and more penetration than reducing atmospheres.^{10,16,23} Thus, it seems to be clear that an oxidizing atmosphere is conducive to penetration. However, since the oxidizing atmospheres were artificially induced, the next question was whether oxidizing atmospheres indeed exist at the mold/metal interface.

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 Bach²⁴ 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 after mold filling 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.

Extensive gas composition analyses were conducted by Scott and Bates^{25,26,27,28} 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.

Measurements of the gas evolution rates from various chemically bonded molds were also performed.^{18,29} 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 cm³/s for chemically bonded molds.

Various sand additives have been claimed to enhance resistance to penetration. They include cereals (0.5-2.0 %),^{17,22,30} and carbonaceous materials.^{21,23,35,31} The beneficial effect of these additives was attributed either to increased pressure in the mold because of the gases resulting from the combustion process of the additives, or because of the reducing atmosphere resulting from their combustion.

Another method known to successfully prevent penetration is coating of the mold. Recommended coatings include talc, coke dust, graphite, zircon sand, colloidal silica.^{12,14,32} The efficiency of coatings or washes can be attributed to decreased wettability and higher bulk density (smaller intergranular spaces).

1.3 Vapor Penetration

Another penetration mechanism advocated by some researchers is vapor state penetration. Sanders³³ hypothesized that iron carbonyl, Fe(CO)₅, is formed by reaction of iron with carbon monoxide at high pressures and low temperatures. However, thermodynamic calculations¹⁴ showed that the pressures required for this reaction to occur are never attained in molds. Nevertheless, some other form of vapor transport may be responsible for metal penetration. According to Svoboda and Geiger,¹⁴ iron from steel castings can be transported either as an elemental vapor or as volatile metal-oxygen molecules, such as FeO₂. While large masses of metal cannot be transported by this mechanism, the metallic materials coats the sand grains and thus decreases the contact angle.

1.4 Explosion Penetration

It was noticed that when using high pressure molds an increased tendency to penetration may occur. This seems to contradict equation (4). However, a different explanation for this phenomenon than mechanical penetration has been proposed by Levelink and van den Berg.³⁴ They suggested that explosive evaporation of water may occur at the mold surface during pouring. The increased pressure in the vicinity of the interface caused by this explosion pushes the metal into the intergranular spaces. This was called explosion penetration. They also noted that the explosion penetration is increased as the mold hardness (compaction) is raised.

More recently, Brümmer *et al.*³⁵ demonstrated that the correlation between mold compaction and explosion penetration is not a simple one. Indeed they obtained the worst penetration for a sand bulk density of 1000 g/cm³. At lower or higher bulk density less severe penetration was obtained.

1.5 Expansion Penetration

Finally, for the specific case of cast iron, another penetration mechanism has been demonstrated to operate. During eutectic solidification, cast iron solidifying with an austenite-graphite eutectic, has been demonstrated to expand significantly. The expanding metal exerts a significant pressure on the mold walls. If the mold is rigid, and if the metal cannot be pushed back in the riser or the gates because they have solidified, this pressure results in metal penetration, termed in the older literature as exudation penetration. In this report it will be called expansion penetration. This type of penetration was first identified by Levelink and Julien.³⁶ They found that there is a direct dependency between penetration and carbon equivalent, as shown in Figure 24, and that inoculated cast iron is less susceptible to penetration than uninoculated iron. They also demonstrated that increasing the phosphorus level up to 0.2% dramatically reduces penetration. The following correlation between penetration depth (length), L_p , and phosphorus content can be calculated based on a figure given by Levelink and Julien:

$$L_p = -102.9 \cdot (\%P) + 23.14 \quad (\text{in mm}) \quad (5)$$

At phosphorus levels in excess of 0.2% high shrinkage is to be expected.

Figure 24. Correlation between penetration depth and carbon equivalent.³⁶

From the above literature review it is seen that most research work on metal 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 the present research program progressed, it became clear that this assumption was not necessarily true. For this reason, this research targeted cast iron exclusively. However, the findings presented in the following paragraphs describe the fundamentals of metal penetration in molding aggregates, which are believed to be valid for all materials. Nevertheless, since they have been verified only for cast iron in this research; their extension to steel is the subject of ongoing research.

2.0 The Physics of Liquid Metal Penetration in Sand Molds

As opposed to previous attempts at understanding and solving the metal penetration problem that were empirical in nature, in this research a fundamental approach, based on the mathematical analysis of the physical process, was used. The basic assumption is that metal penetration can be analyzed and predicted by calculating the pressure balance at the mold/metal interface.^{37,38} Figure 25, which is a graphical illustration of the problem, shows that competing forces act at the mold/metal interface. The liquid metal exerts a static pressure, P_{st} , a dynamic pressure, P_{dyn} , and a pressure because of expansion during solidification (only for cast iron), P_{exp} , that can force the liquid metal into the interstices of the sand grains. On the opposite side of the interface, the liquid metal is retarded from entering the sand aggregate by the pressure drop resulting from the friction between the liquid metal and the sand grains, P_f , and by the pressure resulting from the expansion of the mold gasses, P_{gas} . However, the most important force is that coming from the capillary pressure, P_γ . This pressure is given by equation (4). It has already been noted that, depending on the value of the contact angle, θ , this term can be negative or positive. Thus, the capillary pressure can be beneficial or detrimental in preventing penetration. The governing equation that describes the pressure balance at the mold/metal interface can be written as:

$$P_{st} + P_{dyn} + P_{exp} = P_\gamma + P_f + P_{gas} \quad (6)$$

Figure 25. Pressure balance during metal penetration in a molding aggregate.³⁷

The terms on the left hand side are all pressure exercised on the metal. The terms on the right hand side describe the ease or difficulty with which the metal moves through the sand. When the left hand side of this equation is larger than the right hand side, liquid metal can penetrate into the interstices of the molding aggregate, resulting in penetration. Each of the terms of this equation must be now formulated and discussed. Since the capillary pressure is the most important it will be the first one to be addressed.

2.1 Capillary pressure

In order to understand the origin and the effect of capillary pressure, it is necessary to introduce some elements of surface physics and chemistry.

Within the bulk of a liquid metal, individual atoms are attracted to each other by molecular forces. Since each atom is surrounded by other similar atoms, all the molecular forces are balanced and their resultant is zero. An atom that is at a surface, either liquid/vapor, or liquid/solid, will experience different forces from the atoms in the vapor (or solid) state. Thus, the atoms at the surface will be characterized by a different energy than those in the bulk, coming from the difference between the forces that are exercised on them. This is surface energy, or surface tension. If a liquid droplet is positioned on a solid substrate with which it does not react, the equilibrium shape of the droplet will result from the balance of the surface energy of the three different surfaces, liquid/solid (LS), liquid/vapor (LV), and solid/vapor (SV). The final shape of the static drop, typically referred to as a sessile drop, must be such as to minimize the surface energy. This shape is, in principle, a sphere. However, since a gravitational force is applied on the droplet, the sphere flattens to an elliptical shape, as shown in Figure 26. The equilibrium between the surface energy of the three interfaces is described by Young's equation, as follows:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL} \quad (7)$$

where γ is the surface energy, and θ is the contact angle between the liquid and the solid. Though θ and γ_{LV} can be measured directly, the other two surface energies cannot be easily determined.

Figure 26. Surface energy balance for the liquid metal - solid silica system.

If the liquid is contained in a capillary tube, depending on whether $\theta > 90^\circ$ (non-wetting) or $\theta < 90^\circ$ (wetting), the liquid will be pushed out or drawn into the tube, under a force which is called the capillary pressure. A rigorous derivation of the equation for the capillary pressure has been given in reference³⁹ and was introduced as (4). In this equation, d_e is the diameter of an "equivalent capillary diameter (tube)" which is substituted mathematically for the irregular shape of the pores between the sand grains. It will be called "average pore diameter" in the rest of this paper.

As previously discussed, if $\theta > 90^\circ$ then $P_\gamma > 0$. This increases the right hand side of (6), and thus makes penetration less probable. This is also true for γ_{LV} as long as $\theta > 90^\circ$. It also indicates that there is no reaction between the metal and the mold, and thus, only *mechanical penetration* is possible. Accordingly, it is highly desirable that a high contact angle exists between the liquid metal and the mold. If $\theta < 90^\circ$ then $P_\gamma < 0$, and in most cases spontaneous penetration will occur, because the forces opposing penetration (P_f and P_{gas}) are too small. This also indicates that some chemical reaction occurs between the metal and the mold, resulting in *chemical penetration*.

As discussed later, the value of the contact angle depends on a series of independent factors including temperature, metal and mold composition, atmosphere composition at the mold/metal interface. Because of the importance of the P_γ 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 have been described in reference,³⁷ and will be further discussed in Part II.

2.2 Friction Pressure

The interstices between sand grains in a mold are irregular, and hard to model. However, a sensible way to estimate the resistance that the sand opposes to metal flow is to recognize that compacted sand is a porous medium. A significant amount 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:

$$P_f = \frac{\mu}{K} L_p V_p \quad (8)$$

where 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 20), and V_p is the speed with which the metal moves through the sand during penetration, or L_p divided by the local solidification time.

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

$$K = \frac{(1 - f_d)^3}{180f_d^2} d^2 \quad (9)$$

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 penetration, 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.

2.3 Metallostatic pressure

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

$$P_{st} = \rho gh \quad (10)$$

where ρ is the density of the alloy, g is the gravitational acceleration, and h is the height of the metal in the mold above the area where penetration is occurring. Excessive metallostatic pressure can result in *metallostatic penetration*. The metallostatic pressure is active as soon as metal penetrates into the mold, until significant solid skin forms. At that time it is no longer effective, since liquid is no longer in contact with the mold (Figure 27).

Figure 27. Schematic illustration of the three types of mechanical penetration and their occurrence as a function of time.

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.

2.4 Dynamic Pressure

This is the pressure exerted from the velocity of the metal as it enters the mold during pouring. It can be calculated as:

$$P_{dyn} = \rho V^2 / 2 \quad (11)$$

where V is the velocity of the metal that hits the mold wall where penetration may form. An approximate value of the velocity of the metal can be found from Bernoulli's theorem. In principle, it 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. Excessive dynamic pressure will result in *dynamic penetration*. P_{dyn} goes to zero as soon as the mold is filled (Figure 27).

