Energy NOTES ON TAV R E S N O C

METALCASTING COMPETITIVENESS RESEARCH

Final Report

By
T. S. Piwonka

August 1994

Work Performed Under Contract No. DE-FC07-92ID13163

For
U.S. Department of Energy
Office of Industrial Technologies
Washington, D.C.
By
The University of Alabama
Tuscaloosa, Alabama

DISCLAIMER

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

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

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

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

DISCLAIMER

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

METALCASTING COMPETITIVENESS RESEARCH

Final Report

By
T.S. Piwonka, et al.

August 1994

Work Performed Under Contract No. DE-FC07-92ID13163

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

By
The Metal Casting Technology Center
The University of Alabama
Tuscaloosa, Alabama

CONTENTS

1. PREDICTION OF NON-METALLIC PARTICLE DISTRIBUTION
2. ELECTROMAGNETIC SEPARATION OF INCLUSIONS FROM MOLTEN ALUMINUM ALLOY
3. CLEAN STEEL CASTINGS
4. WASTE STREAM IDENTIFICATION AND TREATMENT
5. ELASTIC WAVE LITHOTRIPSY FOR REMOVAL OF CERAMIC FROM INVESTMENT CASTINGS
6. METAL PENETRATION IN SAND MOLDS
7. MOLD-METAL INTERFACE GAS COMPOSITION
8. IMPROVED ALLOY 718
9. SPECIFICATIONS FOR IRON OXIDE ADDITIONS TO NO-BAKE SANDS
10. CRITERIA FUNCTIONS FOR DEFECT PREDICTION
11. COMPUTER AIDED COOLING CURVE ANALYSIS

METALCASTING COMPETITIVENESS RESEARCH

FORWARD

This report comprises eleven separate reports, each dealing with a separate research task. Except for Tasks 6 and 7, each task is a separate research project, and they are related only insofar as they affect metalcasting in the United States. Each task report, therefore is a separate project report, which is able to stand alone, without reference to other reports. For this reason, the pages in each report are numbered independently of other pages.

Authors of each task report are given on the title page of each report. Objectives and results from each task are summarized below:

Task 1 — Prediction of Non-Metallic Particle Distribution

The objective of this task was to develop a computational method to predict the movement of inclusions in solidifying steel castings, and verify it experimentally. A model was developed, which described whether inclusions would be pushed or engulfed by the growing solid grains. Calculations made using the model were correlated with experimental observations.

Task 2 — Electromagnetic Separation of Inclusions from Molten Aluminum Alloys

The objective of this task was to demonstrate in a pilot plant the ability of electromagnetic fields to remove inclusions from aluminum alloys. A pilot plant was designed, and preliminary experiments indicated that the technology was promising.

Task 3 — Clean Steel Castings

This task was designed to evaluate methods of pouring steel castings which avoid reoxidation of the steel, forming non-metallic inclusions. The results from the project identified a number of promising methods which could be used to significantly improve the cleanliness of steel castings.

Task 4 — Waste Stream Identification and Treatment

The objective of this task was to define the nature of foundry waste streams, where they originate and what products they contain. Emphasis was placed on airborne wastes. A list of those compounds which might be formed and given off as airborne emissions was compiled, as well as a list of vendors capable of treating the emissions.

Task 5 — Elastic Wave Lithotripsy for Removal of Ceramics from Investment Castings

This task was to determine the feasibility of using elastic waves to remove shell material and cores from investment castings. The feasibility of shell removal was demonstrated. The feasibility of removal of ceramic cores was found to be limited by core composition, core geometry, and by the possibility of recrystallization of cast metal.

Task 6 — Metal Penetration in Sand Molds

The objective of this task was to determine the causes of metal penetration in cast iron cast in green sand molds, and determine methods of avoiding the defect. A basic equation capable of evaluating whether a casting/mold/alloy system would be expected to show penetration defects was developed.

Task 7 — Mold-Metal Interface Gas Composition

The objective of this task, which was related to Task 6, was to measure the chemical composition of the gases given off at the mold-metal interface when cast iron is poured into green sand molds. Gas compositions were obtained for green sand molds with and without carbonaceous additions.

Task 8 — Improved Alloy 718

The objective of this task was to modify the composition of alloy 718, a widely-used cast superalloy, so that its properties would be enhanced. A variation of the alloy composition was developed which was approved for use in the upgraded Space Shuttle Main Engine.

Task 9 — Specifications for Iron Oxide Additions to No-Bake Sands

The objective of this task was to develop specifications for iron oxide additions to no-bake sands to improve the surface finish and dimensional reproducibility of steel castings. Characteristics were identified which influenced the action of iron oxide additions to no-bake sands.

Task 10 — Criteria Functions for Defect Prediction

The objective of this task was to develop numerical criteria which are capable of predicting the occurrence of microporosity in aluminum alloy castings. A function was identified which more accurately predicted microporosity than other functions which were previously employed.

Task 11 — Computer-Aided Cooling Curve Analysis

The objective of this task was to develop ways of analyzing cooling curves so as to predict the quality of iron being poured. Analytical methods were developed, and their limitations noted.

Task 3 was performed by Southern Research Institute, and Tasks 8 and 9 by The University of Alabama at Birmingham. In Task 5, Dr. T. Greg Engel, of Texas Tech University assisted. Dr. T.S. Piwonka, Director of the Metal Casting Technology Center at The University of Alabama, was overall program manager.

AUTHORS BY TASK

Task 1	R.V. Phalnikar and D.M. Stefanescu
Task 2	N.H. El-Kaddah
Task 3	C.E. Bates and C. Wanstall
Task 4	M.D. McKinley and I.A. Jefcoat
Task 5	C.R. Evces, A.E. Carden, T.G. Engel and T.S. Piwonka
Task 6	D.M. Stefanescu, S.R. Giese and T.S. Piwonka
Task 7	A.M Lane and R. Pattabhi
Task 8	R.G. Thompson
Task 9	J.B. Andrews
Task 10	J.T. Berry
Task 11	D.M. Stefanescu and S. Viswanathan

Task 1

**PREDICTION OF NON-METALLIC PARTICLE
DISTRIBUTION**

D.M. Stefanescu and R.V. Phalnikar

PREDICTION OF NON-METALLIC PARTICLE MOVEMENT IN STEEL CASTINGS

1.0 Introduction

The solidification microstructure in metals is associated many times with the presence of second phase particles. These particles may be precipitated during solidification due to the supersaturation of certain elements, e.g., precipitation of primary and secondary inclusions in steel, or they may be added intentionally to impart mechanical strength to the metal matrix, e.g., particulate reinforced metal matrix composites (PRMMC). In either case, the structure of the composite in the solidification interval consists of three phases: liquid alloy, solid or liquid particles, and solid grains. The final microstructure would depend on the solidification kinetics that governs the growth of the grains and the interaction between the solid/liquid interface with the second phase particles that determines the distribution of the particles in the final microstructure. As a result of these two simultaneously occurring phenomena, particles may be distributed intergranularly, i.e., found between the grains, intragranularly, i.e., found within the grains, or a combination of both. If the particles are distributed between the grains, they act as stress raisers, which can result in poor mechanical properties. The desirable microstructural requirement is thus a uniform distribution of second phase particles within, and preferably not between the grains.

The interaction of the solid/liquid interface with the particles may result in pushing, engulfment or entrapment of inclusions. Engulfment of a particle occurs when the solid grows around the particle. Pushing of a particle results when the particle is pushed by the advancing solid/liquid interface. If the solidification interface becomes unstable, resulting in the formation of dendrites, then two or more solidification fronts can converge on the particle. Even if the particle is not engulfed by one of the fronts, it will eventually be entrapped in the solid at the end of local solidification. The transition between pushing and engulfment occurs at a certain interface velocity termed the "critical velocity." It has been established that at velocities higher than that critical velocity, particles are engulfed, and at lower velocities, they are trapped..

The objective of this work was to study the distribution of inclusions in steel castings. Keeping the theory of particle/interface interaction in perspective, a part of this work was directed toward studying the pushing/engulfment of inclusions by the advancing solid/liquid interface. The second aspect investigated was the dependence of the size distribution of the inclusions on various processing parameters. Efforts were also directed toward developing a numerical model to predict the distribution of inclusions as a function of the fraction of solid.

2.0 Literature Review

2.1 Theory of particle/interface interaction

The theory of particle/interface interaction postulates a critical interface velocity, V_{cr} , below which particles are pushed and above which particles are engulfed by the advancing solid/liquid interface. From the studies conducted over the last three decades, it can be summarized that the process variables affecting particle behavior at the solid/liquid interface are particle radius, viscosity of the melt, surface energy associated with the particle, liquid and solid, particle shape, convection level in the liquid, density of liquid and particle, liquid/solid interface shape, volume fraction of particles at the interface, and temperature gradient ahead of the interface.

Omenyi and Neumann¹ performed a computer curve fitting analysis of experimental results. They showed that the critical velocity depends on the particle radius, r , according to the equation:

$$V_{cr} = \frac{C}{r^n} \quad (1)$$

where n ranges from 0.28 to 0.90, and C is a constant.

A number of models have been proposed by Uhlmann *et al.*², Chernov *et al.*³, Bolling and Cisse⁴, and by Potschke and Rogge⁵. Stefanescu *et al.*⁶ proposed an analytical model which considered the force balance on the particle. They showed that critical velocity depends on the radius, r , according to the equation:

$$V_{cr} = \frac{1}{6\eta r} \left[\frac{\Delta\sigma_0 d_0}{2} \left(2 - \frac{k_p}{k_L} \right) - \frac{4}{3} r^3 g \Delta\rho \right] \quad (2)$$

where η is the viscosity of the matrix, r is the radius of the particle, $\Delta\sigma_0$ is the surface energy, d_0 is the interatomic distance, k_p and k_L are the thermal conductivities of the particle and matrix respectively, g is the gravitational acceleration, and $\Delta\rho$ is the difference in density between the particle and the matrix.

This model was further developed by Shangguan *et al.*⁷. It involves the solution of the temperature field for the particle/matrix configuration. They obtained the following equation for the equilibrium solidification (interface) velocity for the pushing/engulfment transition:

$$V_e = \frac{\Delta\sigma_0 d}{3\eta\mu r} \left(\frac{a_0}{a_0 + d} \right)^n \quad (3)$$

where η is the viscosity of the matrix, μ is the ratio of the thermal conductivities of the particle and the matrix, r is the radius of the particle, $\Delta\sigma_0$ is the surface energy, d is the particle-interface distance, a_0 is the interatomic distance, and n is a coefficient.

2.2 Inclusions in steel

Inclusions are non-metallic and intermetallic phases embedded in a metallic matrix⁸. They are mostly oxides, sulfides and nitrides of metals and non-metals. Most of the inclusions encountered in metal casting are detrimental to the properties of the metal.

Inclusions can be mainly categorized into (i) exogenous and (ii) indigenous inclusions. Exogenous inclusions are the inclusions derived from external sources, mainly refractories, slag and dross. They are usually macroscopic in size and hence are more prone to float or settle in the melt depending on their density. Indigenous inclusions are compounds derived from the reaction of the metal with the environment during solidification, including precipitation. They are usually microscopic in size and may be present inside the grain or along the grain boundaries. A uniform distribution of the inclusions inside the grains is beneficial as they strengthen the matrix. However, the

inclusions present along the grain boundary are detrimental as they act as stress raisers, thereby degrading the mechanical properties of the metal.

2.2.1. Oxides

The amount of carbon in iron controls the amount of dissolved oxygen. The solid solubility of oxygen in iron is low, and during solidification, oxygen is rejected to the remaining liquid, where it can react with carbon to form CO. The amount of dissolved oxygen in steel castings is reduced by additions of aluminum or silicon. Since Al_2O_3 has a lower free energy of formation than SiO_2 , aluminum is a more effective deoxidizer than silicon. The FeO content is an index of the amount of dissolved oxygen in the steel where the oxygen can also be reduced by carbon⁹, as shown in Figure 1.

Figure 1. Carbon-oxygen equilibrium at 1600 °C⁹.

At a given carbon content, the oxygen can then be reduced by aluminum or silicon to still lower levels, because the free energies for SiO_2 and Al_2O_3 are lower than those for CO or CO_2 at the reaction temperature.

Once oxide inclusions form, their removal rate depends on the nucleation of particles, their growth, and their ultimate agglomeration. Although there is a significant difference in density between the solid particles and the liquid metal, a simple application of Stokes's law is difficult. The problem is dynamic (liquid steel is not stagnant in the mold, as it must be for Stokes's Law to hold) and is influenced by the presence of other inclusion species. Therefore, oxide inclusions are often trapped in the final casting.

2.2.2. Sulfides

Sulfur present in steel combines with iron to form FeS inclusions. Since these inclusions form during the final stages of solidification, they often exist as grain boundary films and are deleterious to the mechanical properties of steel. Hence manganese is often added to steel to produce a more desirable MnS inclusions rather than FeS inclusions with low melting points. These inclusions are classified as Type I, Type II, and Type III respectively¹⁰. Type I inclusions exist as small isolated globules. They are found in steels killed completely with silicon or incompletely with aluminum, zirconium, or titanium. Type II inclusions exist as thin films or chains along grain boundaries. They form when a critical amount of aluminum is added, this being just sufficient to lower the oxygen content of the steel and leave no excess aluminum. This type of inclusions has also been observed in steels strongly deoxidized with zirconium or titanium. Type III inclusions are massive irregular inclusions that are distributed randomly. They result when an excess of aluminum is used for deoxidation. Magnesium when used as a

deoxidizer also promotes Type III inclusions. The typical microstructures of these type of inclusions are shown in Figure 2.

Fig. 2. Illustrations of common inclusion shapes and distributions found in steel. (a) Type I, (b) Type II, (c) Type III.¹¹

MnS inclusions can contain up to 75% FeS in solid solution at the MnS/FeS eutectic temperature (1170 °C), but this decreases to 25% at room temperature. Thus FeS can be precipitated with decrease in temperature or on annealing the material containing MnS inclusions for a long time. From the point of view of properties, Type I and Type III are preferred. Type II has been demonstrated as particularly damaging to the mechanical properties, as it is associated with low ductility.

Sulfur, oxygen, and the type of deoxidizer seem to play a combined role in the type of inclusion. Figure 3 shows this effect and the resulting decrease in structure-sensitive properties such as ductility and impact strength¹². The minimum in the curves is attributed to the formation of Type II inclusions.

The role of aluminum in the modification of inclusion shape and distribution also depends on the oxygen-sulfur equilibrium shift when aluminum is added. The effect of carbon and aluminum on the morphology of sulfide inclusions is shown in Figure 4.

Inclusion shape control becomes a consideration especially if fracture toughness, impact strength, or fatigue resistance must be optimized. Magnesium and calcium additions can be successfully used for shape control, that is, to produce more spherical shapes. Both magnesium and calcium form stable sulfides and oxides.

Several production methods have been employed for calcium or magnesium additions, either as the metallic elements or as compounds.^{23,24} Rare earth elements added in conjunction with calcium, magnesium and aluminum have been reported to enhance the spheroidization and fineness of the inclusions by breaking up the Al₂O₃ galaxies.

2.2.3. Nitrides.

The amount of nitrogen can be controlled by the addition of some alloying elements. For example, vanadium and manganese increase nitrogen solubility, while carbon and phosphorus decrease it. The effect of aluminum on nitrogen solubility has been extensively studied. Other nitride-forming elements such as titanium, zirconium, and vanadium have also been found to be effective. Nitride inclusions are considered to

be beneficial because they pin the austenite grain boundaries, and this results in grain refinement. On the other hand, brittleness results when nitrides become more or less continuous.