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.

2.5 Expansion Pressure

When cast iron solidifies part of the liquid solution of carbon atoms in iron transforms into an austenite-graphite eutectic. The specific volume of the eutectic is larger than that of the liquid, because of the graphite. If the carbon content is higher than 3.6%, the solid expands as compared with the liquid, much like ice does when it solidifies. This expansion is the reason that many iron castings can be made without risers. However, the solidification expansion of cast iron can also cause penetration.³⁶

The mechanism of *expansion penetration* is explained in Figure 28 for the case of an L-shaped casting. Because of the convergent heat flow at the internal corner, heat accumulates in the sand adjacent to that corner (hot spot), and this part of the casting solidifies last. In castings that shrink on solidification, porosity would be expected to be found in this region if the casting were not properly risered. However, if the alloy expands on solidification, as cast iron does, a different situation occurs. The value of P_{exp} at the mold/metal interface is zero until the eutectic temperature is reached (Figure 27), after which it starts increasing. Depending on the design of the rigging, as the casting solidifies the feeding channel may remain open to the end (Figure 28a) In this case the expansion pressure is relieved through the riser. If, on the contrary, the feeding

path is obstructed (Figure 28b), the expansion pressure increases to a high value very quickly and is applied on the mold wall in the region of the hot spot, and the metal is squeezed into the mold, resulting in penetration.

Figure 28. Mechanism of expansion penetration: a) expansion pressure is dissipated toward the riser; b) expansion pressure is exercised on the hot spot and metal penetrates into the molding aggregate.

The penetration defect shown in Figure 20 is a typical case of expansion penetration at a hot spot. Careful examination of the microstructure showed that the metal which has penetrated has the same graphite shape and distribution as that in the bulk of the casting. This indicates 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 29). A thermal analysis showed that there was no progressive solidification from the corner to a riser, and that the last metal to solidify was in this corner.

Figure 29. 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. The ferrostatic head for this casting was 7", so, metallostatic penetration was not the cause of this defect.

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.

The known effect of phosphorus in decreasing penetration (see Equation 5) can now be explained through its influence on the feeding characteristics of the iron. By forming a low melting point phosphide eutectic, phosphorus keeps open channels in the solidifying metal for a long time, allowing communication with the riser and thus, relief paths for the expansion pressure.

The importance of the solidification mechanism on penetration defects 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.

2.6 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.

In this research it was 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. Consequently, in the rest of the theoretical analysis of penetration the contribution of the gas pressure has been ignored.

3.0 The Penetration Equation

In the preceding section the basic equation which governs penetration of cast iron in sand molds was introduced, and each of its terms was formulated and discussed. With this information, it should be possible to evaluate equation (4) and predict the conditions under which penetration will occur.

It was 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 separately for each casting. This cannot be done with a simple analytical equation, as used in the present analysis. However, a straight forward numerical analysis can be attempted to incorporate equation (4) in a solidification simulation model. For this reason, P_{exp} will be dropped from the general analysis.

With this in mind, the various pressure terms can be substituted into equation (4), and it can be solved for the length of penetration L_p . When this is done, the result is:

$$L_p = \left[\frac{d_p^2 t_p (1-f_d)^3}{180\mu f_d^2} (\rho g h + \rho V^2 + \frac{4}{d_p} \gamma_{LV} \cos\theta) \right]^{1/2} \quad (12)$$

This equation can be used to evaluate the contribution of all independent variables included in the formulation on the penetration depth. Since the capillary pressure is the main force opposing penetration, and since it is mostly controlled by the contact angle, it is interesting to study the correlation between penetration depth and contact angle. This can be done by simply plotting this dependency for a number of cases, as presented in Figure 30. From this figure it is seen that, as long as the contact angle remains above a certain value, penetration will not occur. Thus, it is reasonable to conclude that a critical angle for penetration can be defined as the angle above which $L_p = 0$. This is:

$$\theta_{cr} = \cos^{-1} \left[-\frac{d_p}{4\gamma_{LV}} (\rho g h + \rho V^2) \right] \quad (13)$$

It is seen that the critical angle is a function of material (d_p , γ_{LV} , ρ) and process variables (d_p , h , V). Note that, as we will discuss later, the pore diameter, d_p , is both a material and a process variable.

Figure 30. Theoretical evaluation of the influence of contact angle on penetration length calculated with Equation (10). Values used for calculation include $f_d = 0.65$, $h = 200$ mm, $\gamma_{LV} = 1.9 \text{ J m}^{-2}$. Other numbers are given in reference.³⁷

3.1 The Penetration Index

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. They include the mold hardness (it determines d_p), and the height of the casting. In other words, fixing the mold variables establishes the critical contact angle for penetration. If these are changed, a different value for the critical contact angle is found.

Depending on the metal 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*:

$$P = \frac{\theta_A}{\theta_{cr}} \quad (14)$$

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. Note that, since θ_{cr} is always between 90° and 180° (see Equation 11), when the actual contact angle is smaller than 90° , $P < 0$, and penetration will always occur. This is chemical penetration. Accordingly, based on the Penetration Index, three scenarios can be predicted:

- $P > 1$: no penetration;
- $0 < P < 1$: mechanical penetration likely;
- $P < 0$: chemical penetration likely.

To evaluate the Penetration Index it is required to generate values for both θ_A and θ_{cr} . This will be done in the following sections.

3.2 Evaluation of Parameters in the Penetration Index

To calculate the penetration index and thus attempt to predict whether mechanical penetration will occur or not, it is now necessary to calculate the actual and critical contact angles in equation (14). The actual contact angle is simply the angle measured on a sessile drop as shown in Figure 26. The method of measuring this angle is through sessile drop experiments as explained in reference 37. A detailed description of the experimental results will be given in Part II. The actual contact angle is itself a function of the following parameters:

- pouring (melt) temperature
- melt composition
- mold (substrate) composition (type of sand, bentonite content, additives, etc.)
- atmosphere composition at the liquid/mold interface

The critical contact angle depends on the following parameters:

- average pore diameter, in the mold (i.e. the space between the sand grains, that, in turn, depends on sand grain size and sand compaction (bulk density))
- liquid metal surface energy and density
- metallostatic height
- metal velocity in the mold

The evaluation methods as well as the mathematical expressions of all these parameters will be presented in the following paragraphs.

3.2.1 Effect of Pouring Temperature on θ_A

It is well established that the surface energy of liquid metal and the contact angle depend on its temperature. This is shown for cast iron in Figure 31. Higher pouring temperatures lower the contact angle, increasing the opportunity for penetration (it also increases the fluidity of the iron, which also encourages penetration). The proper pouring temperature is, of course, the lowest temperature at which the molten metal fills the mold without causing chill or mottled iron. As the research results show, this also minimizes penetration.

However, a simple contact angle - temperature correlation cannot be used in the penetration index, because the effect of temperature is compounded by that of chemical composition of the metal. Accordingly, a complex relationship between metal composition, temperature and contact angle must be established.

Figure 31. Contact angle of synthetic Fe-C-Si alloy on silica sand (AFS GFN 71) in argon atmosphere as a function of temperature.³⁷

3.2.2 Effect of Metal Composition and Temperature on θ_A

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 Part II. The results obtained showed that the contact angle depends on composition and temperature as follows:

$$\begin{aligned} \theta_A = & 292.837 - 45.159 \cdot [\%C] - 106.134 \cdot [\%Si] - 343.401 \cdot [\%S] - 18.527 \cdot [\%Mn] - \\ & 36.678 \cdot [\%P] + 0.341 \cdot T + 31.813 \cdot [\%C \cdot \%Si] - 0.118 \cdot [\%C \cdot T] + 96.114 \cdot [\%Si \cdot \%S] + \\ & 0.544 \cdot [\%S \cdot T] + 129.745 \cdot [\%Mn \cdot \%P] \end{aligned}$$

where [%C] is the weight percent carbon, [%Si] is the weight percent silicon, [%S] is the weight percent sulfur, [%Mn] is the weight percent manganese, [%P] is the weight percent phosphorus, T is the pouring (superheat) temperature. The statistic parameters are $R^2 = 0.87$, and RMS = 2.893. The model is thus considered to be a satisfactory representation of the relationship. While it cannot be readily observed from this equation, as will be discussed later in this paper, carbon, manganese and sulfur decrease θ_A , while silicon and phosphorus increase it.

3.2.3 Effect of Type of Sand on θ_A

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

Note that the data in Figure 32 are obtained on granular materials. As discussed in more detail in Part II, sand grain size affects the contact angle. However, to evaluate θ_A , it is necessary to use monolithic substrates, since the actual contact angle is an intrinsic material property (does not depend on material shape). Thus, the information obtained on granular substrates cannot be directly used in calculation of θ_A , but is useful for comparing different types of materials.

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). This will decrease the pore diameter, and thus will also lower θ_{cr} . Since θ_A

remains approximately constant, the penetration index will increase. 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.

3.2.4 Effect of Bentonite on θ_A

Because bentonite has a different chemical composition from that of silica sand, its effect on the contact angle was also investigated. However, since bentonite swells during heating, it was impossible to measure the iron/bentonite contact angle. Thus, the effect of bentonite was measured indirectly by measuring the contact angle between iron and sand with increasing bentonite content. The results are shown in Figure 33 for 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. From these results it is difficult to conclude whether bentonite additions increase the contact angle because of the change in the bentonite/metal interface energy, or because bentonite fills in the spaces between the sand, and thus produces a finer material. In any event, it appears that bentonite has a beneficial role on the contact angle.

Figure 33. Influence of temperature and bentonite content of the silica sand on the contact angle of three types of Fe-C alloys.

3.2.5 Effect of Atmosphere at the Mold/Metal Interface

All of the measurements in argon atmosphere produced contact angles greater than 90° , indicating that liquid cast 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, since all of the contact angle measurements were made in argon, the results are strictly valid only if castings are poured in argon. Since it has been shown 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 θ_A can decrease dramatically, and penetration becomes more probable. If θ_A becomes negative, chemical penetration will spontaneously occur.