Figure 3. Combined effect of aluminum and sulfur on the ductility and impact strength of cast and normalized medium-carbon steel.¹²

2.3 Distribution of inclusions in steel

The earlier studies to remove inclusions from steel were concerned with the flotation of these inclusions in the melt. Many researchers^{13,14,15} studied the velocity of flotation of inclusions in the melt. McCance¹⁶ found that inclusions with density of 4000 kg/m³ and size 100 microns floated with a velocity of 80 cm/s whereas those of size 1 micron floated with a velocity of 0.008 cm/s. He also found that all the inclusions above 30 microns in an ingot of length 140 cm. floated up to the surface whereas all the inclusions below 5 microns were entrapped. Another observation was that as the pouring temperature increased, the number of inclusions entrapped decreased. The reason for this could be that if steel is poured from a higher temperature, the inclusions have more time for growth by diffusion, and hence they float with a higher velocity. Another possible explanation is that the inclusions float more easily because the steel has lower viscosity at higher temperatures. Time does not seem to play an important role in the flotation of inclusions.

Earlier, researchers¹³ thought that the non-metallic inclusions were not soluble in steel and that since they were suspensions in steel, they would always be found in the last

liquid to solidify. The former contention was disproved by Sims and Lillieqvist¹⁶, whose experiments indicated that the nonmetallics had limited solubility in steel, and that it changed with temperature, the change being rapid at the freezing point of steel. It was also found that high temperatures increased the solubility of non-metallics and hence very hot steels were dirty.

Figure 4. Effect of carbon and aluminum on the morphology of sulfide inclusions.

Regarding the position of the inclusions after solidification, many researchers once believed that the inclusions which precipitated before the solidification of steel, *i.e.*, the primary inclusions, would be found inside the grains and those which precipitated after the start of solidification of steel, *i.e.*, the secondary inclusions, would be found along the grain boundaries. However, later studies indicated that the primary inclusions may also be found predominantly along the grain boundaries. This led to the concept of pushing/engulfment of the inclusion by the solidification front. Experiments conducted on the metal and organic systems proved that particles/inclusions may either be pushed or engulfed depending on the solidification conditions. Many mathematical and analytical models^{2,3,4,5,6,7} were proposed to determine the critical velocity of solidification front above which the particles would be engulfed in the grains. Work is still going on to predict the particle/inclusion distribution in metals.

Another observation^{13,16} was that small ingots contained small inclusions and large ingots contained large inclusions. It was also observed that the center of heavy castings had larger inclusions than the surface. This is explained by the fact that the size of inclusions depends on the solidification velocity, lower the solidification velocity larger the inclusions.

The shape of inclusions in steel varies between globular, angular to a network along the grain boundaries. Ductile steels have inclusions in the globular or angular form. The globular inclusions are precipitated as liquids in a liquid medium. They retain their globular shape either because they solidify after steel and are forced to retain their shape or because they do not crystallize and cool to a glass. The angular inclusions are precipitated as either liquid or solid in a liquid medium, but are solidified as a crystalline material while the steel is still molten and hence are able to assume their natural crystal shape. The inclusions are in the form of a network when they are precipitated as a eutectic after the solidification of steel has begun.

The nucleation of inclusions in steel may be either homogeneous or heterogeneous. The growth of inclusions may take place by the following mechanisms: (i) diffusion growth, (ii) collisions and coalescence and (iii) diffusion coalescence or Ostwald ripening. Various studies^{15,17,18} were made to predict the growth mechanism of the inclusions in steel. Oxide inclusions were studied by many of these researchers. Turkdogan¹⁷ tried a theoretical analysis of the growth of inclusions by diffusion. Greenwood¹⁸ studied the growth of UPb_3 in liquid lead and of uranium particles in sodium. Torrsell¹⁹, Knuppel *et al.*²⁰ studied the growth of inclusions by collisions and coalescence. Lindborg and Torrsell¹⁹ made a quantitative statistical analysis of the growth and separation of inclusions based on collision theory. All these studies indicate that the three mechanisms contribute to the growth of inclusions to different extents as shown in Figure 5.

Figure 5. Schematic diagram of the typical size of oxide inclusions during the deoxidation period.

It is seen that diffusion growth, which takes place by diffusion of both oxygen and the deoxidizing element, accounts for 3 to 4 microns, whereas the subsequent growth is due to collision and coalescence of inclusions. Collision of inclusions takes place mainly due to the movement of inclusions as a result of Stokes's force and fluid flow. Inclusions grow to a size of 25 to 40 microns after which their separation from the melt takes place. Diffusion coalescence or Ostwald ripening may contribute some growth after very long periods of time, even if separation has partly taken place. The equilibrium oxygen concentration near a small inclusion is higher than that near a larger one. This leads to shrinkage of the smaller particles and growth of the larger ones. This phenomenon is termed as diffusion coalescence or Ostwald ripening. Diffusion coalescence is also noticeable at low contents of oxygen dissolved in steel.

2.4 Methodology for the study of inclusion distribution in steel

The interaction of the inclusions with the growing solid-liquid interface may be expected to play a vital role in determining the position of the inclusions in the final microstructure. According to the theory of particle/interface interaction discussed in section 2.1, there exists a critical velocity^{1,2,3} above which the particles are engulfed in the grain and below which they are pushed along the grain boundaries. Hence, an increase in the velocity of the solid/liquid interface would result in a decrease in the size of the particle that would be pushed. As a result, a velocity of advance of the interface would be reached at which the particles pushed by the interface would be very small or totally absent and thus most of the particles would be present inside the grains. This would enhance the mechanical properties of the metal.

Applying the above concept to steel is somewhat complicated because steel is not an isomorphous system and hence the solidification product in steel is not the final microstructural constituent. The situation is even more complicated for steels undergoing a peritectic transformation. However, plain carbon steel containing 0.6 to 0.7 %C and 0.9 to 2.0 %C can be used for this study. In these steels, the solidification product is austenite. Hence, the inclusions can be found either inside the austenite grains or along the austenite grain boundaries depending on whether they were engulfed or pushed by the growing austenite/liquid interface. Subsequent cooling of the steel does not change this configuration until the formation of the pro-eutectoid phase. The proeutectoid phase will mainly nucleate along the austenite grain boundaries and then grow subsequently. At the eutectoid temperature, the remaining austenite grain will be transformed into pearlite. Hence, the inclusions that were pushed by the growing austenite/liquid interface would be present in the pro-eutectoid phase in the final microstructure and the inclusions that were engulfed by the growing interface would be present in the pearlite. This fact can be used by determining the size of the inclusions present in the proeutectoid phase.

Accurate analysis of the metallographic sample is a vital part of this study. Two approaches can be used for this analysis: (i) Evaluating the maximum size of the inclusion; (ii) Evaluating the average size of the inclusions present on the pro-eutectoid phase. Figure 6 shows some inclusions distributed in a grain. Lines 1-5 denote the plane of the polish. It is desired to determine the size of the inclusion in the grain to the best possible accuracy. According to method (i), the actual size of the inclusion can be taken as to be the size of the largest inclusion in the grain, assuming all inclusions to be equal in size. According to method (ii), the actual size of the inclusion is the average size of all the inclusions present in the grain.

As shown in Figure 6, lines 1, 2, 4 and 5 would give the size of the largest inclusion as d_1 , d_2 , d_3 and d_4 respectively. However, the actual size of the largest inclusion is d_5 . Hence, at least three quantitative analyses should be performed.

Hence the size of the inclusion using method (i) is d_5 and that using method (ii) is

$$\frac{\sum_{n=1}^{n=5} d_n}{5}$$

This size can then be converted into the actual three-dimensional size by statistical methods. This method would give more accurate results.

Figure 6. Schematic diagram of a microstructure.

A plot of the interface velocity vs. the size of the inclusion evaluated using the above methods would give the interface velocity below which the inclusions of a given size would be pushed to the grain boundary. The velocity of the solid/liquid interface can be assumed to be equal to the ratio of the average austenite grain size and the solidification time. As shown in Figure 7, in plain carbon steels which do not undergo the peritectic reaction the austenite grain size, d , can be approximated to the sum of the size of the pearlite colony and the thickness of the pro-eutectoid phase. The interface velocity can then be evaluated from the room temperature microstructure as

$$v = \frac{d}{t_f}$$

where d is the average distance between the center of two proeutectoid ferrite phase crossing a pearlite colony, and t_f is the local solidification time, which can be approximated to the total solidification time in the vicinity of the thermocouple tip. It is obtained from the cooling curve.

Figure 7. Schematic diagram illustrating the phase transformation in steel.

2.4 Identification of silicate inclusions.

Manganese iron silicate inclusions were selected for this study. The reason for selecting these inclusions were: (i) they are easy to identify under an optical microscope; (ii) They are found in most commercial steels. Manganese iron silicate inclusions are found in the presence of manganese, silicon and oxygen. The silicate inclusions can be classified into two types: (1) acidic, (2) basic. The presence of large amount of silicon and small amount of manganese produce acidic inclusions rich in silica. These inclusions are small, transparent and globular in shape. Small amounts of silicon and average amount of manganese results in the formation of basic inclusions. These inclusions have strong coalescing power which makes them grow in size and separate easily.

Complex silicate inclusions are found in the presence of silicon, manganese, oxygen, aluminum, calcium, zirconium, and titanium. These inclusions are difficult to identify. However, in plain carbon steel, complex silicate inclusions are rarely encountered. Depending on the manganese and silicon content, acidic or basic silicate inclusions are predominant. Table I illustrates the method of identification of silicate inclusions by microscopic examination of the unetched section.²¹

Table 1. Microscopic appearance of unetched sections.

Form	Ordinary reflected light	Polarized light with crossed Nicols	Transmitted plain polarized light
Rich in SiO ₂ . Acidic.	Rich in SiO ₂ ; small varying shades of gray to color-less. Sometimes rosettes are present in acidic and appear darker than matrix.	Rich in SiO ₂ ; Optical cross and/or bright spot in center with an annulus near edge. Color white to pale orange.	
Basic	Low in SiO ₂ ; Generally dark green or orange to almost black.	Low in SiO ₂ ; Color green to orange. Second phase may or may not show optical cross.	Low in SiO ₂ . Green to orange.

Photomicrographs of typical silicate inclusions found in steel are shown in Figures 8 and 9.

3.0 Experimental Procedure

The experimental work was aimed at studying the distribution of inclusions in steel castings. It can be broadly categorized as follows:

- (1) Study of the size distribution of the inclusions as a function of the process variables.
- (2) Study of the pushing/engulfment of inclusions by the advancing solid/liquid interface.
- (3) Study of the distribution of inclusions as a function of the fraction of solid.

Figure 8. Large translucent silicate inclusion in cast steel²¹. Unetched. x 1,500.

Figure 9. Glassy silicate inclusions in cast steel²². Inclusion on extreme left shows a smaller inclusion being absorbed by the larger one. Unetched. x 1,000 approx.

3.1 Experimental setup.

The experimental setup used for this work is shown in Figure 10. Steel charges were melted in alumina crucibles using an induction furnace. After adjusting the composition of the melt, it was poured in a resin-bonded mold. The cooling curve was recorded using a platinum-6% rhodium, platinum-30% rhodium thermocouple interfaced to a Compaq II data acquisition system.

Figure 10. Experimental setup.

The samples were cleaned and cut using an abrasive cutoff wheel. They were then polished using polishing papers 80 μm , 120 μm , 240 μm , 320 μm , 400 μm , and 600 μm for coarse polishing and 0.3 μm and 0.05 μm for fine polishing. After the final polishing, the samples were cleaned ultrasonically and dried using acetone. They were then

observed under an optical microscope connected to a Nikon camera and a Zenith image analyzer.

3.2 Influence of holding time

Electrolytic grade iron containing 99 % Fe was melted in an alumina crucible using the setup shown in Figure 10. The carbon, silicon, and manganese levels were adjusted by alloying additions. The melt was then withdrawn after 20, 60, 150, 300, and 500 seconds using a silica tube attached to a vacuum bulb to obtain a cylindrical rod of length 5 cm. and diameter 1 cm. The samples were polished and observed under an optical microscope. The size distribution of inclusions was evaluated using a Zenith image analyzer.

3.3 Influence of carbon content and cooling rate.

Steel was melted in an alumina crucible using the setup as shown in Figure 10. The carbon content was adjusted to the required level by graphite additions. The melt was then poured into resin-bonded sand molds of diameter 15 mm and 20 mm. The cooling curve was recorded using a platinum-6% rhodium, platinum-30% rhodium thermocouple interfaced to a data acquisition system. The samples were polished and observed under an optical microscope. The size distribution of inclusions was evaluated using a Zenith image analyzer.

3.4 Study of the pushing/engulfment of inclusions.

A steel sample containing 0.08% carbon was used for this study. It was melted in an alumina crucible using the setup as shown in Figure 10. The carbon content was adjusted to 0.60, 0.68, and 0.75% by graphite addition. The melt was then poured in pepset molds of diameter 10 mm, 15 mm and 20 mm. The cooling curve was recorded using a platinum-6% rhodium, platinum-30% rhodium thermocouple interfaced with a data acquisition system. The samples were polished and observed under an optical microscope. The size of the inclusions present in the pro-eutectoid ferrite was measured using a Zenith image analyzer. Two methods were used to obtain a fairly accurate size of the inclusions:

- i) Repeated polishing technique. The size of the largest inclusion was measured after polishing. Then the sample was polished again using a 0.05 μm alumina paste. This sequence was repeated three times.
- ii) Averaging technique. The size of all the inclusions present in the pro-eutectoid ferrite was measured. The exact size of the inclusion present in the pro-eutectoid ferrite was then assumed to be the average of the size of all the inclusions present in this phase.

3.5 Study of the distribution of inclusions as a function of fraction of solid.

A computer model to predict the distribution of inclusions in steel castings was constructed. This model used a random number generator to obtain a random distribution of inclusions in the melt. The equiaxed grains were assumed to be spherical. The velocity of the interface was evaluated from the cooling curve and the critical velocity was evaluated using the model described in Section 2.1. The inclusions were pushed or engulfed by the grains depending on the pushing/engulfment criterion. The complete algorithm is given in Appendix A.1.

4.0 Results and Discussion

The objective of this work was to study the distribution of inclusions in steel castings. The work was divided into the following categories:

- a) Study of the size distribution of inclusions as a function of the processing parameters.
- b) Study of the pushing/engulfment of the inclusions by the advancing solid/liquid interface.
- c) Study of the distribution of inclusions as a function of fraction of solid.

4.1 Study of the size distribution of inclusions as a function of the processing parameters

4.1.1 Influence of holding time

The dependence of the size distribution of silicate inclusions on holding time for plain carbon steel containing 0.08 % C is illustrated in Figures 11 to 13 and Table 2.

Table 2. Influence of holding time on the size distribution of inclusions.

Holding time (s)	Maximum size (μm)	No. of inclusions per mm^2 ($\times 10^4$)	Average size (μm)
20	12.40	1.45	2.25
60	17.20	1.84	3.00
150	9.73	1.75	2.31
300	8.00	1.50	2.19
500	7.52	1.40	2.11

Figure 11. Relation between the number of inclusions and holding time.

Figure 12. Relation between the average size of inclusions and holding time.

Figure 13. Relation between the maximum size of inclusions and holding time.

The number of inclusions per unit area, maximum size and average size of inclusions show an initial increase with holding time. However, a subsequent increase in holding time results in a decrease in all three parameters. The initial increase in the number and size of the inclusions can be attributed to the diffusional growth and the

collision and coalescence of inclusions. Subsequent holding results in the flotation and elimination of inclusions from the melt due to Stokes's force resulting in a decrease in the number and size of the inclusions. These results indicate that a holding time of 5 to 10 minutes decreases the number of inclusions by 22%.

4.1.2 Influence of carbon content and cooling rate.

The dependence of the size distribution of inclusions on carbon content for two section sizes (and the two corresponding cooling rates) is depicted in Table 3 and Figures 14 to 17.

Table 3. The influence of carbon content and cooling rate on the size distribution of inclusions.

% C	Cooling rate, 1.3 °C/s			Cooling rate, 3.6 °C/s		
	No. of inclusions per sq. mm.(x10 ³)	Average size (μm)	Maximum size (μm)	No. of inclusions per sq. mm.(x10 ³)	Average size (μm)	Maximum size (μm)
0.50	2.75	1.93	4.68	2.55	2.17	9.40
0.61	1.72	2.10	5.88	1.46	2.20	10.25
0.75	1.50	2.25	6.32	1.28	2.26	11.46
0.95	0.93	2.39	9.60	0.56	2.50	25.38

Figure 14. Influence of carbon content and cooling rate on the number of inclusions.

It is evident from Figure 14 that the number of inclusions decreases with increase in carbon content. This may be due to the reaction of carbon with silica.

As the carbon content of the melt is increased, keeping the amount of the other elements constant, the melt has a higher potential to reduce silica to silicon. This results in a decrease in the extent of the subsequent reaction of SiO_2 with $(\text{Fe}, \text{Mn}) \text{O}$.

Thus the amount of the inclusions decreases with increase in carbon content.

Also, the number of inclusions per unit area is lower for a higher cooling rate and vice-versa. A higher cooling rate provides less diffusion time for the formation and precipitation of inclusions during solidification, resulting in fewer inclusions.

Figure 15. Influence of carbon content and cooling rate on the maximum size of inclusion.

4.1.3 Size distribution of inclusions as a function of their position in the grain

The distribution of inclusions inside the grain and at the grain boundary has been quantified in Tables 4 to 6 and Figures 17 to 19 for three different compositions. Two important aspects of the size distribution of inclusions can be studied from them. For a given composition and cooling rate, the percentage of larger particles engulfed is higher than that of the smaller particles. This suggests that smaller particles are easily pushed by the advancing solid/liquid interface as compared to the larger particles. Secondly, it can be observed that for a given composition, increasing the cooling rate results in an increase in the percentage of inclusions of all size ranges that are engulfed by the solid/liquid interface. A higher cooling rate results in a higher interface velocity, which in turn increases the number of inclusions engulfed by the interface.

Figure 16. Influence of carbon content and cooling rate on the average size of inclusions.

This trend has been observed in all the three compositions that were investigated.

Table 4. The size distribution of inclusions as a function of their position in the grain for 0.6 % C steel.

Size range μm	% of inclusions inside the grain		
	Cooling rate 1.3 °C/s	Cooling rate 3.6 °C/s	Cooling rate 4.7 °C/s
0-4	25	34	53
4-6	45	50	73
6-8	56	60	80
8-17	70	75	84

A polynomial interpolation of the results shown in Table 4 and Figure 17 gave the following relation between the amount of inclusions engulfed (y) and the size of the inclusions (x):

cooling rate 4.7 °C/s. $y = 10.00 + 57.83 x - 16.50 x^2 + 1.67 x^3$.

cooling rate 3.6°C/s. $y = 1.00 + 45.17 x - 14.00 x^2 + 1.83 x^3$.

cooling rate 1.3°C/s. $y = -16.00 + 55.50 x - 16.50 x^2 + 2.00 x^3$.

Figure 17. Size distribution of inclusions as a function of their position in the grain for 0.6 % C steel.

Table 5. The size distribution of inclusions as a function of their position in the grain for 0.73 % C steel.

Size range μm	% of inclusions inside the grain		
	Cooling rate 1.3 °C/s	Cooling rate 3.6 °C/s	Cooling rate 4.7 °C/s
0-3	25.00	33.40	43.80
3-4	40.00	50.00	57.00
4-5	50.00	57.14	66.70
5-15	60.00	67.00	75.00

A polynomial interpolation of the results shown in Table 5 and Figure 18 gave the following relation between the amount of inclusions engulfed (y) and the size of the inclusions (x):

cooling rate 4.7 °C/s. $y = 64.00 - 41.33 x + 23.50 x^2 - 3.17 x^3$.

cooling rate 3.6°C/s. $y = 47.00 - 35.00 x + 18.00 x^2 - 2.00 x^3$.

cooling rate 1.3°C/s. $y = 40.00 - 37.50 x - 20.00 x^2 - 2.50 x^3$.

Figure 18. Size distribution of inclusions as a function of their position in the grain for 0.73 % C steel.

Table 6. The size distribution of inclusions as a function of their position in the grain for 0.93 % C steel.

Size range μm	% of inclusions inside the grain		
	Cooling rate 1.3 °C/s	Cooling rate 3.6 °C/s	Cooling rate 4.7 °C/s
0-3	20	28	43
3-4	25	33	50
4-5	40	50	66
5-15	50	67	72

A polynomial interpolation of the results shown in Table 6 and Figure 19 gave the following relation between the amount of inclusions engulfed (y) and the size of the inclusions (x):

cooling rate 4.7 °C/s. $y = 25.00 + 22.30 x - 3.85 x^2 + 0.35 x^3$.

cooling rate 3.6 °C/s. $y = -4.84 + 53.12 x - 16.91 x^2 + 2.03 x^3$.

cooling rate 1.3 °C/s. $y = 31.67 x - 7.50 x^2 + 8.33 x^3$.

Figure 19. Size distribution of inclusions as a function of their position in the grain for 0.93 % C steel.

4.2 Study of the pushing/engulfment of the inclusions by the advancing solid/liquid interface

An attempt was made to quantify the pushing/engulfment of inclusions by the solid/liquid interface. The interface velocity was approximated to be the ratio of the average grain size and the local solidification velocity. A plot of this interface velocity versus the inclusion radius was compared with the model summarized by Equation (3). Two methods were used to evaluate the inclusion radius:

1. Evaluation of the maximum radius of the inclusion present in the proeutectoid phase by repeated polishing.
2. Evaluation of the average size of the inclusion present in the proeutectoid phase.

The results are given in Tables 7 to 9 and Figures 20 to 22.

Table 7 and Figure 20 contain the data for steel with a carbon content of 0.6%. It is seen that the growth (interface) velocity varies inversely with the size of the inclusion present in the proeutectoid phase. Least squares analysis conducted on this data produced the following relation for critical velocity:

$$V_{cr} = \frac{120.56}{r}$$

Table 7. Dependence of the size of the inclusion present in the proeutectoid phase as a function of the interface velocity for 0.6 % C steel.

Radius of the inclusion in the proeutectoid phase, μm	Interface velocity, $\mu\text{m/s}$
6.55	22.08
7.74	14.80
9.13	9.01

Figure 20. Size of the inclusion pushed as a function of interface velocity for 0.6% C steel.

Table 8 and Figure 21 represent the data of the relation between the interface velocity and inclusion size for steel with a carbon content of 0.68%. A least squares analysis of this data gave the following relation for the critical velocity:

$$V_{cr} = \frac{59.52}{r}$$

Table 8. Dependence of the size of the inclusion present in the proeutectoid phase as a function of the interface velocity for 0.68% C steel.

Radius of the inclusion in the proeutectoid phase, μm	Interface velocity, $\mu\text{m/s}$
2.50	22.49
4.78	14.51
5.37	11.60

Figure 21. Size of the inclusion pushed as a function of interface velocity for 0.68% C steel.

Table 9 and Figure 22 represents the data for steel with a carbon content of 0.73%. Least squares analysis of this data results in the following relation for the critical velocity:

$$V_{cr} = \frac{40.86}{r}$$

Table 9. Dependence of the size of the inclusion present in the proeutectoid phase as a function of the interface velocity for 0.73% C steel.

Radius of the inclusion in the proeutectoid phase, μm	Interface velocity, $\mu\text{m/s}$
2.63	17.28
3.72	9.83
4.45	7.61

4.2.2 Evaluation of critical velocity using the averaging technique

The relation between the interface (growth) velocity and the size of the inclusion present in the proeutectoid phase, evaluated by the averaging technique, is shown in Tables 10 to 12 and Figures 23 to 25.

Table 10 and Figure 23 represent the data for steel having a carbon content of 0.6%. Least squares analysis of this data gives the following relation for the critical velocity:

$$V_{cr} = \frac{45.40}{r}$$

Figure 22. Size of the inclusion pushed as a function of interface velocity for 0.73% C steel.

Table 10. Dependence of the size of the inclusion present in the proeutectoid phase as a function of the interface velocity for 0.6% C steel.

Radius of the inclusion in the proeutectoid phase, μm	Interface velocity, $\mu\text{m/s}$
2.52	22.08
2.85	14.80
3.44	9.01

Table 11 and Figure 24 represent the correlation between the interface velocity and inclusion size for steel with a carbon content of 0.68%. The relation for the critical velocity evaluated by the least squares method is as follows:

$$V_{cr} = \frac{25.93}{r}$$

Table 11. Dependence of the size of the inclusion present in the proeutectoid phase as a function of the interface velocity for 0.68% C steel.

Radius of the inclusion in the proeutectoid phase, μm	Interface velocity, $\mu\text{m/s}$
1.52	22.49
1.59	14.51
1.65	11.60

Figure 23. Size of the inclusion pushed as a function of interface velocity for 0.6% C steel.

Figure 24. Size of the inclusion pushed as a function of interface velocity for 0.68% C steel.

The dependence of inclusion size on the interface velocity for steel with a carbon content of 0.73% is given in Table 12 and Figure 25. A least squares analysis of this data gave the following equation for the critical velocity:

$$V_{cr} = \frac{17.36}{r}$$

Table 12. Dependence of the size of the inclusion present in the proeutectoid phase as a function of the interface velocity for 0.73% C steel.

Radius of the inclusion in the proeutectoid phase, μm	Interface velocity, $\mu\text{m/s}$
1.32	17.28
1.50	9.83
1.61	7.61

4.3 Comparison of the experimental results with the model.

The experimental results were compared with the model⁷ described in section 2.1. Since the value of the surface energy is not available in literature, the experimental results were compared with the model using reasonable values for the surface energy. Two values of the coefficient n in Eq. (3) were chosen, namely, $n=2$ and $n=2.5$. The experimental results using both the repeated polishing technique and the averaging technique were compared.

Figure 25. Size of the inclusion pushed as a function of interface velocity for 0.73% C steel.

4.3.1 Comparison of the experimental data obtained by the repeated polishing technique with the model.

The experimental data obtained using the repeated technique was compared with the particle pushing/engulfment model⁷ described in section 2.1. The results are shown in Figures 26 to 31. Figures 26 and 27 are for 0.6 % carbon steel using the values of n as 2 and 2.5 respectively. It can be seen from Figures 26 and 27 that the experimental data compares well with the model using the surface energy value of 0.05 N/m.

Figures 28 and 29 are for 0.68 % carbon steel using the values of n as 2 and 2.5 respectively. It can be seen from Figures 28 and 29 that the experimental data compares well with the model using the surface energy value of 0.025 N/m.

Figures 30 and 31 are for 0.73 % carbon steel using the values of n as 2 and 2.5 respectively. It can be seen from Figures 30 and 31 that the experimental data compares well with the model using the surface energy value of 0.0125 N/m.

Figure 26. Comparison of the experimental results for 0.6 % C with the model using $n=2$.

Figure 27. Comparison of the experimental results for 0.6 % C with the model using $n=2.5$

Figure 28. Comparison of the experimental results for 0.68 % C with the model using $n = 2$.

Figure 29. Comparison of the experimental results for 0.68 % C with the model using $n=2.5$.

Figure 30. Comparison of the experimental results for 0.73 % C with the model using $n=2$.

Figure 31. Comparison of the experimental results for 0.73 % C with the model using $n=2.5$.

4.3.2 Comparison of the experimental data obtained by the averaging technique with the model

The experimental data obtained using the averaging technique was compared with the particle pushing/engulfment model⁷ described in section 2.1. The results are given in Figures 32 to 37. Figures 32 and 33 are for 0.6 % carbon steel using the values of n as 2 and 2.5. It can be seen from Figures 32 and 33 that the experimental data compares well with the model using the surface energy value in the range of 0.025 to 0.05 N/m.

Figures 34 and 35 are for a 0.68 % carbon steel using the values of n as 2 and 2.5 respectively. It can be seen from Figures 36 and 37 that the experimental data compares well with the model using the surface energy value in the range of 0.0062 to 0.0125 N/m.

Figures 36 and 37 are for a 0.73 % carbon steel using the values of n as 2 and 2.5 respectively. It can be seen from Figures 38 and 39 that the experimental data compares well with the model using the surface energy value of 0.0062 N/m.

Figure 32. Comparison of the experimental results for 0.6 % C with the model using $n=2$.

Figure 33. Comparison of the experimental results for 0.6 % C with the model using $n=2.5$.

Figure 34. Comparison of the experimental results for 0.68 % C with the model using $n=2$.

Figure 35. Comparison of the experimental results for 0.68 % C with the model using $n=2.5$.

Figure 36. Comparison of the experimental results for 0.73 % C with the model using $n=2$.

Figure 37. Comparison of the experimental results for 0.73 % C with the model using $n=2.5$.

4.4 Distribution of the inclusions as a function of the fraction of solid.

The computer model results to predict the distribution of inclusions in steel castings are given in Figure 38. The initial distribution of the particles is given in Figure 38a with fraction of solid equal to zero. The final distribution of the particles is given in Figure 38d with fraction of solid equal to one. Figures 38b and 38c represent the distribution of the particles for fraction of solid equal to 0.4 and 0.8 respectively. It is seen that the particles of size 50 μm are engulfed and those of size 10 and 25 μm are pushed by the advancing solid/liquid interface.

5.0 Conclusions

This study demonstrates the effect of various process variables on the distribution of inclusions in steel castings. The number of inclusions per unit area was found to show a maximum with respect to the holding time. A holding time of 500 seconds decreased the number of inclusions by 22 % as compared to that of 60 seconds. The effect of holding time on the size of the inclusions also showed a similar trend. The initial increase in the number and size of the inclusions can be attributed to diffusional growth and the collision and coalescence of inclusions. Subsequent holding results in the flotation and elimination of inclusions from the melt due to Stokes's force, resulting in a decrease in the number and size of the inclusions.

The number of inclusions per unit area decreased with increasing carbon content, other factors remaining constant. This may be due to the reaction of carbon with silica. As the carbon content of the melt is increased, keeping the amount of the other elements constant, the melt has a higher potential to reduce silica to silicon. This results in a decrease in the extent of the subsequent reaction of SiO_2 with $(\text{Fe}, \text{Mn})\text{O}$. Thus, the amount of inclusions decreases with increasing carbon content. It was observed that for a given carbon content, the number of inclusions per unit area was lower and the size of the inclusions was higher for a higher cooling rate and vice-versa.