Previous researchers have demonstrated that an oxidizing atmosphere can react with the metal and produce iron oxide, which in turn can react with silica to produce fayalite. 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 often this result was mistakenly extrapolated 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 gas 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, as well as and the experimental method are given in Part III. 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 34 and Figure 35 show 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. When no carbon was added to the mold, the atmosphere

was oxidizing enough for the first four minutes to react with pure iron (Figure 34). The interfacial atmosphere was never oxidizing in experiments where carbon was added to the mold (Figure 35). 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. 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.

The question is now "why was there no evidence of iron oxidation at the mold/metal interface, since at least in one instance oxygen was present at the interface?" The reason is that the carbon in the gray iron protects the iron by oxidizing first. The oxygen solubility in cast iron ranges from 4 to 10 ppm. Thus, at the casting interface, the oxygen saturation in cast iron can be achieved rapidly from the diffusive dissolution of oxygen. 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.

Figure 34. Gas composition in a mold without seacoal additions.

Figure 35. Gas composition in a mold with 4.9% seacoal additions.

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 36 shows the variation of the contact angle and oxygen concentration versus time.

The sessile drop 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 increase in the oxygen concentration, as indicated during the first four minutes on Figure 36. 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 increased because of the depletion of dissolved carbon to reach 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/mold interface as long as carbon is present in the metal. Therefore, it is impossible for chemical penetration to occur when pouring cast iron in sand molds.

A model of transport and reaction of chemicals in the interfacial region was developed to answer the fundamental question of the mold-metal atmosphere tests. It is detailed in Part III.

Figure 36. Contact angle of a synthetic Fe-3.68%C-1.25% Si alloy on silica sand 108+ 9% sodium bentonite in 95% argon + 5% oxygen atmosphere.

3.2.6 Evaluation of Average Pore Diameter

The equivalent pore diameter, d_p , can be calculated or measured experimentally for different molding aggregates. For the closed packed three-dimensional case it was demonstrated that:³⁸

$$d_p = 1.1 \cdot d(1 - f_d)^{1/3} \quad (15)$$

Thus the pore diameter is simply a function of average grain density, d , and of fractional density. It decreases, and makes penetration less probable, as the sand grain size decreases and as the fractional density increases. The pore diameter is also directly related to the permeability of the sand as measured by the AFS test.

The fractional density of a molding aggregate can be calculated as the ratio between the bulk density and the true density. It is also equivalent to the percent solids ($f_d \cdot 100$). Since both the bulk density and the true density of molding materials can be measured, the fractional density can be obtained directly from experimental measurements. Typically, the fractional density of green molding sands varies between 39 and 70. The fractional density of dry molding sands varies between 54 and 64. It has been shown that, a direct relationship exists between fractional density and the hardness of compacted green sand.³⁸ As the hardness of the sand increases, the fractional density also increases.

Experimental evaluation of the average pore diameter can be done with a mercury porosimeter. The method and the significant experimental results are presented in Part II of this paper. The experimentally evaluated pore diameter has then been correlated empirically with typical sand tests, including permeability, mold hardness and mold quality indicator (MQI).

For green sand (3% Western bentonite, 3% water) the following relationships were obtained:

$$d_p = 2.73 \cdot 10^{-2} \cdot \ln(0.123 \text{ Perm}) \quad (16a)$$

$$d_p = \exp(-6.35 \cdot 10^{-2} \cdot HD + 1.638) \quad (16b)$$

$$d_p = 0.112 - 1.662 \cdot 10^{-4} \cdot MQI \quad (16c)$$

where *Perm* is the permeability of sand measured with the standard Permmeter and *HD* is the hardness of the sand measured with the ball indenter (Dietert).

For a resin bonded sand (PepsetTM Part I/Part II ratio 55/45, 1.3% binder based on Part I) the correlations between the equivalent pore diameter and sand tests are as follows:

$$d_p = 3.245 \cdot 10^{-2} + 2.797 \cdot 10^{-4} \cdot \text{Perm} \quad (17a)$$

$$d_p = 1.74 - 2.161 \cdot 10^{-2} \cdot HS \quad (17b)$$

$$d_p = -4.61 \cdot 10^{-2} \ln(9.87 \cdot 10^{-4} \cdot MQI) \quad (17c)$$

where *HS* is the mold hardness measured with a scratch indenter.

From these data it is concluded that the pore diameter decreases as permeability decreases and as mold hardness and MQI increase. Remember that as the pore diameter decreases the penetration tendency also decreases, because the critical contact angle, θ_{cr} , decreases (see equations (13) and (14)).

3.2.7 Liquid Metal Surface Energy

From the analysis of (1) it can be seen that when the metal is not wetting the mold ($\theta > 90^\circ$) a decrease in γ_{LV} will result in increased penetration. Unfortunately, as shown in Figure 37, increased contents of any elements decrease the surface energy of iron.⁴⁰ Oxygen, sulfur and nitrogen have a particularly strong influence. Thus, an increase in the content of any elements will be conducive to higher penetration tendency, unless the contact angle is increased.

The surface energy of liquid metals can be measured by a number of methods. Attempts at measuring it from the shape of the sessile drop in this work have been unsuccessful, because of the sensitivity of the measurement to the digitization of the shape of the droplet. Thus only literature data have been used.

Figure 37. Effect of various elements on the surface energy of liquid iron at 1550-1570 °C.⁴¹

3.2.8 Metal Velocity in the Mold

As previously discussed, a first order evaluation of the metal velocity can be done through the Bernoulli equation. However, the velocity in the penetration equation is that of the metal impacting the mold wall in the specific spot where penetration is evaluated. This can be only obtained from a model that allows calculation of the metal velocity throughout the casting during mold filling. Such models are now commercially available. Thus, incorporation of the penetration model in some commercial code is the next logical step.

To evaluate the importance of metal velocity the Penetration Index was plotted in Figure 38 as a function of metal velocity. All other parameters were chosen in such a way as to give $P = 1$ when the metal velocity was zero. It is seen that velocities of up to 0.5 m/s do not affect the Penetration Index. However, as the velocity increases above this limit P decreases rapidly, suggesting high probability of penetration.

Figure 38. Influence of metal velocity in the mold on the Penetration Index.

3.3 Other Effects Not Directly Included in the Penetration Index

3.3.1 Volume Expansion

While the Penetration Index is not applicable if conditions for expansion penetration exist, it is still important to achieve a quantitative understanding of volume expansion, because the penetration model as described above could predict expansion penetration if incorporated in a solidification model.

Some simple calculation can be used to predict the amount of expansion of cast iron as a function of composition. Assuming equilibrium solidification conditions exists, the following equation can be used to estimate the maximum solubility of carbon in austenite:

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

where the %Si, %Mn, %P, and %S are the average element concentration in the melt. The fraction of austenite and graphite in the solid 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 of the austenite phase can be determined from the following relationship:⁴¹

$$v_{\gamma} = 0.1330 + 0.0013 (\%Si - \%C) \quad \text{at } 1155^{\circ}\text{C}$$

The specific volume of the liquid cast iron, v_L , is the sum of the weighted average of the specific volume fraction of the austenite, v_γ , and graphite, v_{Gr} , 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 as:

$$\Delta v = \frac{v_S - v_L}{v_L} \quad (18)$$

Thus, if the specific volume of solid cast iron is greater than the specific volume of the liquid, $\Delta v > 0$ there will be volume expansion during eutectic solidification. 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, resulting in expansion penetration.

A spreadsheet program was designed to calculate the magnitude of the volume change which can be expected during solidification based on the model presented above. In the example shown in Figure 20, the expected expansion was 0.88% — just enough to force a small but significant amount of metal into the sand. Note that the highlighted region of the casting shown in the figure is the area with the highest modulus, and it corresponds to the area where penetration was found.

3.3.2 Effect of Sand Additives and Mold Coatings

It is generally accepted that addition of certain additives such as silica flour or coal to the sand, and mold coatings or washes can significantly decrease the penetration tendency. The simplest explanation for this effect can be that all of these addition decrease the pore diameter, thus decreasing the critical contact angle and increasing the penetration index. For steel and added benefit is that some of these coatings will include additives (e.g., zircon flour) that have a higher contact angle than silica.

For seacoal a more detailed discussion is necessary. 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 39. 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 39. Enlarged area of metal penetration shown in Figure 20. The large dark areas on the photograph are silica sand grains surrounded with bentonite. The lighter gray areas between the metal and sand grains are vitreous carbon. Since no iron oxide or fayalite are present this is strictly mechanical penetration. Magnification 250x.

4.0 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 in the mold do not significantly change the gas composition.

5.0 The Penetration Prognosticator

The *Penetration Prognosticator Program* calculates the value of P , and also calculates the amount of expansion which can be expected from the composition of the iron. It is a spreadsheet program written in Excel 5.0, using Visual Basic. The program accepts input data provided by the user in terms of foundry variables. The program runs on DOS (a version is also available for Macintosh systems) and requires 3 MB of RAM. This makes it possible to carry onto the foundry floor.

In using the program, first the value of P is calculated. If it is greater than 1, indicating that penetration is not likely, but penetration is present, the graphite expansion should be calculated. If the expansion is positive, then casting and/or gating redesign are necessary to eliminate penetration.

5.1 Validation of the Program

The Penetration Prognosticator was validated in the laboratory and at four other foundry sites. In all cases predicted results came close to the measured ones. Details of the laboratory casting validation are given below.

A number of bottom gated cylindrical castings having 58.6 cm height and 15.2 cm diameter were poured in green sand molds. The clay content of the sand was 7.8% and the sand fineness was GFN 60. The pouring velocity was 0.23 m/s (1 lb/s through a 3/4" diameter sprue). Other data regarding sand and mold properties, and the chemical compositions of the castings are given in Table 7.