The study of the distribution of the inclusions in a grain revealed two important aspects of the size distribution of inclusions. It was found that for a given composition and cooling rate, the percentage of larger inclusions engulfed was higher than that of the smaller inclusions. In particular, about 80% of the inclusions in the size range 8 to 15 μm were found to be inside the grains whereas only 20 to 25% of the inclusions in the size range 0 to 3 μm were found inside the grains. This suggests that smaller particles were easily pushed by the advancing solid/liquid interface as compared to the larger particles. Secondly, it was also observed that for a given composition, increasing the cooling rate results in an increase in the percentage of inclusions of all size ranges that are engulfed by the solid/liquid interface. A higher cooling rate results in a higher interface velocity, which in turn increases the number of inclusions engulfed by the interface.

The critical growth (interface) velocity was found to decrease with the increase in the radius of inclusion pushed by the solid/liquid interface for all three compositions of steel and two methods of evaluation of inclusion size that were used for the investigation. The following relation was obtained:

$$V_{\text{cr}} = \frac{C}{r}$$

a

b

c

d

Fig. 38. Computed distribution of inclusions in steel containing 5 % inclusions of size 10, 20, and 50 μm : a) $f_s = 0$, b) $f_s = 0.4$, c) $f_s = 0.8$, d) $f_s = 1$.

This study thus illustrates that small inclusions are readily pushed by the advancing solid/liquid interface, whereas very low interface velocities are required to push larger inclusions.

The significance of the above results is that i) the process variables can be adjusted in the right amounts to decrease the number of inclusions. ii) the size distribution of the inclusions can be controlled by combining the process variables, namely the holding time and cooling rate, for a given composition. iii) For a given size distribution of inclusions, an approximate interface velocity can be evaluated using which most of the inclusions can be obtained inside the grains after solidification.

References

1. S.N. Omenyi and A.W. Neumann, *J.Appl.Phys.*, 1976, vol. 47, no. 9, p. 3956.
2. D.R. Uhlmann, B. Chalmers and K.A. Jackson, *J.Appl.Phys.*, 1964, vol. 35, no. 10, p. 2986.
3. A.A. Chernov, D.E. Temkin, and A.M. Melnikova, *Sov.Phys.Crystallogr.*, 1976, vol. 21, no. 4, p. 369.
4. G.F. Bolling and J. Cisse, *J.Cryst.Growth*, 1971, vol. 10, p. 56.
5. J. Potschke and V. Rogge, *J.Cryst.Growth*, 1989, vol. 94, pp. 726-738.
6. D.M. Stefanescu, A. Moitra, A.S. Kacar, and B.K. Dhindaw, *Met.Trans.*, 1990, vol. 21A, pp. 231-239.
7. D. Shangguan, S. Ahuja, and D.M. Stefanescu, *Met.Trans.*, 1992, vol. 23A, pp. 669-680.
8. S. Katz, General Motors Research Laboratory, Principles of Liquid Metal Processing, *Metals Handbook*, vol. 15, pp. 88-98.
9. S. Katz, General Motors Research Laboratory, Principles of Liquid Metal Processing, *Metals Handbook*, vol. 15, p. 92.
10. T.R. Allmand, Microscopic identification of inclusions in steel, British Iron and Steel Research Association, p 51.
11. C.E. Sims and F.B. Dahle, The Effect of Aluminum on the Properties of Medium Carbon Cast Steel, *Trans. AFS*, 1938, vol. 46, pp. 65-132.
12. S. Katz, General Motors Research Laboratory, Principles of Liquid Metal Processing, *Metals Handbook*, vol. 15, p. 93.
13. A. McCance, *J. Iron Steel Inst.*, 1918, XC7, p. 240.
14. R. Gunn, *Science*, 1965, vol. 150, p. 695.
15. U. Lindborg and K. Torssell, *Trans. AIME*, 1968, vol. 242, p. 94.
16. C.E. Sims and G.A. Lillieqvist, *Trans. AIME*, 1932, vol. 100, p. 154.
17. E.T. Turkdogan, *J.Iron.Steel.Inst.*, 1966, p. 914.
18. G.W. Greenwood, *Acta Metallurgica*, 1956, vol. 4, p. 243.
19. K. Torssell, *Jernkontorets Ann.*, 1967, p. 151.
20. H. Knuppel, K. Brotzmann, and N.W. Forster, *Stahl Eisen*, 1965, vol. 85, p. 675.
21. T.R. Allmand, Microscopic identification of inclusions in steel, British Iron and Steel Research Association, p 51.
22. S.F. Urban and J. Chipman, Non-Metallic Inclusions in Steel, *Trans. A.S.M.*, 1935, vol. 23.

APPENDIX A.1

Figure. A.1. Model for inclusion distribution in castings.

Task 2

**ELECTROMAGNETICSEPARATION OF INCLUSIONS FORM
MOLTEN ALUMINUM ALLOY**

N.H. El-Kaddah

ELECTROMAGNETIC SEPARATION OF INCLUSIONS FROM MOLTEN ALUMINUM ALLOYS

1.0 Introduction

This project, on the use of an electromagnetic field to separate inclusions from molten aluminum alloys, focused on the industrial implementation of the Electromagnetic Separation System (EMS) developed at The University of Alabama.¹ To meet this goal, the program was divided into three principal tasks:

1. Design of a continuous flow system for filtering large quantities of molten aluminum.
2. Fabrication and installation of the system.
3. Evaluation of system performance under industrial conditions.

The industrial partner in this project was the Aluminum Company of America (Alcoa), who entered the project after two previous industrial partners withdrew, one for financial reasons (it was a division of a larger corporation, and was divested during the period of the project) and a second because of inability of the University and corporation to agree on patent and legal rights to the technology under development. This meant that Alcoa entered the project late, and much of the project work that they carried out was done after DOE funding had expired. Researchers at the University had the responsibility to design the system, and Alcoa was responsible for fabricating and testing the system, at their Research Center.

Alcoa's interest in this technology was primarily for cleaning molten aluminum in the continuous casting process. In general, most in-line filtration systems for continuous casting are only effective in removing inclusions larger than 50 microns.² To meet the demands for cleaner melts, it was decided to test the system capability in removing particles 20 microns and larger. As a first step in the industrial implementation of this technology, it was agreed to determine the system performance in cleaning a continuous stream of molten metal flowing at the rate of about 30 lb/min., from a 3500 lb holding furnace.

2.0 The University of Alabama Electromagnetic Separation System

The University of Alabama's Electromagnetic Separation System is a hybrid system that involves the application of both an electromagnetic field and conventional filters. It is a small, compact device that can be easily retrofitted to all types of pouring ladles, and even could be placed in the runner systems of large castings. It is shown schematically in Figure 1.

It consists of a rectangular refractory box with an inlet nozzle at the top and an outlet nozzle at the bottom. There are two elements for removal of inclusions in the box, a long refractory block with open channels (called the "baffle block") for electromagnetic separation, and a standard filter. The baffle block sits above the filter, which is located just above the exit nozzle.

In electromagnetic separation, the inclusions are driven out of the melt by the application of an external electromagnetic force field. This is similar to inclusion removal by flotation where the external force is gravitational. The buoyant force generated by the

Figure 1. Schematic Diagram of the Separation Chamber

electromagnetic field depends on both the difference between electrical conductivities of the metal and the inclusion, and the strength of the field. Because the electrical conductivity of metals is an order of magnitude larger than that of nonmetallic inclusions, the same electromagnetic buoyant force is exerted on all forms of inclusions, regardless of their chemical composition or physical form.

Figure 2. Required Force Field Distribution in the Baffle Block

The direction of the electromagnetic separation forces depends on the induction coil configuration that generates the force field. In the University of Alabama EMS, the electromagnetic forces are normal to the vertical walls of the separation chamber. This forces the inclusions to migrate to the side walls where they are trapped by the

refractories. The only requirement is that the electromagnetic force vectors be parallel and normal to the walls of the separation chamber, as shown in Figure 2.

3.0 System Design

3.1 Design Criteria

Design of the electromagnetic separation element essentially involved the design of the induction coil and chamber configuration in the baffle block (i.e., the proper positioning of the vertical walls of the chambers in the block) to meet the force field configuration requirements described above. In addition, the time required to transport the inclusions to the side walls by electromagnetic forces must be less than the time it takes for the metal to flow through the chamber (the "residence time" of the melt).

Generally, these two design criteria cannot be met by trial and error; without a computer-aided design tool it is impossible to meet all the strict requirements simultaneously. Although a process design model was available for computing the electromagnetic and velocity field in the system, this model was substantially revised and refined during the design phase of the project. The model was upgraded to compute the electromagnetic force distribution for any given chamber design and inductor configuration as well as the rate of particle removal from the system. These refinements were necessary to improve the accuracy of the model, thus reducing the number of industrial trials required to achieve optimal performance from the system.

3.2 Process Design Model

The removal of inclusions in the EMS system is influenced by:

1. electromagnetic force field distribution in the separation chamber
2. the corresponding velocity field
3. particle dynamics in the melt.

These three aspects are interrelated as the force distribution dictates both fluid flow and particle history in the separation chamber. For successful removal of inclusions, melt stirring by electromagnetic forces must be eliminated. Thus calculation of the velocity field is necessary to ensure that this condition is met in the system.

Electromagnetic Field Equations

Maxwell's equations for a general three-dimensional system take the following form:

$$\nabla \cdot \mathbf{J} = 0$$

$$\nabla \cdot \mathbf{B} = 0$$

$$\nabla \times \mathbf{B} = \mu \mathbf{J}$$

$$\nabla \times \mathbf{E} = - \partial \mathbf{B} / \partial t \quad (1)$$

where

$$\mathbf{J} = \sigma [\mathbf{E} + \mathbf{U} \times \mathbf{B}] \quad (2)$$

$\mathbf{J}$ is the electric current density, $\mathbf{E}$ is the electric field, $\mathbf{B}$ is the magnetic flux density, μ is the magnetic permeability, $\mathbf{U}$ is the velocity, and σ is the electrical conductivity of the material.

Fluid Flow Equations

The most efficient removal of inclusions will take place when the fluid is stagnant. Since this is impossible in a flowing stream, the next best condition is for the fluid to be flowing under laminar flow conditions. Fluid flow equations are therefore

$$\nabla \cdot \mathbf{U} = 0 \quad (3)$$

$$\rho (\mathbf{U} \cdot \nabla) \mathbf{U} = -\nabla P - \nabla \cdot \boldsymbol{\tau} + \mathbf{J} \times \mathbf{B} \quad (4)$$

where P is the pressure, and $\boldsymbol{\tau}$ is the viscous shear stress tensor.

Particle Dispersion Model

To describe the behavior of a population of inclusion particles with different sizes in the melt during separation realistically, the particle history of the inclusions was represented by a population balance. The total number of particles in the melt, N , is expressed in terms of particle density $f(r)$, i.e., the distribution of particles having a radius r , by:

$$N = \int_0^{\infty} f(r) dr. \quad (5)$$

The particle number balance equation is given by:

$$\frac{\partial f}{\partial t} + \nabla \cdot (\mathbf{U}_p f(r)) + \int_0^{\infty} \frac{\partial G(r)}{\partial r} f(r) dr = S(r) \quad (6)$$

where $G(r)$ is the growth function, $\mathbf{U}_p$ is the velocity of a given particle, and $S(r)$ is a source and sink term which can be used to represent the removal of the particles at the melt boundaries.

Equations (1) to (6) constitute a complete statement of the problem. These equations are solved simultaneously using previously published techniques.^{3,4}

Solution of these equations gave the necessary dimensions of the baffle block. This included block length, which was determined by the residence time required for the system to remove inclusions, the actual shape of the opening between the baffles, the magnetic flux density and electric current density required for operation of the coil. The other quantities are defined by the alloy selected.

3.3 The Electromagnetic Separation System at Alcoa

The EMS consists of two basic components: the inductor and the electromagnetic separation chamber. These two elements must be carefully matched to produce the precise field strength and structure in the channels of the chamber for optimal removal of inclusions. The field strength and structure in the chamber are determined by the coil configuration and the coil operating conditions (coil current and frequency) as well as the location and dimensions of separation channels in the baffle block.

To reduce the cost of the planned experiments, which, as previously noted, were to clean 3500 lb of molten aluminum alloy flowing at a rate of 30 lb/min., Alcoa chose an existing 150 kW mains frequency (60 Hz) power supply. Design calculations, using the model of section 3.2, were carried out to determine the coil configuration and the coil current that would remove inclusions larger than 20 microns.

Figures 3 and 4 show the configuration of the coil designed for these experiments. It was a water-cooled 20-turn two-parallel plate inductor. Each plate was 600 mm long and 289 mm wide. The distance between the two plates was 174 mm, slightly larger than the width of the separation chamber. The calculated resistance and inductance of the coil were 0.04 Ohm and 133 μ Henry respectively. The water flow rate through the coil at 60 psi was estimated to be 100 liters per minute. On the basis of electrical data and water flow rate, the coil was capable of carrying electric current up to 300 Amps per turn, which was three times the current needed for removal of inclusions larger than 20 microns. Figure 5 shows the coil which was built.

In the process of designing the baffle block for this test, a number of practical problems emerged in implementing the original baffle block design shown in Figures 1 and 2. These revolved around the need for a large power supply with this baffle block configuration to remove 20 micron inclusions, and the high cost to manufacture the baffle block because of radially skewed arrangement of the separation channels in the block. To alleviate these problems several modifications were made to the baffle block design. These modifications involve the use of smaller separation channels to reduce the time required for inclusion removal, and the use of magnetic shields to modify the force field distribution and improve its alignment in the chamber. The use of smaller channels reduced the separation time and the force field requirement for effective separation of small inclusions. The purpose of using the magnetic shield was to align the separation channels parallel to each other. This significantly simplified the fabrication of the baffle block and lowered its manufacturing cost.

Figures 6 - 8 show the design of the baffle block for the electromagnetic separation chamber used for Alcoa's experiments. The size of the separation chamber for these experiments was relatively small, 148 x 268 x 480 mm. The baffle block contained 48 rectangular cross-section channels, arranged symmetrically around the center planes of the block. In designing the baffle block, the cross sectional area of the channels was made non-uniform, decreasing towards the center of the block (where the field strength is minimum), to have the same separation time in all of them. The hatched 10 x 10 mm square at the top left corner of the block, shown in Figure 7, indicates the location of the magnetic shield in the baffle block. In design calculations copper was used as a shielding material as it has a higher electrical conductivity and melting point than aluminum (the metal to be cleaned). Below the baffle block a 10 ppi filter was placed in the same position as shown in Figure 1 to regulate and ensure laminar flow through the channels.

4.0 Fabrication, Installation and Test Results

4.1 Fabrication and Installation

The coil was fabricated at the University of Alabama and was fully insulated and leak tested at 60 psi.

The separation chamber was fabricated to the new design shown in Figures 6 and 7 by Hi-Tech Ceramics, Inc. The baffle block was made of 92% alumina reticulated ceramic

Figure 3. Sketch of Coil Winding

Figure 4. Coil Configuration of the Electromagnetic Separation System

Figure 5. Coil, as fabricated.

Figure 6. Plan view at the middle of the baffle block

Figure 7. Quarter section of baffle block, showing detailed dimensions

filter material. Processing the baffle block involved depositing a ceramic slurry of alumina 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 a temperature above of 1500 C to form a fully sintered ceramic product. After fabricating the baffle block, the copper magnetic shield was installed in the grooves of the two sides of the block. The assembly was then enclosed in a ceramic box having a 2" diameter hole in the top and bottom. The box was made from 3/4" thick alumina plates supplied by the Norton Co. The plates were cemented together using a high temperature refractory cement and the whole assembly was dried overnight at 60 C.

Figure 8 shows a schematic sketch of the experimental arrangement at Alcoa. The EMS system was placed under the trough of the holding furnace. As seen, the inlet nozzle of the chamber was connected to the bottom of the trough. In this set-up the metal was discharged from the chamber into a drain pan. The inlet nozzle was a 3" graphite tube with an inner diameter of 1". The exit nozzle was made of a 5" graphite tube with a 1" hole in the center. To control the flow through the chamber a 1" boron nitride tube was inserted in the exit nozzle. A special stand was designed and constructed at Alcoa to support the EMS system (the coil and the separation chamber).

Figure 8. The Alcoa experimental Electro-Magnetic Separation (EMS) system schematic.

4.2 Test Results

Magnetic field measurements were carried out to calibrate the electromagnet and to examine the uniformity of the field within the inductor in the region occupied by the chamber. Figure 9 shows the measured magnetic field strength at the center of the inductor at different coil currents. It is seen that the magnetic flux density increases linearly with the inductor current, as expected. The magnetic flux density at 1080 Amps (used in the separation experiments) was 0.0816 Tesla. This value is very close to the

calculated value obtained from the mathematical model. The field within the inductor was found to be uniform to within $\pm 5\%$.

Figure 9. Variation of the magnetic field with coil current

Before conducting the melt filtration experiments, a series of trials was carried out to ensure the safety of the system and to establish the experimental procedure. During these trials numerous engineering problems were discovered, all relating to the necessity to preheat the chamber before exposing it to molten metal (so that the metal would not freeze in the chamber and block flow). Although problems of this type are common in large scale experiments involving new concepts, three of the five chambers available for experimentation fractured during these trials. The two final chambers were used in experiments that permitted some flow of molten metal to be obtained. The limited results obtained were very encouraging. Examination of the metal that flowed through the filter showed it to be substantially free of inclusions larger than 20 microns, as was expected, thus establishing the feasibility of the process. In other words, the model which was developed was successful in producing a workable design for a commercial installation.

However, these experiments did not produce results sufficient to permit a quantitative economic analysis of the efficiency of the process to be made. The program was put on hold by Alcoa. Their conclusion was that the technology was sufficiently promising to warrant further work to complete implementation, but that the timing of this work would have to wait for improved economic conditions in the aluminum industry.

5.0 Conclusions

1. The feasibility of using the electromagnetic separation process to remove inclusions from molten aluminum has been established.
2. A mathematical model has been developed which is capable of designing a commercial sized inclusion removal system for aluminum alloys.
2. Significant engineering problems remain to implement the system in a commercial application.

REFERENCES

- ¹N.H. El-Kaddah, "Apparatus and a Method for Improved Filtration of Inclusions from Molten Metal," U.S. Patent # 4,909,836, 1990.
- ²A.T. Engh, *Principles of Metal Refining*, Oxford University Press Inc., New York (1992).
- ³N. El Kaddah, "A Comprehensive Mathematical Model of Electromagnetic Separation of Inclusions in Molten Metal," *IEEE IAS Conf. Proceedings*, 1988, p. 1162.
- ⁴L. Marechal, N. El-Kaddah and P-Y Menet, "Influence of Convection on Agglomeration and Removal of Non-Metallic Inclusions in Molten Aluminum," *Light Metals 1993*, p. 907.

Task 3

CLEAN STEEL CASTINGS

C.E. Bates and C. Wanstall

CLEAN STEEL CASTINGS

1.0 Introduction

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 project involves:

1. conducting a thorough literature search to identify new approaches that might be adapted to produce cleaner castings,
2. exploring filters for their ability to remove inclusions as metal is poured,
3. conducting water modeling experiments to explore methods for minimizing air entrainment during pouring.

This report presents a summary of work completed in the first year of the project.

2.0 Significant Conclusions

1. This report summarizes the published literature on the effects of processing and pouring steel in air on steel casting cleanliness.
2. Molten steel oxidizes extremely rapidly in air.
3. Stream surface area must be minimized during pouring.
4. Air entrainment during handling and pouring must be minimized.
5. Filtration of carbon steel in the current program was found to reduce inclusions by 50% with a corresponding reduction in weld repair time.
6. Care must be taken in filter selection because some commercial filter materials are not sufficiently resistant to molten steel.
7. In water modeling trials with bottom pour ladles the ladle depth, nozzle opening and sprue length had significant effects on the amount of entrained air
8. The stopper opening produced about 70% of the variation in air entrainment, with deeper ladles producing more entrainment than nearly empty ladles.

9. Sprue length caused about 10% of the variation in air entrainment.
10. Teapot ladles generally produced less air entrainment than bottom pour ladles.
11. The experimental system developed for water modeling allows processing variables to be systematically changed and their effects on air entrainment to be quantitatively measured.
12. Water appears to be a good physical model for pouring steel because it has approximately the same density to viscosity ratio which permits Reynolds number matching in a one-to-one scale model.

3.0 Summary of the Literature on Clean Steel Castings

Oxygen can come from several sources including air, water in refractories, molding sand, or oxidizing slag, and react with steel to produce reoxidation products. Mechanical entrapment of oxides such as refractories and sands also is a possibility. Mechanical entrapment is an obvious source and has often been cited as the major source of oxide macroinclusions. However, many sources of inclusions exist and are summarized in Table 1.¹⁻¹⁵ The major sources include reoxidation of the metal during pouring and entrapment of sand.

Reoxidation

There is substantial evidence that reoxidation is a major cause of oxide macroinclusions. Reoxidation is considered to be the reaction of elements in steel with oxygen after the steel has been deoxidized.

The formation of deoxidation and reoxidation products is schematically illustrated in Figure 1.¹⁶ Deoxidation products are small, typically 10µm or smaller in diameter, and are primarily composed of alumina (Al₂O₃) in aluminum deoxidized carbon and low alloy steels. In reoxidation products, the alumina particles lie in multiphase globules formed by the oxidation of aluminum followed by silicon, manganese and iron.^{14,16,17} The oxide matrix in which the alumina particles lie is typically rich in manganese and silicon, but in extreme cases may contain some iron oxide. The presence of iron oxide may cause carbon monoxide gas holes to be formed within the inclusion as the iron oxide is reduced by carbon during solidification.

Typical oxide macroinclusions are green to white powders. The inclusions consist of corundum (alumina) crystals or a mixture of corundum, silica and manganese oxide. The presence of corundum indicates that the inclusion began as a reaction product between oxygen and dissolved aluminum. Most refractories are composed of mullite or lower alumina content materials and are not expected to produce corundum.^{15,6,8,10,18,19}

If reoxidation is a major cause of inclusions, then the deoxidized metal composition should have some effect on the composition of inclusions formed. This has been found to be the case in both carbon steels and high alloy steels. Increasing the manganese-to-silicon ratio increased the manganese oxide and decreased the silicon oxide content of inclusions in low alloy steels. Aluminum deoxidation increased the amount of aluminum oxide in inclusions and reduced the manganese + iron oxide contents.^{1,12}

Not only does reoxidation inclusion composition depend on the composition of the metal, but the volume of inclusions has been related to the amount and composition of deoxidizers added. Increasing the concentration of even a mild deoxidizer, such as manganese, resulted in an increase in the number of inclusions.¹² Increasing the amount of strong deoxidizing additions, such as aluminum, zirconium and titanium, also increased the weight of inclusions formed. Most reports indicate that subsurface oxide macroinclusions, which are so detrimental to tool life, are much more frequent when aluminum is used compared to when silicon is used. It appears that shallow surface inclusions can be attributed to a higher silica content than the subsurface white powder inclusions composed primarily of alumina.^{1,12,20}

Figure 1. Stylized formation of inclusions in as-cast steel/ deoxidized with aluminum.
($> 0.01\% \text{ Al.}$)

Table 1. Sources of Oxide Macroinclusions by Source of Oxygen.

A. REOXIDATION - reaction of liquid metal with oxygen

SOURCES	MECHANISM OF FORMATION	PREVENTION
A. Air	liquid steel reacts quickly during pouring with air as a function of surface area exposed and time of exposure	must minimize exposure to air by fast pouring, ladle alignment low to mold, compact pouring streams.
2. Refractories	moisture or poor refractories can be reduced by deoxidizers in steel.	must use dry, high quality refractories. must recondition ladles to remove slag and metal attack and expose good refractory - patching must be dry and good quality.
3. Slag	furnace slags high in FeO can contribute to reoxidation slags and are especially harmful if left on refractories in ladle in spout or bottom pour area.	must not pour slag into casting - must clean slag out of ladle between uses.
4. Mold	mold binders high in moisture or other oxidizing components can contribute to reoxidation.	use organic additives or organic binders to produce a more reducing atmosphere.

B. ENTRAPMENT - capture of an existing oxide in liquid metal

SOURCES	MECHANISM OF CAPTURE	PREVENTION
1. Slag	slags high in FeO are very fluid and apt to be entrapped in pouring.	avoid large amounts of furnace slag, clean old slag from ladle pouring areas, avoid mixing acid and basic slags.
2. Refractories	metal can attack binder areas of refractory and allow erosion.	use good refractories resistant to metal attack and erosion, especially in the area of pouring.
3. Mold	scabbing or erosion can lead to trapped sand or mold wash.	use a proper sand mix and gating design to prevent scabbing and erosion.

Proper gating and filtering can help reduce oxide macroinclusion.

Reoxidation problems increase with the quantity and strength of the deoxidizers added as does the volume of oxide macroinclusions. This trend is shown in Table 2 which relates the machined cleanliness of "B" turning bars to the deoxidation practice.⁽²¹⁾ As the deoxidizer changed from weaker titanium to stronger aluminum and from less to more deoxidizers added, the cleanliness rating decreased.^{12,21}

Radioactive cerium (Ce141) has been added to steel during aluminum deoxidation and to the slag in efforts to determine the source of oxide inclusions.²² Almost no trace of radioactive cerium was found in ingots where the slag was activated. The small amount of radioactivity found in the inclusions was attributed to reduction of the oxides in the slag and not to slag carryover. The trials with the activated deoxidizers showed significant amounts of activity in the slag. High radioactivities also were found in the large inclusions near the top surface of ingots. These experiments indicate that reoxidation and not slag carryover was the major cause of inclusions.²²

Reoxidation is implicated by the composition and volume of inclusions, which is related to the amount and composition of the deoxidizers. Control of reoxidation can be accomplished by limiting the exposure of the metal to oxygen in all forms since deoxidizer additions are necessary in steel to produce sound castings.

Reoxidation by Exposure to Air

Oxidation of molten steel in air occurs very rapidly as illustrated in Figure 2.¹⁶ The oxygen concentration in steel shot reduced by hydrogen increased from near zero to 0.08% in about 0.25 seconds when exposed to air. The rate of reaction is probably limited only by the ability of oxygen to diffuse through the nitrogen rich layer surrounding the steel to replace oxygen already reacted at the liquid metal surface. In a foundry environment a major exposure of molten steel to air occurs when pouring the steel into molds through air and when air is entrained in the pouring stream.

The size distribution of reoxidation products formed during tapping from a furnace are shown in Figure 3.²¹ Reoxidation particles can grow within a minute to macroinclusion size and float out of the liquid in about two minutes. It has been estimated that in each pouring or tapping operation, from three to nine pounds of oxides are produced for each ton of metal transferred. A loss of about 1.6 lb. manganese, 0.3 lb. carbon, 0.9 lb. silicon, and 0.9 lb. aluminum per ton of steel has been reported during metal transfer in some wrought steel operations.²³ Greater pouring heights result in more reoxidation from stream breakup and from longer exposure to air. Throttling a bottom pour ladle results in a higher surface area of liquid metal exposed, increased air entrainment and longer pouring times. The loss of aluminum, manganese and silicon associated with each metal transfer is an indication of the amount of reoxidation.

In many transfer operations, the large reoxidation products have time to float from the liquid. However, pouring into a casting cavity forms products that are likely to be trapped under the cope surface. In continuous casting, proper shrouding to exclude exposure to air

has been found to reduce oxide inclusions by 90%. It has been estimated that in excess of 60% of the inclusions in steel castings are a result of reoxidation during casting.^{14,16,24}

Many types and sizes of ladles are in use in the steel casting industry. For many years bottom pouring was considered to produce the cleanest castings. However, with the improvements in refractories in the past 15 years, it is no longer certain that bottom pouring practices produce cleaner castings than well maintained teapot ladles or well skimmed lip pour ladles. Bottom pour ladles certainly have the advantage of requiring minimum foundry floor space, but they suffer from the need to throttle the stream when the ladle is full and when pouring small castings from large ladles. Throttling produces stream flaring, and the flared metal has a high surface area which invites reoxidation. Large bottom pour ladles also have high head pressures which produce high metal velocities that aggravate sprue and runner erosion. Teapot and lip pour ladles require more foundry floor space but permit pouring compact streams with a minimum head pressure and metal velocity.

The type of pouring ladle used has a significant effect on the amount of air exposure. A lip pour or teapot ladle may allow metal to fall a relatively long distance if the ladle is not held close to the mold. The lip pour ladle also may allow slag to be carried into the casting more easily than bottom pour ladles. However, bottom pour ladles create higher velocity conditions in the nozzle and sprue area which may increase the tendency for erosion. The bottom pour ladle is often throttled during pouring which results in a flared pouring stream that entrains air and exposes a high metal surface area to air. Both factors favor reoxidation.^{1,12,25}

In any event, pouring must be done with the minimum of exposure to air and without entraining slag or eroding ladle refractories. Minimum air exposure is accomplished by fast pouring, low pouring heights, good nozzle or lip design, and a compact pouring stream.

Shrouding and submerged pouring to eliminate air exposure has been successfully used in continuous casting of steel but has had very limited success in reducing oxide inclusions in static castings. No conclusive improvement in casting cleanliness has been found using this system.²⁶

Reoxidation and Entrapment of Mold Materials

Molds are often blamed for inclusions, but eliminating sand by pouring castings in graphite molds does not eliminate the inclusions. This fact implies that while sand may contribute to inclusions, it is certainly not the only factor. Reoxidation in the mold can occur by reactions between metal and the air in the cavity, oxygen in the binder, and with entrapped sand grains. Entrapped sand grains may come from erosion, loose sand, or expansion defects on the mold.^{1,3,12,27-29}

621-778
5-407

Figure 2. Oxygen pickup by falling droplets. Droplets were mold-quenched under nitrogen.

Table 2. Effects of deoxidation on the cleanliness of grade "B" turning bar castings.

DEOXIDANTS	NUMBERS OF CASTINGS	FREQUENCY OF CLEANLINESS					AVERAGE NO.	POUNDS EQUIVALENT OF AI ADDED PER TON
		1	2	3	4	5		
5 lb titanium per ton	5	-	-	-	-	5	5	0.00
8 lb (Fe-Ti-Si-Mn-Al-Zr alloy) per ton	3	-	-	-	1	2	4.7	1.04
8 lb (Fe-Ti-Si-Mn-Al-Zr alloy) plus 1lb aluminum per ton	6	1	1	1	2	1	3.2	2.04
2.5 lb aluminum plus 3 lb (Fe-Si-Ti-Ca alloy) per ton	12	3	2	2	4	1	2.9	2.50
4 lb aluminum plus 3 lb (FeSi-Ti-Ca alloy) per ton	8	4	2	1	1	-	1.9	4.00

*RATING NUMBER

RATING GRADE

- 5 Excellent. 0-5 microinclusions, (0.0079-0.0158 inches diameter) first cut
- 4 Very good. 6-15 microinclusions, (0.0079-0.0158 inches diameter) first cut
- 3 Good. 16-30 microinclusions, 0.3 macroinclusions (0.0625 inches diameter) first cut
- 2 Poor. 31-50 microinclusions, 0.3 macroinclusions (0.125 inches diameter) first cut
- 1 Very poor. 50+ microinclusions, 3+ macroinclusions larger than 0.125 inches diameter

Figure 3. Particle size of deoxidation products from tapping to pouring

Reoxidation by reaction with air in the mold has the same effect as pouring through the air which was previously discussed. However, attempts to purge molds with nitrogen and other inert gases have not been successful in substantially reducing oxide macroinclusions.