Table 7. Sand and mold properties and chemical composition of casting used for Prognosticator validation tests

Casting no.	Mold properties				Chemical composition, wt%					
	Water content, %	Compact-ability	Hardness	Permeability	C	Si	Mn	S	P	CE
1	4.4	62	92	225	3.61	2.24	0.15	0.007	0.013	4.30
2	4.6	64	93	250	3.48	2.19	0.16	0.006	0.014	4.16
3	4.2	57	93	230	3.46	2.83	0.17	0.009	0.013	4.34
4	4.4	60	91	215	3.66	2.91	0.35	0.007	0.015	4.56
5	4.1	58	94	220	3.49	2.71	0.12	0.006	0.012	4.33
6	4.2	58	90	190	3.08	2.30	0.14	0.007	0.012	3.79
7	4.0	60	94	195	3.18	2.26	0.12	0.006	0.011	3.88

Penetration was observed in all castings above a certain height. The measured and predicted penetration heights (from the bottom of the casting) are recorded in Table 8. The pouring temperatures required for calculation of the penetration index and of the predicted penetrated height are also included in the table. As clearly shown in Figure 40, the measured and predicted penetration heights agree reasonably well. Further analysis of the data in Table 8, presented in Figure 41, shows that, as expected, carbon and silicon contents significantly affect the tendency for mechanical penetration. First, it is seen that as the carbon equivalent increases the penetration height decreases. This simply confirms the sessile drop data in Figure 32, showing that the actual contact angle increases with carbon equivalent. Both calculated and measured set of points on the graph follow the same trend. The scatter of data is probably because of the variation in the pouring temperature. In addition, Figure 41 reveals that carbon and silicon have opposing influence on penetration; silicon decreases the penetration height, while carbon increases it.

Table 8. Comparison between measured and predicted penetration height, and casting temperatures

Casting no.	Pouring temperature, °C	Measured height, mm	Predicted height, mm
1	1358	5.7	7.1
2	1422	7.7	10.7
3	1370	4.3	2.9
4	1368	4.7	3.1
5	1422	4.3	3.6
6	1474	11.6	13.1
7	1556	6.4	6.9

Figure 40. Comparison between measured and predicted (calculated) penetration heights (in cm) for some experimental castings.

Figure 41. Comparison between measured and calculated penetration height as a function of chemical composition.

A major advantage of the Penetration Prognosticator is that it not only indicates when a problem is probable, it also indicates what corrective action is possible. Figure 42 through Figure 44 show three graphs which are displayed by the program. In Figure 42, 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. Figure 43 also shows

that changing the phosphorous, sulfur or manganese levels will probably not have much effect on the penetration index.

Figure 42. Graph of metal variables used in verification experiment for a metallostatic height of 16". This gives a penetration index of 0.97. This height was selected to show all variables on the graph.

Figure 43. Since sulfur and phosphorus additions are made in small quantities, another metal graph is included in the software program identifying the effect of phosphorus and sulfur on the penetration index.

Figure 44 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 44. Graph of the mold variables generated from the software program. The graph used the same input variables as shown in Figure 42.

Part II: Experimental Evaluation of Some of the Main Parameters Responsible for Penetration

1.0 Introduction

It has been demonstrated (see Part I) that the penetration tendency of liquid metal into a molding aggregate can be evaluated with the help of the Penetration Index, given by the following equation:

$$P = \frac{\theta_A}{\theta_{cr}} = \frac{\theta_A}{\cos^{-1} \left[-\frac{d_p}{4\gamma_{LV}} (\rho g h + \rho V^2) \right]} \quad (14)$$

where θ_A is the actual contact angle between the metal and the mold material, θ_{cr} is the critical contact angle at which penetration is likely to occur in a molding aggregate having an average pore diameter d_p , by a metal having the surface energy γ_{LV} , the density ρ , the metallostatic height h , and the velocity V .

It has also been shown that if $P > 1$, no penetration is expected; if $1 > P > 0$, mechanical penetration is likely to occur; when $P < 0$, chemical penetration will occur. A detailed discussion of the contribution of all these parameters to penetration has been given in Part I of this paper. However, the details of the experimental evaluation of the actual contact angle and of the average pore diameter has not been provided. The purpose of this paper is to describe the experiments conducted to determine the values of θ_A for irons of different compositions and temperatures, and of d_p for various molding aggregates. While no measurements of the surface energy were done in this work, some useful data from the literature, and comments will be included in the body of this paper.

2.0 Evaluation of Actual Contact Angle

2.1 The Sessile Drop Method

The most accurate technique presently available for measuring contact angles, particularly at high temperature, is the sessile drop method. 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, is 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.³⁹ The force balance between the surface energy and gravity intrinsically gives the sessile drop an elliptical shape in appearance for a non-wetting liquid.

As discussed in some detail,³⁹ the equilibrium configuration of a non-wetting liquid droplet resting on a flat, chemically inert solid surface is determined by the surface energy 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 45. The contact angle θ can be measured directly. It is used as a parameter in determining the wetting characteristics of the liquid metal on ceramic substrates. If the contact angle is greater than 90° , the liquid metal is considered non-wetting, and wetting when the contact angle is less than 90° . The value of the contact angle is an intrinsic material property. However, it is also a function of temperature and surface roughness.

Figure 45. Surface energy balance for the liquid metal -- solid silica system.

2.2 Experimental Procedure

2.2.1 Experimental Apparatus

Sessile drop measurements require in principle a furnace that can melt the material under investigation. The furnace must be provided with a system that allows continuous recording of the shape of the sessile drop and of the temperature. In this research it was necessary to use neutral, oxidizing and reducing atmospheres above the sessile drop. Because of this two different furnaces were used: a furnace with the heating elements in the melting chamber, that could operate under vacuum, inert or reducing atmosphere, and a tube furnace with the heating elements outside the melting chamber, that could operate under oxidizing atmosphere.

The Vacuum Furnace. Figure 46 shows a schematic diagram of the Centorr furnace chamber assembly used for sessile drop experiments. The furnace chamber was evacuated using a mechanical pump and a diffusion pump capable of decreasing and maintaining pressure down to 10^{-5} to 10^{-6} Torr (10^{-7} to 10^{-8} atm.). The furnace was operated under vacuum or in an argon atmosphere.

Figure 46. Schematic drawing of the vacuum furnace for the measurement of the wetting angle and of the surface energy.

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 at two minute intervals. The temperature was recorded for each photograph.

The Tube Furnace. 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 (see below) as those prepared for the vacuum furnace. Figure 47 shows the experimental setup used for the tube furnace experiments.

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

Figure 47. Schematic drawing of the tube furnace.

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 minutes. A photograph was taken at this time to record the shape of the sessile drop.

2.2.2 Experimental Design

Two distinct groups of experiments were performed: exploratory experiments, followed by statistically designed experiments. Accordingly, 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, including some exploratory experiments and the statistically designed array of experiments, since the results obtained from this study would closely represent the surface energy conditions experienced during actual casting operations. A detailed description of the materials used for these experiments is given in the following paragraphs.

2.2.3 Sessile Drop Sample Preparation

All metal samples were prepared either in a resistance furnace or in an induction furnace. The synthetic grade alloys were based exclusively on pure elements. The second type, commercial grade alloys, were 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 spectrometer. Discs, 5 mm high and 5 mm in diameter were sectioned from the rods for the sessile drop experiments. Before each experiment the metal sample was polished using fine emery grinding paper and 97% isopropyl alcohol, to remove any oxides on the surface. The sample was then dried in acetone and immediately placed on the substrate.

The chemical compositions of the iron-base samples used in these experiments are given in Table 9. The numbers in bold indicate the significant element for the particular experiment run.

Table 9. Chemical analysis (wt%) of ferrous alloys used in the exploratory experiments

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

For the statistical array of experiments, as shown in Table 10, four base alloys were prepared from high purity pig iron in a 50 lb. 100 kW 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.

Table 10. Abbreviated L32 array with main factors only.

Alloy number	%C	%Si	%S	%Mn	%P	Superheat temperature
1	3.04	1.81	0.02	0.09	0.03	150°C
2	3.04	1.81	0.02	0.09	0.03	250°C
3	3.08	1.75	0.03	0.66	0.12	150°C
4	3.08	1.75	0.03	0.66	0.12	250°C
5	3.04	1.75	0.12	0.10	0.11	150°C
6	3.04	1.75	0.12	0.10	0.11	250°C
7	3.06	1.78	0.13	0.70	0.02	150°C
8	3.06	1.78	0.13	0.70	0.02	250°C
9	3.04	2.41	0.02	0.06	0.13	150°C
10	3.04	2.41	0.02	0.06	0.13	250°C
11	3.09	2.33	0.01	0.67	0.02	150°C
12	3.09	2.33	0.01	0.67	0.02	250°C
13	3.08	2.38	0.14	0.08	0.02	150°C
14	3.08	2.38	0.14	0.08	0.02	250°C
15	3.09	2.33	0.11	0.67	0.13	150°C
16	3.09	2.33	0.11	0.67	0.13	250°C
17	3.59	1.74	0.02	0.07	0.11	150°C
18	3.59	1.74	0.02	0.07	0.11	250°C
19	3.55	1.80	0.02	0.71	0.03	150°C
20	3.55	1.80	0.02	0.71	0.03	250°C
21	3.56	1.77	0.14	0.08	0.03	150°C
22	3.56	1.77	0.14	0.08	0.03	250°C
23	3.62	1.76	0.14	0.70	0.12	150°C
24	3.62	1.76	0.14	0.70	0.12	250°C
25	3.62	2.39	0.02	0.08	0.03	150°C
26	3.62	2.39	0.02	0.08	0.03	250°C
27	3.57	2.35	0.02	0.69	0.13	150°C
28	3.57	2.35	0.02	0.69	0.13	250°C
29	3.64	2.32	0.10	0.08	0.12	150°C
30	3.64	2.32	0.10	0.08	0.12	250°C
31	3.67	2.29	0.10	0.69	0.03	150°C
32	3.67	2.29	0.10	0.69	0.03	250°C

Several types of materials were used to evaluate the role of molding aggregate on the contact angle. They included monolithic quartz and several sand substrates. The sands used are listed in Table 11 along with their sieve analysis. The chemical composition for chromite and silica sand is reported in Table 12. For substrates containing no clay binder additives, the crucible (35 mm height by 6 mm dia.) 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.