Reoxidation caused by reactions with mold binder decomposition products has been shown to be a factor in inclusion formation in some cases. High water contents and high pouring temperatures both aggravate the occurrence of inclusions. High pouring temperatures aggravate reoxidation problems, as shown in Figure 4.²⁷

Water produces a more oxidizing atmosphere in the mold compared to organic binders. In at least one plant, the use of baked oil bonded sand instead of green or dry sand caused some reduction in inclusion occurrence. In other experimental studies, baked oil sand was shown to be only slightly better than green sand.¹

The use of oil bonded sand does not give a completely reducing atmosphere, however, since it contains some oxygen and usually some cereal or cellulose. Organic binder systems can be produced with relatively low oxygen contents, and the low oxygen content coupled with high strength and resistance to erosion does improve casting cleanliness.

Silica sand is another source of oxygen. If a sand grain is entrapped in the metal, strong deoxidizers may react with it to produce a reaction rim around the grain. The entrapment of sand may occur from pickup of loose sand in the gate or mold cavity, erosion of the gate, core, or mold, or by mechanical failure caused by sand expansion.

Figure 4 . The effect of pouring temperature on cerioxide severity.

Pickup of loose sand by flowing liquid metal is not as straightforward as it might appear. Experiments have been conducted where loose sand was placed in a runner or mold cavity. Quite often the sand was not picked up by the liquid metal. Clean deoxidized metal does not wet silica sand, and consequently the liquid metal does not readily entrap the sand on contact. Turbulent flow conditions or the presence of slag or reoxidation products are needed to entrap loose sand. If reoxidation products are present or formed during pouring, the oxides can wet and cause loose sand to be picked up by the metal.

The pouring practice may have a significant effect on mold erosion. Long pouring times, high metal drop heights, and high pouring temperatures increase the amount of sand erosion and spalling. More ramming and higher mold densities decrease the amount of erosion, but excessive ramming leads to an increase in expansion defects.

In summary, the sand content of nonmetallic inclusions in steel castings can range from small values when the inclusions are principally caused by reoxidation to almost 100% sand when formed by mold scabbing. Reoxidation products can wet and partially dissolve loose sand to form nonmetallic inclusions that may range widely in the amount of contained sand. Inclusions are often present in the absence of sand such as in castings poured in graphite molds. These inclusions are a result of either reoxidation or refractory erosion. Good sand practice and clean molds help minimize the sand contribution to oxide macroinclusions, but they do not eliminate these inclusions.

Gating to Minimize Inclusions

While the primary function of the gating system is to transmit metal poured from the ladle into the mold cavity, it can have a significant effect on the occurrence of oxide macroinclusions in castings. Good gating systems help retain oxides in the gating system and prevent reoxidation and erosion products from entering the mold cavity.

Other than some rules of thumb, there is little in the literature about gating systems for steel castings. Mathematics and principles for risering steel castings are far more advanced than principles for gating.

Three empirical pouring time formulas are given in equations 1-3.

$$t = W/1.5 \quad (1)$$

$$t = (1.73 - .26 \log W)/W \quad (2)$$

$$t = W \quad (3)$$

where t = pouring time (sec) and
 W = casting weight (lb)

The third formula applies only to small castings. Other rules of thumb are that the rate of metal rise in the mold should be one inch per second but the pouring time should never exceed 60 seconds. Long pouring times result in radiant heating of the mold cope surface, sand expansion, and spalling of the cope into the casting. Excessive pouring times also lead to binder decomposition, loss of binder strength, and erosion in the sprue, runner, and ingates.

Several generally accepted ideas about gating include:

- (1) pour as fast as possible, but size the runner so that runner velocities do not exceed 40 inches per second,
- (2) pour as cold as possible to minimize the thermal load on the binders,
- (3) bottom gate when possible to minimize metal tumbling into the casting cavity which aggravates both reoxidation and erosion.

Gates must be properly designed to prevent erosion, scabs, and loose dirt from forming and being carried into the casting. Ceramic tile runners are effective in preventing erosion and are widely used in the production of larger castings. Tile runner systems must be properly aligned and the joints seated to avoid erosion or entrained sand at the joints.

Many gate designs have been proposed and tested for maximizing the cleaning effect. The published results indicate that streamlined gates and whirlgates are the most effective. Drag runners with cope ingates provide some residence time for metal in a full runner and allow oxides to float and stick to the cope. The whirlgate also allows flotation coupled with centrifugal force to separate oxides from the liquid metal.³⁰

Gating Design

The gating ratio is the ratio of the total cross sectional area of the sprue to the runner and gate. The sprue base area is normally considered to be the basis number. A ratio of 1:1:1 means that the runner and ingates have the same cross-sectional area as the sprue base. The gates typically have the same total cross-sectional area as the runner and exit the runner from the cope.

If the gate exits from the side or bottom of the runner, the total ingate area is usually the same or smaller than the sprue. For cope gates, typical sprue: runner: gate ratios range from 1:1.5:1.5 to 1:3:3. The most popular steel casting gating ratio is 1:2:2. High ratios of 1:4:4 produce low runner velocities that can lead to reoxidation of the metal in the runner. Consequently, a ratio of 1:4:4 is used only on small castings.³¹

When bottom pouring castings through tile runners, the gating ratio often includes the ladle nozzle size as the first number in the ratio sequence. A common recommendation is to use 1:2:2:2 ratio as a minimum when bottom pouring.

Gating systems usually consist of a pouring cup, sprue, runners and gates. The pouring cup should be large enough to hit without splashing and deep enough to minimize vortexing of the metal as it leaves the cup and enters the sprue. Offset pouring basins slow the pouring rate without improving the quality of the metal, and they sometimes allow more slag into the mold. Both box and conical pouring cups seem to work well. Usual rules of thumb indicate that the pouring cups should be 2.5 to 3 times the sprue diameter in width and as deep as they are wide. The pouring cup and sprue connection should be smooth and moldable to allow good sand compaction and minimum erosion.³¹

The sprue design must consider several factors such as cope height, sprue cross-sectional area, taper, shape, base design, and material. The sprue height is normally defined by the flask equipment and casting placement. Short sprues produce lower ferrostatic pressures and allow lower metal velocities, which in turn, reduce metal splashing and mold erosion. Taller sprues lead to higher velocities and a greater probability of metal oxidation and mold erosion.

Sprue sizes are usually determined by the weight of castings to be poured or by the nozzle size in the bottom pour ladle. In practice, the sprue size for bottom pouring is usually equal to the nozzle size when pouring castings weighing less than 1000 lbs, 1/2" larger in diameter than the nozzle when castings weigh from 1000-50,000 lbs and 1" larger in diameter than the nozzle when castings weigh above 50,000 lbs.

Tapered sprues are recommended to minimize reoxidation and provide flow control when pouring smaller castings. It is often suggested that the sprue area at the top should be four times the sprue area at the bottom. However, the use of tile precludes the use of tapered sprues, and many straight tile sprues are used successfully.

Round and rectangular sprues have been used in casting production. Rectangular shapes are supposed to minimize vortexing, but no improvement of casting quality has been reported.

The sprue well serves as the transition zone to change the metal flow direction from vertical to horizontal. It is generally considered that the sprue well should be at least twice the diameter of the sprue base and as deep as the runner plus 1/2-1". The connection of the

sprue to the well and well to the runner should eliminate sharp corners and allow good sand compaction.

Runners are used to deliver metal from the sprue to the gates, and the runner is the last area where nonmetallic inclusions might stick and be removed from the metal. Runners must be kept full, and the metal velocity must not be excessive. Factors influencing the runner design include: (a) the distance from sprue to the first gate, (b) runner area, (c) runner shape, (d) area reduction after each gate, and (e) runner traps. The cross-sectional area of the runner depends on the gating ratio chosen, but the runner cross section is normally 1.5 to 4 times the area of the sprue cross section to reduce the metal velocity.

The proper cross-sectional shape of the runner has been the matter of considerable debate. Shape recommendations have been made ranging from circular to shallow and rectangular. The runner should be easy to mold in order to avoid soft spots and erosion. It is believed that runners should be shallow to provide short flotation distances for nonmetallics, and it should have flat cope surfaces to provide the maximum area for nonmetallic particles to stick; however, because of the turbulent flow conditions in the runners, flotation is unlikely to occur. These requirements are best met with a shallow triangular or tapered rectangular (width twice the depth) runner. Square, round, and half round runners are not as moldable or as efficient as shallow ones. Shallow triangular or rectangular shapes have a higher wetted surface area that increases boundary layer flow.³²

Traps are used in the runner system in an effort to catch oxide particles before they enter the casting cavity. Most traps are extensions of the runner system past the last gate. However, wells above or below the runner, alternating the runner from the cope to the drag, and saw tooth runner tops have been used. It has been observed in water modeling and x-ray observations of mold filling that traps, including runner extensions and runners alternating between cope and drag, are unlikely to be effective.

Gates deliver metal from the runner to the mold cavity. Factors that must be considered in gate design include: (a) connection to runner, (b) cross-sectional area, (c) cross-sectional shape, (d) number, and (e) connection to mold cavity. The connection of the gate to the runner should be streamlined to avoid erosion, hot spots, and restraint. The best option is to put the runner in the drag and the gates in the cope; thus the runner stays full to minimize erosion and splashing in the gate. If the gate is below the runner, then the choke must be in the gate or dirt will be carried into the mold cavity.

The cross-sectional area of the gate is established by the choice of the gating ratio. Individual gate areas are determined by dividing the total gate area by the number of gates. The gate area should be the same as the runner area if the gates come from the top of the runner. If the gates exit from the side or bottom of the runner, the gate areas normally range from 0.7 to 1 times the sprue area to keep the runner full. If the individual gates are too small, excessive metal velocity can cause erosion.

The shape of the ingate is normally rectangular with a depth of half the width. Thin ingates freeze quickly and minimize feeding the casting from the runner. Multiple gates are beneficial in minimizing erosion, misruns, and warpage.

The gate should introduce metal into the bottom of the mold cavity where possible. Bottom gating of steel castings significantly improves quality. However, bottom gating is

difficult to achieve in many cases because of casting design. It is more important to use bottom gates with larger castings.³¹

Whirlgates

Whirlgates utilize the density differences between oxide particles and liquid steel to cause separation by gravitational and centrifugal forces. Liquid steel containing oxide particles is usually fed into a cylindrical cavity on a tangent to cause a circular flow of the metal. The heavier metal flows at the outer rim touching the cavity wall and the lighter oxide particles are forced into the center and do not exit from the whirlgate. This makes the whirlgate a special trap to catch the oxide particles.

Several whirlgate designs have been suggested as being effective at eliminating oxide particles. One design for large castings recommends that the intake diameter (d) be less than four tenths (0.4) the diameter of the whirlgate (D). The height above the intake should be greater than $0.5D$, and the intake should be 1 to $1.5D$ above the exit. The intake should be tangential and the exit radial to the whirlgate.^{33,34}

Whirlgates have been used primarily on larger castings but some development has been done on whirlgates for small castings. The particle separation efficiency was highest when the ratio of the inlet diameter to whirl diameter was less than 0.3 in castings with a head height of 1.5 meters (4.9 ft.). Higher ratios produced higher efficiencies when the head height increased to 3.5 meters (11.5 ft.). The height to diameter ratio of the whirlgate was also an important factor with higher ratios producing a higher particle collection efficiency. It does take some metal flow to establish the proper flow for separation, as shown in Figure 5.³³ It may be possible to use whirlgates to clean up the metal, but they have not been widely applied because of the loss in metal yield.

4.0 Filtration of Carbon Steel

The experimental work on filtration focused on the ability of commercial filters to remove inclusions from a steel containing about 0.20% carbon. Previous research has shown that stainless steels can be filtered and the use of filters is economically justifiable. Filtration of carbon steel was of particular interest in the current study because of the relatively low superheat normally used when pouring carbon steel castings and the reported difficulty encountered with priming of filters with these alloys. The filter trials were conducted using a statistically designed matrix with the following broad objectives:

1. determine if a measurable improvement in casting cleanliness could be obtained using filtration and
2. determine if the extent of improvement would justify the cost of adding filters to the mold.

4.1 Filter Characteristics

The filters used in this study were selected by participants in the study based on prior experience in the steel casting industry. The trials were conducted using two different types of filters to pour valve bodies from ASTM A216 WCB steel.

621-788

5-424

Figure 5 . Separation efficiency of particles introduced to the ladle stream at varying intervals after the start of pouring.

Filter 1 had a cellular structure produced by extrusion. The filter was made of mullite-alumina material and coated with an exothermic compound. The nominal filter dimensions were 2.9 inches square by 0.64 inches thick with ten pores per linear inch (10 ppi or 100 cells/in²). The apparent (bulk) density of the filter was 1.05 gm/cc as determined by measuring the three filter dimensions, weighing the filter, and dividing the total weight by the total volume. The filter weight and specific heat are important in determining how easy or difficult it is to prime the filter during the initial stages of pouring. The apparent filter material density was 3.29 gm/cc as determined by an immersion density measurement in alcohol.

Filter 2 had a reticulated structure and was made of partially stabilized zirconia. The filter was 3 x 4 x 1 inch and had an apparent (bulk) density of 1.034 gm/cc and an apparent material density of 5.633 gm/cc as determined by immersion in alcohol.

4.2 Metal Filtration Experimental Design

An experimental filtration matrix was developed based on four considerations:

- (1) The availability of a suitable casting with defect incidence data produced in sufficient quantities to allow the conduct of a designed experiment,
- (2) Foundry specific processing variables that might be included in the study (ladle size, deoxidation, practice, etc.).
- (3) Established inspection techniques in the plant, and
- (4) Statistical considerations necessary to design an experiment, conduct the experiment, and gather and analyze the resulting data.

4.3 Casting Selection

The casting was selected for filtration experiments to meet several criteria. First, the casting must have a recognized cleanliness problem, for which filters might be a solution. Historical cleanliness data should be available so the proper number of castings could be selected and poured to allow statistically valid conclusions to be drawn from the data.

Second, the pattern board must have sufficient space to accommodate gating modifications necessary for the addition of filters. Finally, the casting must be produced in quantities and lot sizes sufficient to permit the production of the desired number of castings in a few days.

The casting best meeting these criteria was a fifty-eight pound valve body illustrated in Figure 6. The pattern had four cavities per mold, with a total poured weight of 514 lbs. The alloy poured was ASTM A216 WCB. All molds were made with PepSet bonded silica sand. The pouring temperature was nominally 2850°F, and the pouring times ranged from 21 to 27 seconds with an average value of 25 seconds.

4.4 Casting Processing Variables

The primary objective of the study was to determine if a statistically significant improvement in casting cleanliness could be achieved using filtration and to define the magnitude of this improvement. Filter suppliers were involved in all aspects of the gating system modification to ensure that the experimental results would be based on cumulative supplier experience. The number and size of filters used, placement relative to the downsprue, filter orientation, and runner geometry changes necessary to transition the flow from the filter to the runners were made by the individual filter suppliers.

Relatively large sample sizes are required to establish the statistical significance of a variable in processes where the measured variations are small. Large sample sizes can sometimes permit the effects of secondary variables to be assessed if these variables can be measured and incorporated into the experimental array.

The foundry participating in this trial had developed a "Clean Steel Technology" program, and procedures to serialize heats and castings, conduct a layered inspection, and keep adequate records. Each casting could be identified by heat and cavity number in the mold.

Three statistical considerations were involved in setting up the experimental matrix including: (1) the available historical casting cleanliness data, (2) desired statistical

confidence in the results, and (3) the ability to randomize the pouring sequence for the molds.

Based on statistical and production considerations, the experimental matrix illustrated in Table 3 was developed. The primary variable was filtration using two types of commercial filters. Filter 1 was extruded and contained an exothermic surface coating. Filter 2 was a reticulated magnesia stabilized zirconia filter. The results obtained with these two filters were compared with a conventional pouring practice that did not employ a filter.

616-209a

Figure 6. Fifty-eight Pound Valve Body Used in Filtration Experiments

TABLE 3. FILTER EXPERIMENT MATRIX

TABLE 3. FILTER EXPERIMENT MATRIX							
FILTER CONFIGURATION							
	FILTER 1		NO FILTER		FILTER 2		
	MOLDS FROM 700# LADLE	MOLDS FROM 3500# LADLE	MOLDS FROM 700# LADLE	MOLDS FROM 3500# LADLE	MOLDS FROM 700# LADLE	MOLDS FROM 3500# LADLE	TOTAL MOLDS PER HEAT.
Heat 1	2	3	2	3	2	3	15
Heat 2	2	3	2	3	2	3	15
Heat 3	2	3	2	3	2	3	15
Heat 4	2	3	2	3	2	3	15
Heat 5	2	3	2	3	2	3	15
Total Molds Per Config	10	15	10	15	10	15	-
Total Molds	25		25		25		75
Total Castings Per Config	40	60	40	60	40	60	-
Total Castings	100		100		100		300
Notes:							
1. Each matrix number indicates the quantity of molds poured for the configurations.							
2. 30 total molds poured from the 700# ladle.							
3. 45 total molds poured from the 3500# ladle.							
4. There are four castings per mold.							

4.5 Experimental Results

All of the castings were poured with WCB steel as previously noted. The average pouring temperature, as determined in the pouring ladle, for the five heats used to produce the 300 test castings was 2900, 2906, 2878, 2870, and 2906°F respectively. The average pouring time without a filter was 25.2 seconds compared to 24.1 seconds pouring through Filters 1 and 2.

The statistical test used establishes the probability that observed differences in the defect rates, under the two test conditions, are real differences. The alternative explanation is that the observed defect rate differences are simply a consequence of random sampling from a single population. The statistical significance in column 8 of Table 4 is the likelihood that a different defect rate exists for the factor being evaluated than is at work under the baseline conditions. This statistical test assumes a normal (Gaussian) approximation to the binomial probability distribution.

The primary factor of interest was filtration. There were 14 castings diverted for weld repair out of the 100 unfiltered castings poured. This represented a 14% defect rate for the standard (unfiltered) practice under the conditions existing during this experiment. Filter 2 produced 7 castings requiring weld repair out of 100 castings poured from the same heats. It can be concluded with 95% confidence that different defect rates did in fact exist between the filtered and unfiltered metal.

4.6 Conclusions from Filtration Experiments

The following conclusions can be drawn from the carbon steel filter experiments conducted in this program.

1. Some current commercial filters can be used to pour carbon steel castings without spalling. The filters primed and metal flowed through them. All WCB castings primed and filled the reticulated PSZ filters at pouring temperatures as low as 2870°F.
2. It can be stated with about 95% confidence that filtration using a stabilized zirconia reticulated filter decreased the weld repair rate in the carbon steel valve body casting used in this study.
3. Filtration through Filter 2 resulted in a 50% reduction in the weld repair time on castings, but the cost savings associated with the reduced welding time do not justify the cost of putting filters in the molds for this casting.

5.0 Water Modeling of Pouring Practices

The primary purpose of the water modeling task was to conduct physical modeling trials to explore several techniques that may be used to reduce reoxidation during handling and pouring of metal in air.

Water is a useable modeling fluid for molten steel because it has approximately the same density to viscosity ratio as steel, which permits Reynolds number matching in a one-to-one scale model. This establishes, in the model, flow conditions similar to those in a

TABLE 4. STATISTICAL SIGNIFICANCE OF WELDING RESULTS

Baseline Data			Factor Data			Statistics	
Baseline	Quantity Welded/ Sample Size	Rate Defective	Factor	Quantity Welded/ Sample Size	Rate Defective	Z Statistic	Statistical Significance
Unfiltered	14/100	14%	Filter 2	7/100	7%	1.615	94.68%
3500#	9/120	7.5%	700#	12/80	15%	1.695	95.45%
1,3,4,5	12/160	7.5%	Heat 2	9/40	22.5%	2.768	99.72%
1,2,3,5	19/160	11.9%	Heat 4	2/40	5%	1.269	89.78%
1,2,3,4			Heat 5				
1,2,3	17/120	14.2%	Heats 4 & 5	4/80	5%	2.072	98.09%
1,2,4	19/150	12.7%	Cavity 3	2/50	4%	1.731	95.83%

foundry. One-to-one scaling of geometric dimensions and fluid velocities ensures that Froude Number matching is satisfied and all geometric ratios are maintained.

Air entrainment rates are a function of boundary geometries, fluid flow characteristics, fluid properties, and the availability of constant air pressure. Similitude permits a dimensionless air entrainment rate to be expressed as a function of the Reynolds, Froude, Weber, and Euler numbers and unchanged geometric ratios. Air entrainment rates for steel flow can thus be modeled with some accuracy using water under identical pouring conditions.

Several factors thought to influence the amount of air entrained during bottom pouring are illustrated in Figure 7. The liquid height in the ladle and the distance between the ladle and the mold affect the liquid velocity and stream impingement velocity in the sprue. The nozzle opening has a significant effect because it controls stream fragmentation as liquid leaves the ladle and drops through air into the pouring basin and sprue. Sprue length, shape, and orientation affect the flow characteristics between the ladle and mold. The gating ratio and ingate velocity may have an effect by influencing the stream jetting behavior as the stream leaves the runner and enters the mold cavity.

5.1 Experimental Arrangements

Bottom Pouring. The specific conditions considered in the experimental bottom pouring series described in this report are schematically illustrated in Figure 8. Water was poured from a bottom pour ladle having a capacity of 4 cubic feet (approximately 2000 lbs. of steel) through a 1 7/8 inch diameter nozzle. Four variables were considered in the experimental series including:

1. liquid depths of 11" and 26" in the ladle,
2. stopper openings of 0.25" and 2.5",
3. sprue lengths of 5" and 10", and
4. the use of a 5" long nozzle extension to produce some stream compaction.

Water was poured directly into the pouring cup and sprue. The sprue was a commercial shell molded sprue with a nominal diameter of 2" that had been sealed to prevent its degradation under water. Water exited the downsprue and entered the liquid bath as illustrated.

A load cell on the pouring ladle was used to determine the initial and final gross ladle weights. The difference in gross weights was used to accurately calculate the volume of liquid poured. A switch on the stopper lifting mechanism allowed the precise start and end of pour to be determined. The time difference between the start and end of pouring provided the pouring time.

Both the water from the ladle and the entrained air entered the mold box. The water stayed in the mold box which caused some air initially in the mold to be displaced. Both the entrained air and displaced air exited the mold box through a vent and was collected in a

sealed bag. After the pouring experiment was over, the total volume of air in the sealed bag was determined by pumping the air through an air turbine which functioned as a volumetric flowmeter. The total air volume minus the displaced air volume (determined from the volume of water poured) was the entrained air volume.

The volume of entrained air was divided by the volume of water poured, to correct for slight variations between the quantity of water poured. This normalized the data for direct comparison and provided an air entrainment ratio, the cubic feet (cf) of air entrained per cf of liquid poured. Each experimental series was organized so the results could be statistically analyzed to draw conclusions with an established level of confidence. Three replicates of each experimental configuration were made to assess the data variability under similar pouring conditions.

Teapot Ladle Pouring. The variables included in the initial teapot pouring experiments included depth of liquid in the ladle, distance from the ladle lip to the pouring basin, sprue length, and angle of inclination (tilt) of the sprue from the vertical. The teapot ladle was a commercial ladle provided by a participating foundry. The ladle had a gear box so the rate of ladle tilt could be controlled by the rate of angular rotation of the ladle wheel. When the teapot assembly was put in the ladle, the ladle capacity was approximately 2.7 cubic feet (cf) equivalent to approximately 1200 lbs. of steel.

The teapot for the ladle was constructed of a 3" diameter pipe cut at an angle of 60° from the horizontal at the bottom of the ladle. Water entered the bottom of the spout and exited the ladle over a hemispherically shaped lip with a diameter of 2.5". The pouring rate was controlled manually and the rates were usually as high as possible without splashing water from the sprue.

5.2 Experimental Results

Several series of bottom pour experiments have been conducted using various combinations of ladle depth, stopper opening, nozzle extension, and sprue length. The data presented in this report is representative of the data being obtained.

Experimental series 2 used a bottom pour ladle, a 1 7/8" nozzle, a 2" diameter sprue with a variable sprue lengths (5.25" and 10.25"), variable ladle depth (11" and 26"), variable stopper opening (0.25" and 2.5"), and a 5" long nozzle extension in some cases. The structure of the matrix and the experimental results obtained are presented in Table 5.

The columns in Table 5 list the experiment number, ladle depth, stopper opening, whether a 5" long nozzle extension was used or not, and the sprue length. The subsequent columns contain the volume of air entrained in triplicate experiments, the mean entrainment rate, the standard deviation in entrainment, and the mean and standard deviations in pouring times.

BOTTOM POUR: AIR ENTRAINMENT FACTORS

7605-2-1 A

Figure 7 - Schematic of Possible Bottom-pour Air Entrapment Factors

BOTTOM POUR: AIR ENTRAINMENT

CONSTANT FACTORS
 1 7/8" NOZZLE, 2" Ø SPRUE

VARIABLE FACTORS
 LIQUID DEPTH 11", 26"
 STOPPER OPENING 1/4", 2 1/2"
 SPRUE LENGTH 5', 10'

7605-2-1B

Figure 8- Schematic of Bottom-pour Experimental Series 2.

TABLE 5. BOTTOM POUR FACTORS - EXPERIMENTAL SERIES 2
Constant Factors: 1 7/8" nozzle, 2" diameter sprue
Variable Factors: Sprue length, ladle depth, stopper opening, nozzle extension

Orthogonal L8 Experimental Array

Trial	Ladle Depth	Stopper Opening	5" Extension	Sprue Length	Air Entrainment Data (ft ³)	Data Mean (ft ³)	Data Standard Deviation (ft ³)	Mean & Standard Deviation Pour Time (secs)
1	11"	1/4"	No	5 1/4"	.456 .476 .479	.470	.012	29.4 ± 1.1
2	11"	2 1/2"	Yes	5 1/4"	.145 .152 .148	.148	.004	6.6 ± 0.1
3	26"	1/4"	Yes	5 1/4"	.388 .492 .531	.470	.074	10.1 ± 0.9
4	26"	2 1/4"	No	5 1/4"	.188 .168 .158	.171	.015	4.4 ± 0.4
5	11"	1/4"	Yes	10 1/4"	.464 .634 .628	.575	.097	23.1 ± 10.3
6	11"	2 1/4"	No	10 1/4"	.175 .170 .195	.180	.013	7.3 ± 0.5
7	26"	1/4"	No	10 1/4"	1.095 .937 .879	.970	.112	14.9 ± 0.5
8	26"	2 1/2"	Yes	10 1/4"	.158 .145 .153	.152	.007	4.4 ± 0.5
L8 Col. #	2	4	7	1	.392	.392	Overall Mean	---

Trial 1 involved a liquid depth in the ladle of 11", a stopper opening of 1/4", and the sprue length was 5 1/4". The air entrained in three experiments was 0.456, 0.476, and 0.479 cubic feet (cf) for an average value of 0.47 cf with a standard deviation of 0.012 cf per cf of liquid poured. (All of the entrainment data are on a per cubic foot basis.) For example, about 0.47 cubic feet of air were entrained in the first trial per cubic foot of water poured. The mean pouring time in these experiments was 29.4 seconds with a standard deviation of 1.1 seconds.

The second trial was similar except the stopper was completely open, and a nozzle extension allowed a full compact stream of liquid to exit the ladle and enter the sprue. The volumes of air entrained were 0.145, 0.152, and 0.148 cf with an average value of 0.148 cf per cf of liquid poured. The pouring time dropped to 6.6 seconds with a fully open nozzle. The volume of air entrained was reduced by about 65% compared to pouring through a throttled nozzle.

The third trial was conducted with a water depth in the ladle of 26", using a stopper opening of 1/4", a nozzle extension, and a 5 1/4" long sprue. Triplicate experimental results resulted in entraining about 0.47 cf of air per cf of water poured. The pouring time was about 10 seconds with this experimental arrangement.

The next experimental arrangement involved a 26" ladle depth, a completely open stopper nozzle, no nozzle extension, and a 5.25" long sprue. These conditions resulted in entraining 0.17 cf of air per cf of water poured. The pouring time with the fully open nozzle was 4.4 seconds.

The next four pouring trials were similar to the first four except the sprue length was increased to 10.25", and there was a reversal of conditions for the 5" nozzle extension. Pouring with an 11" ladle depth, 1/4" stopper opening, with an extension on the nozzle into the 10.25" long sprue resulted in the entrainment of about 0.58 cf of air per cf of liquid poured. A fully open nozzle in trial group 6 without the nozzle extension reduced the entrainment to 0.18 cf air.

Throttling the nozzle without a nozzle extension on the full ladle increased the entrainment to about 0.97 cf of air per cf liquid poured. This was the highest mean value of entrained air for this series of experiments. The full ladle coupled with an open nozzle and the use of a nozzle extension resulted in an entrainment air volume of 0.15 cf air per cf water as shown by the data in trial group 8.

The orthogonal structures of this experimental series permitted an analysis of variance (ANOVA) to be conducted on the data. This test is used to establish that a difference exists between the mean values for two groups of data. This conclusion means that the observed differences between data groups are probably not due to differences in random sampling from a single population. Rather, the data groups represent different populations, each having its own mean. The results of the statistical analysis are presented in Table 6. The information presented in each column of the table includes the source of variation, the variation sum of squares, degrees of freedom, variance, Fisher's F ratio, test statistic, and statistical confidence. Also included are two additional columns which provide a breakdown of the observed variability by source.