Table 11. Characteristics of Ceramic Materials

Sieve number	Carbon sand	Silica sand 108	Silica sand 71	Chromite sand	Zircon sand 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	0.34	-	-	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 12. Chemical composition (wt%) of two sands used for substrate preparation

Chromite sand		Silica sand	
Cr ₂ O ₃	46.5	SiO ₂	99.779
SiO ₂	0.85	Fe ₂ O ₃	0.016
FeO	24.5	Al ₂ O ₃	0.07
Al ₂ O ₃	14.87	TiO ₂	0.014
MgO	10.4	CaO	0.012
CaO	0.15	MgO	0.003

For the substrates containing clay binders, dry sand and clay binder were added to 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 alumina crucible and leveled. The packed crucible was then dried in a furnace at 100 °C for 4 hours to remove the excess water.

2.2.4 Contact Angle Measurements

Measurements of the contact angle between the sessile drop and the substrate were performed by projecting the photograph image on 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.

2.2.5 Furnace Validation Experiments

It was important to ensure that results of experiments performed on the vacuum/argon 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 48 are similar, demonstrating that furnace itself did not influence experimental results.

Figure 48. Furnace comparison of synthetic Fe-3.68% C-1.25% Si alloy on monolithic quartz in argon atmosphere at 1235 °C.

2.2.6 Sample Geometry and Experimental Error

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 vacuum/argon 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 49 show that the results are practically independent of sample geometry for the first minute. A sudden discrepancy is noted after about 75 seconds. This jump is probably the result of some inadvertent vibration of the furnace assembly, since any changes in contact angle will occur gradually as a result of thermodynamic and kinetic effects.

Figure 49. 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.

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. It was calculated that the mean contact angle was of 122.7° with a standard deviation of 1.1°.

3.0 Results

3.1 Results of Preliminary Experiments on Influence of Iron Composition

The chemical composition of iron dramatically influences the surface energy and therefore the contact angle as discussed in reference 41. 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 contact angle. Only quaternary alloys, Fe-C-Si-X, were considered.

The experimental results in terms of average contact angle for commercial alloys on monolithic quartz substrates, and for synthetic alloys on silica sand with 9% western bentonite additions substrates, under argon atmosphere, are shown in Figure 50. 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 energy. 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. Indeed, as shown in a theoretical discussion by Kaptay and Stefanescu,³⁹ as the oxygen content in a Fe-C melt increases the contact angle decreases rapidly.

Figure 50. Influence of minor elements on the contact angle at 1300 °C under argon atmosphere for binary Fe-3.6 C and quaternary Fe-C-Si-X alloys on two types of substrates.

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 + bentonite substrates. For discussion, the results obtained on monolithic quartz will be used since the presence of western bentonite and surface roughness in the sand substrate experiments affect the contact angle. Manganese and phosphorus showed little influence on the contact angle. This is in line with their influence on surface energy, discussed later in this paper. Sulfur additions significantly decreased the contact angle. This was expected since sulfur is considered to be a surface active element in cast iron.

Magnesium showed the highest specific influence in decreasing the contact angle. This finding may seem surprising to the ductile iron metal caster, who normally observes that ductile iron wets the mold less than gray iron. In other words, the presence of magnesium in commercial irons results in increased contact angle. However, in commercial ductile iron magnesium deoxidizes and desulfurizes the melt, effectively increasing the contact angle because of the removal of these elements. In this experiment, initially, the liquid melt was deoxidized by the addition of silicon. Magnesium was then added immediately afterwards. Since the melt was already deoxidized and low in sulfur content, the magnesium did not

combine with oxygen and sulfur. Thus, magnesium acting as a solutal addition to the melt only will decrease the contact angle.

3.2 Results of Designed Experiments on the Influence of Iron Composition

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. The data discussed above allow an understanding of the individual influence of minor elements on the contact angle. However, calculation of the actual contact angle in the Penetration Index requires the combined influence of the minor elements and temperature. The influence of the interactions between alloying additions in the melt and melt temperature could not be determined from the exploratory study. Accordingly, commercial alloys were used in a statistically designed experiment to study the main effect of the alloying additions and superheat temperature. An equation was formulated to predict the contact angle based on these variables.

Table 10 shows the chemical composition and superheat temperature for the L32 experimental array used for this study. The measured contact angle for these alloys are given in Table 13. The computed effects for each main variable are given in Table 14. As expected, silicon showed a positive response on the contact angle (i.e., it increases 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 neutralized 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 energy of cast iron based on data presented by Keene.⁴³ However, Levelink and Julian³⁶ have shown that the depth of penetration decreases with increasing concentrations of phosphorus, as explained in Part I, this is because of the effect of phosphorus on the graphite eutectic expansion of cast iron (phosphorus additions decrease eutectic graphite expansion).

A multiple regression model was run using the data presented in Table 10 and Table 13 to predict the contact angle for the chemical compositional and temperature 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:

$$\theta_A = 292.837 - 45.159 \cdot [\%C] - 106.134 \cdot [\%Si] - 343.401 \cdot [\%S] - 18.527 \cdot [\%Mn] - 36.678 \cdot [\%P] + 0.341 \cdot T + 31.813 \cdot [\%C \cdot \%Si] - 0.118 \cdot [\%C \cdot T] + 96.114 \cdot [\%Si \cdot \%S] + 0.544 \cdot [\%S \cdot T] + 129.745 \cdot [\%Mn \cdot \%P]$$

where [%C] is the weight percent carbon, [%Si] is the weight percent silicon, [%S] is the weight percent sulfur, [%Mn] is the weight percent manganese, [%P] is the weight percent phosphorus, T is the pouring (superheat) temperature. The coefficients of determination are $R^2 = 0.87$, and $RMS = 2.893$. The model is thus considered to be a satisfactory representation of the relationship. It must be noted that this equation is only valid for variables in the range used in the statistical array, that is: 3.04 - 3.67% C, 1.74 - 2.41% Si, 0.07 - 0.71% Mn, 0.03 - 0.13% P, 0.01 - 0.14% S, and melt temperature of 1300 - 1400 °C.

Table 13. Contact angle of alloys in Table 10 on monolithic quartz substrate

Alloy no.	1	2	3	4	5	6	7	8	9	10	11
Contact angle, °	130	136	124	125	122	124	110	122	124	122	125
Alloy no.	12	13	14	15	16	17	18	19	20	21	22
Contact angle, °	115	126	126	122	129	128	120	119	113	120	116
Alloy no.	23	24	25	26	27	28	29	30	31	32	
Contact angle, °	113	111	135	127	131	125	129	128	120	119	

Table 14. Variable and interactions effects on contact angle response

Variable	Effect results
Carbon	-1.75
Silicon	4.4
Sulfur	-3.875
Manganese	-5.625
Phosphorus	1.125
Temperature	-1.25

3.3 Results of Experiments on Influence of Substrate Composition

The combined effect of substrate composition and carbon equivalent of iron have already been presented in Part I of this report. The main conclusion was that there was little change in the contact angle of cast iron with silica, chromite, zircon or carbon sand.

4.0 Surface Energy of Cast Iron

4.1 Influence of Metal Composition

When a solute is added to the bulk liquid, the surface energy, as well as the contact angle, changes as a 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 by Allen.⁴⁰ His data have been summarized in Figure 49 in reference 43. Additional data on the influence of oxygen are given in Figure 51.⁴⁴

Figure 51. Calculated influence of oxygen on the contact angle in the Fe-O/SiO₂ system.⁴⁴

Similar effects of element additions were found for cast iron by Cosneanu,⁴⁵ as shown in Figure 52. It is seen that while Ni, Cu and Si slightly reduce the surface energy, Ca, Mg, Ce, S, Se, and Te have a much stronger effect.

Extensive research performed by Washchenko and Rudoy⁴⁶ on cast iron also showed that carbon, silicon, and phosphorus slightly decrease the surface energy, while sulfur and magnesium additions have significant effect. In Figure 53, it can be seen that the influence of manganese is significant at contents above 1.5% Mn. Below this level manganese has little effect. This is because it is neutralized by sulfur through the formation of MnS, which is insoluble in cast iron.

Figure 52. Influence of some elements on the surface energy of liquid iron at 1400 °C.⁴⁵

Figure 53. The effect of manganese on the surface tension of cast iron.⁴⁶

The influence of magnesium is more complex, as shown in Figure 54, and merits additional discussion. Magnesium reacts with both sulfur and dissolved oxygen. The formation of MgS and MgO , which are both insoluble in cast iron, will increase the surface energy of cast iron by removing these surface active components from the liquid. This occurs up to 0.018% Mg . Beyond this content, the surface energy decreases, as a direct consequence of the solution of the remaining free magnesium.

Figure 54. Variation of the surface energy of Mg treated iron with residual magnesium.⁴⁵

4.2 Effect of Temperature

As the temperature of the system is increased, the atoms in the bulk liquid begin to vibrate more and escape the interface monolayer more frequently. The intermolecular forces holding the bulk atoms decrease allowing the bulk and the monolayer surface to expand. As a 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.³⁸

In general, surface tension decreases in a nearly linear fashion with increasing temperature, provided there is no phase changes in either bulk phase with increasing temperature. On the basis of experimental evidence it was concluded that there is a general linear relationship between the contact angle and temperature:

$$\cos \theta = 1 + K_1(T - T_{CS}) \quad \text{or} \quad \cos \theta = 1 + K_2(\gamma_{CS} - \gamma_{LV}) \quad (19)$$

where K_1 is the slope of contact angle with temperature, T_{CS} is the critical temperature for spreading, *i.e.*, the temperature at which the contact angle approaches zero, K_2 is the slope of the surface energy with temperature, 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} .

A qualitative analysis of equation 19 is in order to demonstrate how surface energy data can be used to correlate contact angle data. Clearly, the values for the $\cos \theta$ term ranges from -1 to +1. Therefore, the term $K_2(\gamma_{CS} - \gamma_{LV})$ or $K_1(T - T_{CS})$ must have a range between 0 and -2. The sign of the slope K_1 , has to be positive since the difference in the spreading temperature and actual temperature will always be negative. Similarly, the sign of the slope K_2 , will be negative since $\gamma_{LV} \leq \gamma_{CS}$. Qualitatively, using equation 19 with the data presented earlier, an increase in

the surface energy 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 energy will result in a decrease in the contact angle.

5.0 Evaluation of Average Pore Diameter and Related Sand Tests

5.1 The Mercury Penetration Porosimetry

The average pore diameter was determined using mercury penetration porosimetry. The mercury penetration porosimetry is based on the amount of pressure required to force the mercury into the pores of the sand, and an average pore diameter is calculated from the pressure versus volume intruded. The average pore diameter can also be empirically correlated to several foundry sand tests including, permeability, mold hardness, and mold quality indicator (MQI).

The intrusion of mercury into a pore is the result of a force balance coming from the surface energy of mercury and the contact angle of mercury against the pressure applied to the mercury (Figure 55). The governing equation of this phenomenon is:⁴⁷

$$r = \frac{2\gamma |\cos\theta|}{P} \quad (20)$$

where, r is the pore diameter, γ is the surface tension of mercury (0.485 N/m), θ is the contact angle of mercury (140°), and P is the pressure applied to the mercury. If all the pores have the same size, the volume of mercury penetrated in the sample will only depend on the total pore volume once the pressure exceeds the value calculated from the above equation (Figure 56a). However, since in real sand systems a pore size distribution must be taken into account, the volume of mercury penetrated will increase as pressure increases, and will reach the maximum at the pressure required by the smallest size pores (Figure 56b). From the experimental graph the variation of volume penetrated with pressure, dV_i/dP , can be calculated. It can be demonstrated that the pore volume distribution function can then be calculated as:⁴⁷

$$v(r) = \frac{dV_i}{dP} \frac{P}{r} = \frac{dV_i}{dP} \frac{P^2}{2\gamma |\cos\theta|} \quad (21)$$

The volume averaged mean pore radius, r_m , can then be calculated as:

$$r_m = \frac{\int r \cdot v(r) \cdot dr}{\int v(r) \cdot dr} \quad (22)$$

Then the average pore diameter is simply $d_p = 2 \cdot r_m$.

Figure 55. Penetration of mercury into a pore.

Figure 56. Hypothetical results of mercury penetration porosimetry experiments: a) cylindrical pores of equal size; b) pores of different sizes.

5.2 Sand Tests Related to Average Pore Diameter

The *permeability* of the sand is the volume of air that is forced through the sand per second. The AFS Permeability Number is defined by:

$$\text{AFS Permeability Number} = 3007.2 / t \quad (23)$$

where, t is the time(s) required to force 1 liter of air through a standard AFS 3 ram sample when using an AFS permeability testing machine. The permeability of the sand will increase with increasing pore diameter.

The mold hardness of clay bonded sand is measured with a spring-loaded ball. The depth of the indentation is measured on a scale of 0 to 100 with 100 being the hardest mold. The scratch indenter used for resin bonded sands scratches the surface of the sand while a constant pressure is applied by a spring to make an indentation in the sand surface. The depth of the scratch is also measured on a scale of 0 to 100 with 100 being the deepest penetration. The hardness should decrease as the fractional density of the sand decreases, which is directly related to increasing pore diameter.

The Mold Quality Indicator (MQI) is an inverse of permeability. In MQI testing air is forced into the mold at the surface, and the back pressure is associated with the MQI number which increases with increasing back pressure. MQI provides a quick measurement of a mold quality that can be performed in an operating foundry. MQI will decrease with increasing pore diameter.

5.3 Experimental Procedure

A commercially washed silica sand was separated into four single samples through sieving, as follows: -35+50, -50+70, -70+100, and -100+140. For green sand samples, each sample was mixed with 3% Western Bentonite and 3% water. A standard AFS three ram 2 inch sample was prepared from each of the four sands. Permeability, MQI, and mold hardness tests were performed on each of the four samples in that order. The samples were then stripped from the tube and placed in an oven at 200 °F for 4 hr. to remove the moisture. For the resin bonded sand, the four sample sands were each combined with Pepset™ binder using a ratio of 55/45 (Part I/Part II) and 1.3% binder based on Part I. Standard AFS 2 inch three ram specimens were again prepared, and the sand tests were performed in the same order, using the scratch indenter for mold hardness.

For the mercury porosimetry experiments, a small sample, approximately 0.5 g, was removed from the 2 inch specimen and weighed on an analytical balance. The sample was placed in the sample cell as shown in Figure 57. The sample cell was sealed, and a stainless sheath with a ground wire was placed over the cell stem and inserted into the horizontal vacuum jar (Figure 58) and held in place with the cell retainer. The vacuum pump was turned on, and the rate control valve was opened after the selector valve was set to vacuum. The maximum rate

valve was opened when the pressure dropped below 2 psia. When the vacuum dropped below 50 $\mu\text{m Hg}$, both the maximum rate valve and the rate control valve were closed, and the selector valve was turned to vent. The vacuum jar was then rotated down to a position where approximately 1 in. of the stainless steel sheath was submerged in the mercury, and the volume was zeroed. The rate control valve was slowly opened and left open until there was a large volume change (usually occurred at 1 to 2 psia with a magnitude of approximately -0.700 cm^3). This indicated that the sample cell was filled with mercury. When the volume changed, the rate control valve was quickly closed. The vacuum jar was then rotated back to the horizontal position, and the volume was re-zeroed. The data acquisition system was started, and the rate control valve was slightly opened. The data was collected until the intruded volume became constant with changing pressure. Then the average mean pore radius was calculated with equation 22. The process was repeated three times for each of the samples for both green sand and resin bonded sand, and the results averaged.

Figure 57. Schematic drawing of the sample cell with a sample in place.

Figure 58. Schematic drawing of the vacuum jar with sample cell and stainless steel sheath inserted. The sample and cell retainer are located to the left of the figure.

6.0 Experimental Results and Discussion

The results of the mercury porosimetry tests and the sand tests for the green sand samples are shown in Table 15. A plot of the sand test values versus the average pore diameter with the best fit regression lines is shown in Figure 59. It is seen that the mold hardness and the MQI values decrease with increasing pore diameter, while permeability. The empirical correlations and r^2 values for the average pore diameter with sand test values are as follows:

$$d_p = 2.73 \cdot 10^{-2} \cdot \ln(0.123 \text{ Perm}) \quad r^2 = 0.928 \quad (24a)$$

$$d_p = \exp(-6.35 \cdot 10^{-2} \cdot HD + 1.638) \quad r^2 = 0.971 \quad (24b)$$

$$d_p = 0.112 - 1.662 \cdot 10^{-4} \cdot MQI \quad r^2 = 0.917 \quad (24c)$$

where *Perm* is the permeability of sand measured as discussed previously and *HD* is the hardness of the sand measured with the ball indenter.

Table 15. Experimental data for silica sand with 3% Western bentonite and 3% water, except for average pore diameter where the sand is dry.

Sand	Average pore diameter (mm)	AFS Permeability	Mold Hardness (Scale B)	MQI Number
-35+50	0.096	269	63	109
-50+70	0.078	175	65	159
-70+100	0.072	88	68	277
-100+140	0.050	53	73	374

Table 16 shows the results of the mercury porosimetry tests and the sand tests for the resin bonded sands. As with the green sand, the MQI number and the mold hardness decreased with increasing average pore diameter, and the permeability increased with increasing average pore diameter (Figure 60). The values for MQI for resin bonded sands are larger than those for green sand, but the values for permeability are larger for green sands. This is to be expected because the bonded resin decreases the pore diameter as shown in Table 15 and Table 16. The results of the best fit regressions are as follows:

$$d_p = 3.245 \cdot 10^{-2} + 2.797 \cdot 10^{-4} \cdot \text{Perm} \quad r^2 = 0.967 \quad (25a)$$

$$d_p = 1.74 - 2.161 \cdot 10^{-2} \cdot HS \quad r^2 = 0.973 \quad (25b)$$

$$d_p = -4.61 \cdot 10^{-2} \ln(9.87 \cdot 10^{-4} \cdot MQI) \quad r^2 = 0.904 \quad (25c)$$

where *HS* is the mold hardness measured with a scratch indenter.

Table 16. Experimental data for a resin bonded silica sand.

Sand	Average pore diameter (mm)	AFS Permeability	Mold Hardness (Scratch Indenter)	MQI Number
-35+50	0.107	278	76	107
-50+70	0.091	193	77	138
-70+100	0.059	97	78	217
-100+140	0.046	51	79	462

Figure 59. Plot of sand test values versus average pore diameter with the best fit regression lines for silica sand with 3% Western bentonite and 3% water.

Figure 60. Plot of sand test values versus average pore diameter with best fit regression lines for resin bonded silica sand.

The mercury porosimetry experiments were performed at room temperature which could affect the degree of accuracy of the regression equations for predicting the average pore diameter at the temperatures that cast iron is poured (approx. 1400 °C). The expansion of the silica sand will make the average pore diameter smaller for the green sand and the resin bonded sand. However, the resin will also be burning off at the pouring temperature which could lead to a larger pore diameter. This is probably insignificant because the layer of resin is extremely thin. Therefore, the average pore diameter at pouring temperatures will be smaller than that predicted by the regression lines. This will lead to less penetration in the casting.

Part III: Measurement of Mold/Metal Interfacial Gas Composition

1.0 Introduction

As described in Part I of this report, penetration of liquid metal into molding media may be caused by mechanical or chemical means. Mechanical penetration occurs when the forces on the liquid metal, such as metallostatic head force the liquid into the sand. Chemical penetration occurs when the surface of the metal reacts chemically with the sand to produce a compound which penetrates the sand, or is attached to the surface of the casting.

For ferrous alloys poured in green sand, the existence of an oxidizing atmosphere within the mold during pouring and solidification produced penetration defects whereas the presence of neutral or reducing atmospheres did not.⁹ Analysis of the surface of castings which were oxidized during solidification showed the presence of fayalite, Fe_2O_4 , which resulted from the reaction of iron oxide, FeO , on the surface of the mold with sand, SiO_2 , in the mold.

The first step in the chain of events which causes chemical penetration is the oxidation of liquid iron to form iron oxide, FeO . FeO is liquid at the temperature of solid steel, and can react with and dissolve silica to form fayalite.^{15,21,48} When this happens, fayalite penetrates the mold, followed by liquid iron, which then solidifies. Oxidation of the liquid iron could result either from the oxygen present in air when the mold is initially poured, or from the reaction of iron with water vapor, which is present at steam when the casting is poured. To determine whether iron oxide can form, it is necessary to determine the composition of the atmosphere at the mold/metal interface during pouring and solidification.

Gas composition has been measured previously. In one experiment, gas was collected from the interface or was collected from the mold cavity.^{23,24} The gas analyses showed that the gas was primarily composed of hydrogen and carbon monoxide, with smaller amounts of methane and carbon dioxide present as well. In these experiments, the gas was collected during solidification and subsequently analyzed using gas chromatography. This method does not allow the gas composition to be continuously monitored during solidification. In addition, most experiments were out on steel, rather than cast iron. Because of the higher carbon content of cast iron, results from steel experiments may not be assumed to be valid for cast iron.

This investigation, therefore, focused on measuring the gas composition produced at the mold/metal interface when cast iron is poured into green sand molds.

2.0 Technical Approach

A designed experiment was used to determine the effects of mold moisture content, seacoal and cellulose content, and pouring temperature on gas composition. The gas was analyzed by on-line mass spectrometry, and mathematically corrected so that real-time gas compositions were determined. Casting surfaces were then examined for evidence of

penetration, and the surface condition correlated to gas composition. A schematic drawing of the experimental arrangement is shown in Figure 61.

2.1 Experimental Procedure

Experiments were carried out on a casting six inches in diameter with a height which was normally 12 inches high, and could be increased to 24 inches. The casting was molded in the cope, and gas sampling probes and thermocouples were placed in the drag, as shown in Figure 62. The casting was gated through the bottom. Stainless steel tubes were used as pressure and gas composition probes; they were fixed to a support bar in the drag so that their ends were 1/8 inch from the mold/metal interface, the closest distance at which the molten metal would not plug the tube. Castings were well-vented, as the cope did not cover the top of the casting.

Temperature at the mold/metal interface was measured using a type K chromel-alumel thermocouple coated with zirconia paste. Temperature readings were recorded at one second intervals. The pressure was determined using a psi-millivolt pressure transducer fixed to one of the 1/4 inch tubes in the drag. Results were recorded on a strip chart recorder, and the transducer was calibrated to read in the 0 to 15 psig range.

One hundred pounds of washed silica sand with an AFS grain fineness of 71 were muller for ten minutes in a closed muller. New sand was used for each mold to avoid contamination from previous experiments. Western bentonite (7%) and cellulose (1%) were added to the sand. Moisture and seacoal content were varied as part of the designed experiment. Cellulose was added after the bond addition; if seacoal was to be added, it was added after the cellulose. Molds were hand rammed to a hardness of 80-85.

Loss on ignition (LOI) tests were used to determine the actual carbonaceous addition to the sand. An LOI sample was taken after the cellulose addition, and a second LOI sample after the seacoal addition. Cellulose content was determined from the first sample, and seacoal content was determined by difference between the first and second samples. Moisture content was determined by weighing a fresh sample, then drying it at 100 °C for three hours and re-weighing.

Commercial pig iron was melted in a 100 kW high frequency induction furnace. Chemical adjustments were made to achieve aim composition of 3.5% carbon, 1.8% silicon, 0.7% manganese, 0.12 phosphorous, and 0.12% sulfur. Pouring temperature was a variable in the designed experiment.

The gas composition was drawn from the interface through a 1/8 inch diameter stainless steel tube by using a vacuum pump at a rate of 6 - 10 cc/min. The small amount of gas thus removed from the surface is not enough to alter gas composition at the surface. The gas passed through a humidity probe, a 2 micron filter and was dried by passing it through a desiccant (CaSO₄). The desiccant does not absorb any of the gases analyzed, so did not alter the measured gas composition. A capillary tube carried the dry gas to the mass spectrometer.

Figure 61. Experimental setup to measure gas composition, pressure, and temperature at the interface.

Figure 62. Schematic of pattern and flask used, showing position of support bar and probes.

The mass spectrometer used was a Leybold Inficon Transpector with an electron multiplier and a Faraday cup detector. It continuously scanned the mass range from 1 to 100 atomic mass units (amu). The mass spectrometer measures concentration for each amu. Data was collected at four second intervals.

Provision was made to remove dry gas across septa by taking an injection for analysis by gas chromatograph to distinguish between nitrogen and carbon monoxide, which have the same molecular weight and amu (28), and thus cannot be differentiated by the mass spectrometer. To resolve this an HP5890 gas chromatograph was used with a Haysep D column, a thermal conductivity detector and helium as the carrier gas.

The gas had to travel a substantial distance from the mold to the mass spectrometer, which meant that the gas was actually analyzed after a delay of about five minutes from the time it was generated at the interface. The line had areas where significant mixing could take place. To account for the delay and the mixing effects, the system was modeled as a series of ideal plug and mixed flow regions.⁴⁹ Time constants of the system were determined by subjecting the sampling tube to a step change of nitrogen and helium gas concentrations. By using this model and transforming the data from the interface, real time gas concentrations at the mold/metal interface could be determined.

Calibration of both the mass spectrometer and the gas chromatograph was necessary because the response of these instruments is non-linear. This means that the calibration requires a large number of data points. On the basis of a review of literature and theoretical thermodynamic calculation of the likely products of combustion (which indicated that the atmosphere should be mostly nitrogen and oxygen at the beginning of pouring, and mostly hydrogen and carbon monoxide with a little carbon dioxide and methane mixed in at the end of solidification) calibration was carried out using mixtures of pure gases in the following ranges:

Hydrogen	0% to 80%
Nitrogen	15% to 79%
Oxygen	0% to 21%
Methane	0% to 5%
Carbon monoxide	0% to 100%
Carbon dioxide	0% to 5%

2.2 Experimental Design

An L16 designed experiment was used to determine the level of four variables on gas evolution. These four variables, each held at two levels, were sand moisture content, seacoal content, cellulose content, and pouring temperature. The experimental design is shown in Table 17. In addition, one casting was poured in resin-bonded (phenolic urethane) sand, two extra castings were poured in green sand, and three castings were poured using non-vented molds, to determine the effect of venting on pressure and gas composition at the interface. In the non-

vented molds, the top of the casting was covered with a six inch high cope, so that the casting itself was actually poured as the cheek section of the three-piece mold.

Table 17. Experimental Design

Experiment #	Moisture %	Seacoal %	Cellulose %	Pour Temp. °C
0-1	3.7	0	0	1400
0-2	2.3	0	0	1400
1	3.7	4.9	0.5	1440
2	3.7	4.9	0.5	1357
3	3.7	4.9	0.2	1440
4	3.7	4.9	0.2	1357
5	3.7	2.1	0.5	1440
6	3.7	2.1	0.5	1357
7	3.7	2.1	0.2	1440
8	3.7	2.1	0.2	1357
9	2.3	4.9	0.5	1440
10	2.3	4.9	0.5	1357
11	2.3	4.9	0.2	1440
12	2.3	4.9	0.2	1357
13	2.3	2.1	0.5	1440
14	2.3	2.1	0.5	1357
15	2.3	2.1	0.2	1440
16	2.3	2.1	0.2	1357

3.0 Results

Actual mold properties obtained are given in Table 18. Not all of the objectives of the designed experiment were realized. Green sand properties can be difficult to control, and the scatter, while disappointing, is not considered to invalidate the experiments. Note that control of cellulose to the levels desired in the designed experiment was not obtained, and so its effect could not be determined.

3.1 Gas Composition

Mold/metal gas compositions were measured as a function of time after pouring for all molds prepared. Test results were highly reproducible, as shown in Figure 63, which compares the data obtained for three experiments using the same sand and pouring temperature. Because of this high reproducibility, gas composition traces will be shown only for representative molds

showing no carbonaceous (seacoal or cellulose) addition (Figure 64), a low level of seacoal addition (Figure 65), and a high level of seacoal addition (Figure 66).

Table 18. Actual Properties of Molds Poured

Mold	Mold Hdns	Compaction, %	AFS Gas Perm	Moisture %	Seacoal %	Cellulose %	Pour Temp °C
0-1	85	35	105.4	3.3	-	-	1397
0-2	85	30	119.0	2.8	-	-	1400
1	78	40	112.1	4.4	4.8	1.2	1395
2	79	30	97.0	4.2	4.9	1.5	1358
3	82	30	94.0	3.2	5.1	1.3	1443
4	84	25	103.7	3.4	4.8	1.1	1357
5	83	35	106.1	4.2	1.7	1.2	1359
6	88	35	107.4	4.3	2.2	1.1	1415
7	84	35	89.4	4.1	2.2	1.1	1440
8	84	30	96.9	4.3	2.1	1.1	1364
9	77	15	94.0	2.3	5.0	1.5	1452
10	79	30	89.8	2.9	4.7	1.1	1350
11	83	25	107.4	2.5	4.8	0.9	1436
12	81	25	79.2	3.2	4.7	1.2	1349
13	80	25	127.6	2.9	2.1	1.4	1424
14	-	-	-	2.8	2.2	1.1	1368
15	88	30	129.6	2.9	2.1	0.9	1420
16	83	35	114.3	3.1	2.1	1.0	1358
17	90	25	121.7	2.7	4.5	1.3	1393
18	88	30	99.4	2.9	-	-	1460
Resin	-	-	-	-	-	-	1352
NV1*	87	25	85.9	3.8	-	-	1440
NV2*	88	35	82.9	4.5	5.0	1.3	1446
NV3*	89	30	95.0	4.1	4.5	1.2	1389

* non-vented

Figure 63. Reproducibility of gas composition obtained at the mold/metal interface form similar sand compositions and mold temperatures.

Figure 64. Gas composition at the mold/metal interface in the carbon-free mold.

Figure 65. Gas composition at the mold/metal interface in the low level carbon-containing mold.

Figure 66. Gas composition at the mold/metal interface in the high level carbon-containing mold.

In each case there was an initial transient period, which lasted less than four minutes. During this period, the oxygen and nitrogen contents (which represented the air initially in the mold) fell off to zero, and the hydrogen and carbon monoxide contents increased, until each was about 40 to 60% of the total gas at the interface. Some methane was also formed, as was carbon dioxide.

Gas measurements are on a moisture-free basis. In three experiments a humidity meter was placed just after the sample tube exited the mold. The temperature and relative humidity of the sample gas were recorded, and the moisture content of the gas was calculated. Each experiment showed that the sample gas contained about 2 mole per cent water. This is a minimum concentration, as water may also have condensed out in the tube before reaching the humidity meter.

In all cases, the nitrogen and oxygen contents fall off rapidly, as the air in the mold is expelled by the vaporization of moisture in the mold. Water in the mold reacts with carbon in the alloy to produce carbon monoxide and hydrogen. Sand moisture content does not appear to affect the gas concentration significantly. Omission of carbonaceous additions causes an initial increase in the ratio of CO_2 to CO ratio, as shown in Figure 67, which then falls off rapidly as the CO_2 is reduced by the carbon in the molten alloy. A carbonaceous addition to the molding sand such as seacoal thus does prevent this initial production of carbon dioxide, but increasing the amount of this addition does not change the interfacial atmosphere significantly. Higher values of seacoal increased the hydrogen, and somewhat decreased the carbon monoxide and dioxide quantities. Higher temperatures slightly decreased the amount of carbon monoxide.

In no case did the CO_2/CO ratio remain greater than 0.1 after four minutes after pouring. Below this ratio and at temperatures above 1200°C , it has been shown²¹ that no oxidation of iron can be expected. Thus, as FeO does not form, fayalite cannot form, and there can be no chemical penetration in cast iron. The castings were carefully inspected for evidence of penetration, and no evidence was found. Theoretical calculations using reaction thermodynamics verified that the gas formed will always consist of carbon monoxide and hydrogen, and therefore be reducing, as long as there is free carbon at the liquid metal interface; in cast irons, the carbon content is sufficiently high that it is always available at the interface to produce carbon monoxide gas.

As expected, the atmosphere in the resin-bonded mold was also reducing. Again, as no oxidizing gas forms, no chemical penetration is expected in castings poured in resin-bonded molds.

3.2 Gas pressure at the Mold/Metal Interface

In all casting poured, vented and non-vented, the increase in pressure at the mold/metal interface was measured to be about 0.01 psig. This suggests that the gas generated at the interface can diffuse through the mold to the surface of the mold (or along the parting line), where, as it is reducing, it burns on contact with the oxygen in the air surrounding the mold.

Figure 67. Ratio of carbon dioxide to carbon monoxide at the mold/metal interface in carbon-free, low level and high level carbon-containing molds.

There was no accumulation of gas at the interface. These results are consistent with those of earlier investigators.^{16, 22}

4.0 Discussion

Pouring temperature, seacoal content and moisture level of the sand were considered to be the most important process variables affecting the atmosphere at the mold/metal interface when cast iron is poured into green sand molds. These were tested at levels representative of industrial use in iron foundries. There was little effect on the mold atmosphere composition after the initial transient period.

When metal initially contacts the mold, there is a huge increase in temperature, and the condensed water near the interface vaporizes, expanding in volume over 1000 times. This rapid expansion displaces the air originally in the mold. The water which vaporizes is an oxidizing gas at the elevated temperature of liquid cast iron, and the carbon in the iron reacts:

where C indicates that the carbon is in solution in the metal (the cast iron can be either liquid or solid). Water vapor could also react with the carbonaceous additions to the mold or with the liquid iron itself. However, the free energies of formation are such that the reaction shown is preferred. Note that the equation indicates that equal volumes of each gas are to be expected.

The dissolved carbon is present at the surface of the casting. When it reacts with water, it forms carbon monoxide and leaves the surface of the casting. This establishes a concentration gradient, and more carbon diffuses to the surface, where it, in turn, reacts. This process continues until the casting solidifies. The carbonaceous additives also react, but much more slowly, as they must be heated up by the heat transferred from the cooling casting to the mold.

A reducing layer of CO/H₂ gas, in roughly equal proportions, forms at the interface. It then grows outward. At the same time, water vapor which is being formed by the heat of the cooling casting diffuses inward to the casting surface where it continues to react with the carbon at the surface. After a short while a pseudo-equilibrium is established at the interface. The carbon in the metal diffuses to the interface to replace the carbon consumed in the reaction. Water vapor diffuses through the growing product layer of carbon monoxide and hydrogen to replace the water consumed in the reaction. The rate of gas generation depends on the diffusion rates of carbon and water vapor to the interface.

Note that when carbonaceous additives are omitted from the mold, there is an initial period when carbon dioxide is formed instead of carbon monoxide. This indicates that the initial carbon at the surface of the mold is rapidly depleted, and a period of time results when carbon must diffuse to the casting surface. There is initially a great deal of water vapor available at the interface; however, after it is consumed in the reaction, the reaction cannot continue until more water vapor diffuses to the interface. Because the diffusion of water vapor is slower than the

diffusion of carbon, the carbon content can build up at the interface to continue the reaction at a pseudo-steady state until the casting solidifies.

A number of interfacial gas determinations were made in sponsor foundries, using their production sand which had been re-cycled, in contrast to the new sand used for laboratory experiments. The CO/H₂ ratios found in these foundries were generally higher (around 60% CO/40% H₂) than that found in the laboratory experiments, possibly as a result of resins present in the recycled sand. No chemical penetration was observed in any sponsor foundry.

IV. Conclusions

A. Clean Cast Steel Technology

Modeling of Steel Pouring Practices.

1. Throttling of a bottom pour ladle increases air entrainment by about 100% compared to a fully open stopper.
2. The new gating design increased air entrainment by about 100% compared to the original gating system in the fully open stopper condition. This increase correlated well to the 115% increase in inclusions observed at the foundry when the new gating system was used.
3. A ten inch sprue length increased air entrainment by about 18% compared to a five inch sprue.
4. A 30 degree slanted sprue increased air entrainment by about 17% compared to a straight sprue with a teapot sprue.
5. Higher pouring rates with the slanted sprue produced increased stream turbulence with the teapot ladle.
6. A slanted sprue reduced air entrainment by about 20% compared to the straight sprue.
7. A short channel length reduced air entrainment by about 20% compared to a long channel length.
8. A round lip shape reduced air entrainment by about 38% compared to a square lip shape on the quadrant ladle.

Lip Pour Trials Weighing Less Than 250 lbs.

9. The use of reticulated filters reduced weld repair time by about 90%.

10. A minimum metal temperature of 2920 °F was needed to ensure priming of the filter.
11. Filtration resulted in a net savings of \$16 per casting for the foundry.

Stream Shrouding of Bottom Poured Castings.

12. Gas shrouding and mold purging did not improve casting quality as determined by weld repair time.
13. Defects removed from sample castings indicate entrapment of shrouding gas in the casting. Inclusion oxide material was not observed in the defects examined. Improvement of the gas shrouding system may eliminate gas entrainment in to the casting.
14. A combination of a filter/riser combination and a mechanical shroud significantly improved casting quality compared to a conventionally poured casting.
15. Mechanical shrouding alone produced erratic results. Molding sand may have been dislodged by the shroud during pouring producing erratic cleanliness ratings.
16. The use of reticulated filters on a 900 lb. stainless steel casting reduced weld repair and cleaning room time by about 65% compared to nonfiltered castings.
17. The use of filters resulted in a net savings of \$985 per casting for the foundry.
18. Concentration of oxidizable elements in the metal at block and at final were important indicators of metal quality in the heat-to-heat variation trials.
19. General housekeeping such as furnace and ladle repair were also important factors in metal quality.

Castings Produced By Special Pouring Techniques

20. The trials with the quadrant pour ladle were not successful. The inability of the ladle to be moved and the location of the pouring cup increased the pouring time and resulted in cold metal defects in the casting. Improvements in gating design and in foundry location should allow a reliable appraisal of the quadrant pour ladle to be made.

B. Electromagnetic Separation of Inclusions from Ferrous Melts

Despite being unable to complete the project for lack of funding, the calculations indicated that removal of inclusions from the flowing stream using electromagnetic means is feasible.

C. Cast Iron Penetration in Sand Molds

1. Penetration of cast iron into sand molds is caused by the physical movement of liquid metal into the sand. Because the high carbon and silicon present in the chemistry of cast iron prevents iron from oxidation, 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. Thus, in the vast majority of cases, only mechanical penetration can be expected in cast iron. The mechanisms of mechanical penetration can be analyzed by a simple pressure balance equation. This equation can be solved by a spread sheet program suitable for use on a lap-top computer. Use of this program 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.
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. 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. Although further confirmation is necessary, it appears that seacoal is effective in countering penetration by plastic deformation 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. This obstructs any movement of liquid metal into the mold.
7. After an initial transient period, the atmosphere at the interface of an iron casting solidifying in green sand is a roughly equal ratio of carbon monoxide and hydrogen, containing small amounts of methane and carbon dioxide.

8. Pouring temperature, seacoal additions and moisture contents have only a slight effect on the composition of the interfacial atmosphere. In all cases, the resulting atmosphere is reducing.
9. The complete absence of carbonaceous additions permits a period of less than four minutes when oxidizing conditions exist at the mold/metal interface. These conditions give way to a reducing mixture of gas, and do not produce chemical penetration.
10. Based on the determinations of mold atmosphere composition at the mold/metal interface in the laboratory and in the field, it is concluded that chemical penetration does not exist in cast iron poured in green or resin-bonded sand molds.
11. The main parameters influencing cast iron penetration in molding aggregates, the actual contact angle and the average pore diameter in the molding aggregate, have been measured experimentally. The sessile drop method has been used successfully to evaluate the contact angle and the mercury penetration porosimetry method to evaluate the average pore diameter. The average pore diameter was also related to typical sand tests including permeability, mold hardness and MQI. The empirical equations obtained in this study have been implemented in the Penetration Prognosticator.

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