TABLE 6. - BOTTOM POUR FACTORS - EXPERIMENTAL SERIES 2 RESULTS

Results from analysis of variance (ANOVA) of air entrainment data

Variation Source	Sum of Squares (SS) *10,000	Degrees of Freedom (v)	Variance (V) *10,000	F	Test Stat	Statistical Confidence	Observed Variation from Mean (%)	Observed Variation from 0 (%)
Mean	36,926	1	36,926	1059	8.53	99%	--	66.9
Stopper Opening	12,622	1	12,622	362.1	8.53	99%	69.0	22.9
Sprue Length	1429	1	1429	41.00	8.53	99%	7.8	2.6
<u>Mixed Interaction</u> (Stopper Opening) * (Sprue Length and/or (Ladle Depth) * (Extension)	1317	1	1317	37.79	8.53	99%	7.2	2.4
Nozzle Extension	745.9	1	745.9	21.40	8.53	99%	4.1	1.4
<u>Mixed Interaction</u> (Stopper Opening) * (Ladle Depth) and/or (Sprue Length) * (Extension	600.0	1	600	17.21	8.53	99%	3.3	1.1
Ladle Depth	570.3	1	570.3	16.36	8.53	99%	3.1	1.0
<u>Mixed Interaction</u> (Stopper Opening) * (Extension) and/or (Ladle Depth) * (Sprue Length)	443.7	1	443.7	12.73	8.53	99%	2.4	0.8
Error	557.7	16	34.85	n/a	--	n/a	3.0	1.0
TOTAL	55,213	24	n/a	n/a	--	--	100.0	100.0

77

The sources of variation in the table include:

- (1) the stopper opening,
- (2) sprue length,
- (3) some combinations of interactions between stopper opening and sprue length, and between ladle depth and nozzle extension,
- (4) nozzle extension,
- (5) mixed interactions between the stopper opening and ladle depth, and between sprue length, and nozzle extension,
- (6) ladle depth, and
- (7) an additional group of mixed interactions between stopper opening and nozzle extension, and between ladle depth and sprue length.

All of the effects investigated in this series of experiments were significant at the 99% confidence level. However, nozzle opening effects accounted for most of the variation from the mean, about 69%. Sprue length and mixed interactions involving stopper opening, sprue length, and ladle depth accounted for about 7% each of the variation, with other variables having smaller but statistically significant effects.

Columns 8 and 9 of Table 6 describe the degree to which the measured variability can be attributed to a single factor. Column 8 is calculated by dividing the sum of squares for the factor by the difference between the tested sum of squares and mean sum of squares for all the different experimental conditions.

Column 9 is calculated by dividing the sum of squares for the factor by the total sum of squares. Column 8 indicates variability relative to the data measured in the experiment. Column 9 indicates variability on an absolute basis, relative to the "no-entrainment" ideal.

The mean effects of the bottom pour factors are graphically illustrated in Figure 9. The horizontal line at the mean air entrainment of 0.39 represents the mean entrainment for all experimental conditions conducted in this series. The first diagonal line crossing the mean line illustrates the effect of the nozzle with and without a nozzle extension. The mean air entrainment ratio was 0.45 without an extension and 0.34 with the extension. The extension undoubtedly produced some stream compaction that reduced the amount of entrained air.

The effect of sprue length is illustrated by the second diagonal line. The mean air entrainment ratio was 0.32 with a 5" long sprue and 0.47 cf/cf with a 10" sprue. The longer sprue increased the fluid velocity, provided more opportunity for mixing between air and fluid, and resulted in higher impact velocity. More air was entrained during this process.

The effect of ladle depth is illustrated by the third diagonal line. The air entrainment ratio was 0.34 with the 11" deep ladle and 0.44 with the 26" deep ladle. The higher metal pressure created by a greater ladle depth produced a higher impingement velocity which caused more air entrainment.

Stopper throttling had the greatest effect. A 1/4" gap between the stopper and the nozzle resulted in a mean air entrainment ratio of 0.62 while a fully open stopper resulted in a mean air entrainment of 0.16 cf/cf.

Figure 9. Effects of Bottom-pour Variables on the Mean Air Entrainment Ratios, Measured During Experimental Series 2.

5.3 Teapot Ladle Pouring

Two series of teapot ladle pouring experiments were conducted using the apparatus schematically illustrated in Figure 10. Water was poured from a full teapot ladle and from a ladle that had been tilted 40° from the vertical. Water was poured from the ladle through sprues that were 5 and 10" long. Many of the experiments were conducted with a conventional sprue oriented vertically in the mold but some experiments were conducted where the sprue was tilted 30° from the vertical.

The experimental matrix and the results obtained are summarized in Table 7. The first four experiments were conducted with a full ladle using $5\frac{1}{4}$ and $10\frac{1}{4}$ " long sprues with and without a slight tilt. Experiments 5 through 8 were conducted after the ladle had been tilted 40° from the vertical. The sprue length conditions and the sprue tilt conditions were repeated in this second group of experiments.

The greatest amount of air entrained was obtained with a full ladle, sprue length of $10\frac{1}{4}$ ", and with a conventional vertical sprue. The least amount of air entrainment occurred after some liquid had been poured from the ladle to produce an initial ladle tilt of 40° and when pouring the metal through a $5\frac{1}{4}$ " long sprue tilted 60° from the horizontal. These conditions resulted in an air entrainment of 0.20 cf.

The factors that had a significant effect on the amount of air entrainment are summarized in Table 8. The sprue tilt, sprue length, tilt and length interaction, and ladle depth all had significant effects with a confidence of 99% or greater. The greatest effect was produced by the sprue tilt but the remaining factors listed above were all significant. The mean effects graph is illustrated in Figure 11.

Pouring from a ladle containing less liquid reduced the average air entrainment from .26 to .25 cf. Pouring through a 10" sprue compared to a 5" sprue increased the amount of air entrainment from .23 to .27 cf. Pouring through a vertical sprue produced a mean air entrainment of .28 cf compared to a mean value of .22 cf when pouring through a tilted sprue.

5.4 Conclusions Regarding Water Modeling

1. Different rates of air entrainment existed for each condition of all the factors evaluated.
2. Stopper opening effects resulted in 69% of the observed variation in air entrainment in bottom pouring simulations.
3. Sprue length was the second most significant source, causing about 8% of the variation.
4. The next significant source is probably the interaction between stopper opening and sprue length, but since two interactions are confounded, a definite statement cannot be made.
5. The remaining factors caused less than 5% of the variation about the mean.

CONSTANT FACTORS
 TEAPOT
 2" Ø SPRUE
 ROUND SPLASH SURFACE

VARIABLE FACTORS
 LADLE DEPTH: FULL, 40" TILT
 SPRUE LENGTH: 5", 10"
 SPRUE TILT: 90°, 60°

NOTES:
 1. LADLE-TO-MOLD HEIGHT IS MINIMUM
 (<1") AT END OF POUR.
 2. VERTICAL POSITION OF LADLE IS
 CONSTANT DURING POUR.

REQ. BY	Southern Research Institute BIRMINGHAM, ALABAMA 35255	TEAPOT POUR: EXPERIMENTAL SERIES 5: SCHEMATIC	
ENGR.		SIZE	REV.
DRWN P. MILLER		B	7605-02-01-L
CHK.		SCALE	
PROJ. 7605-02	DATE 4/12/93		SHEET

Figure 10. Schematic of Teapot Pouring Apparatus.

TABLE 7 - TEAPOT POUR FACTORS - EXPERIMENTAL SERIES 5

Constant Factors: Teapot, 2" diameter sprue, curved sprue cup splash surface

Variable Factors: Ladle depth, sprue length, sprue tilt

Orthogonal L8 Experimental Array (Full Factorial)

Trail	Ladle Depth	Sprue Length	Sprue Tilt	Air Entrainment Data (ft')	Data Mean (ft')	Data Standard Deviation (ft')	Mean & Standard Deviation Pour time (secs)
1	0° tilt	5 1/4"	90°	.257 .271 .263	.264	.007	24.7 ± 2.8
2	0° tilt	5 1/4"	60°	.232 .217 .196	.215	.018	23.8 ± 0.9
3	0° tilt	10 1/4"	90°	.338 .325 .358	.340	.017	24.9 ± 1.3
4	0° tilt	10 1/4"	60°	.195 .264 .238	.232	.035	22.8 ± 2.1
5	40° tilt	5 1/4"	90°	.222 .218 .237	.226	.010	28.0 ± 1.9
6	40° tilt	5 1/4"	60°	.213 .211 .180	.201	.007	26.5 ± 1.7
7	40° tilt	10 1/4"	90°	.335 .292 .276	.301	.031	31.0 ± 3.7
8	40° tilt	10 1/4"	60°	.217 .217 .209	.214	.214	22.1 ± 2.4
L8 Col. #	1	2	4	.249	.249	Overall Mean	--

TABLE 8. - TEAPOT POUR FACTORS - EXPERIMENTAL SERIES 5 RESULTS

Results from analysis of variance (ANOVA) of air entrainment data

Variation Source	Sum of Squares (SS) *10,000	Degrees of Freedom (v)	Variance (V) *10,000	F	Test Stat	Statistical Confidence	Observed Variation from Mean (%)	Observed Variation from 0 (%)
Mean	14,905	1	14,905	3655	8.53	99%	--	96.3
Sprue Tilt	268.7	1	268.7	65.89	8.53	99%	47.4	1.7
Sprue Length	124.7	1	124.7	30.57	8.53	99%	22.0	0.8
<u>Interaction</u> (Sprue Tilt) * (Sprue Length)	55.51	1	55.51	13.61	8.53	99%	9.8	0.4
Ladle Depth	44.55	1	44.55	10.92	8.53	99%	7.9	0.3
<u>Interaction</u> (Sprue Tilt) * (Ladle Depth)	7.82	1	7.82	1.92	1.42	75%	1.4	0.1
<u>Interaction</u> (Sprue Tilt) * (Ladle Depth)	0.12	1	0.12	0.03	1.42	none	--	--
<u>3rd Order Interaction</u>	0.03	1	0.03	<0.01	1.42	none	--	--
Error	65.24	16	4.08	n/a	n/a	--	11.5	0.4
TOTAL	15,472	24	n/a	n/a	--	--	100.0	100.0

MEAN EFFECTS OF TEAPOT-POUR FACTORS

2" Ø sprue, curved splash surface

Figure 11. Mean Effects Diagram for Factors Influencing Air Entrainment During Teapot Pouring.

6. On an absolute basis, "experimental error" contributed 1% of the total variation from zero. This experimental error includes slight variations in the pouring conditions between nominally identical events, unidentified factors (noise), and measurement errors in the load cell and gas flow meter.
7. The greatest amount of air entrained in teapot pouring was observed when pouring from a full ladle with longer sprues. Short sprues and pouring through a tilted sprue reduced the entrainment.
8. In general, pouring from a teapot ladle produced less entrainment than pouring from a bottom pour ladle.
9. The experimental system developed for water modeling allows processing variables to be systematically changed and their effects on air entrainment to be quantitatively measured.
10. Water appears to be a good physical model for pouring steel because it has approximately the same density to viscosity ratio which permits Reynolds number matching in a one-to-one scale model.

USE OF THIS REPORT AND INFORMATION CONTAINED THEREIN

Publicity

This report and the information contained therein is the property of the individual or organization named on the face hereof and may be freely distributed in its present form. However, Southern Research Institute hereby reminds Sponsor that no advertising or publicity matter, having or containing any reference to Southern Research Institute, shall be made use of by anyone, unless and until such matter shall have first been submitted to and received the approval in writing of the Institute. (The Institute does not usually approve any type of endorsement advertising.)

Limitation of Liability

Southern Research Institute has used its professional experience and best professional efforts in performing this work. However, the Institute does not represent, warrant or guarantee that its research results, or product produced therefrom, are merchantable or satisfactory for any particular purpose, and there are no warranties, express or implied, to such effect. Acceptance, reliance on, or use of such results shall be at the sole risk of Sponsor. In connection with this work, Southern shall in no event be responsible or liable in contract or in tort for any special, indirect, incidental or consequential damages, such as, but not limited to, loss of product, profits or revenues, damage or loss from operation or nonoperation of plant, or claims of customers of Sponsor.

Report No. : SRI -MMER- 93 - 615 - 7605 - III

To: Steel Founders' Society of America

455 State Street

Des Plaines, IL 60016

Date: July 15, 1993

7605UA1 . FNL

References

1. W. Stuart Lyman and F. F. Boulger, "An Investigation of Factors Producing the Cerioxide Defect on Steel Castings: Part I--Composition and Sources," SFSA Research Report No. 48, February, 1961.
2. George J. Vingas, Arthur H. Zrimsek, and LeRoy Carney, "Cerioxide Origins, A Tracer Program, " *AFS Transactions*, Vol 72, pp 1-8 (1964) .
3. M. C. Ashton and S. G. Sharman, "Control of the As-Cast Quality of Steel Castings, " *AFS Transactions*, Vol. 90, pp 719-728 (1982).
4. *International Atlas of Casting Defects* published by American Foundrymen's Society, 1974, pp 269, 275, 280, 283, 288 and 290.
5. R. A. Flinn, L. H. Van Vlack and G. A. Colligan, "Macroinclusions in Steel Castings," *AFS Transactions*, Vol. 74, pp 485-512 (1966).
6. R. E. Preece, "Identification of Surface and Subcutaneous Macroinclusions, " *AFS Cast Metals Research Journal*, pp 12-20 (September 1965).

7. G. A. Colligan, L. H. Van Vlack, and R. A. Flinn, "The Effect of Temperature and Atmosphere on Iron-Silica Interface Reaction," *AFS Transactions*, Vol 66, pp 452-458 (1958).
8. L. H. Van Vlack, R. A. Flinn and G. A. Colligan, "Nonmetallic Macroinclusion Causes in Steel Castings Deoxidized with Aluminum," *AFS Transactions*, Vol 74, pp 132-135 (1966).
9. L. H. Van Vlack and R. A. Flinn, "Reactions Between Refractories and Molten Steel Containing Aluminum," *AFS Transactions*, Vol 68, pp 136-144 (1960).
10. R. A. Flinn and L. H. Van Vlack, "Deoxidation Defects in Steel Castings," *AFS Transactions*, Vol 67, pp 295-299 (1959).
11. G. R. Fitterer, J. W. Linhart, B. B. Rosenbaum, J. B. Kopec, S. Poch and W. G. Wilson, "Acid Open Hearth Slag Fluidity and Its Significance," *Bulletin #1 of Acid Open Hearth Research Association, Inc.* (September 1945)
12. J. B. Caine, "A Method of Control of Oxides and Cases in Steel for Castings," *Steel Founders' Society of America*, Vol 3, pp 2-11, May, 1940.
13. Norman F. Koch, "A Study of the Snotter Cope Defect and Eroded Sand," *Steel Foundry Facts*, pp 5-11, July 1956.
14. L. J. Heaslip, A. McLean, and I.D. Sonunerville, "Chemical and Physical Interactions During Transfer Operations," *Continuous Casting*, Vol 1, pp 1 -122.
15. J. Savage and J. Lavender, "The Use of Radioactive Tracers for Determining the Source of Exogenous Sand Inclusions in Steel Castings, *Journal of Steel Castings Research* #26 July 1962.
16. "Inclusions Originating from Reoxidation of Liquid Steel" Summerville Farrell, Bilek and Hilty.
17. Olga Repetylo, Michel Olette and Paul Kozakevitch, "Deoxidation of Liquid Steel with Aluminum and Elimination of the Resulting Alumina," *Electric Furnace Proceedings*, pp 7-11 (1966).
18. Arthur H. Zrimsek and George J. Vingas, "Inhibitors for Elimination of Cerioxides in Steel Castings," *Modern Castings*, Vol 43, pp 203-20 (1963).
19. J. Brokloff, H. C. Chao, L. H. Van Vlack and R. A. Flinn, "Macroinclusion Studies in Steel Castings," *AFS Transactions*, Vol 71, pp 783-790 (1963).
20. A. More, "The Formation and Growth of Oxide Inclusions in Austenitic CrNi Steels," *Journal of Steel Casting Research*, No. 53, December 1970.
21. Peter F. Wieser, "Deoxidation of Steel for Steel Castings", *Steel Foundry Facts*, February 1970, pp. 2-11.
22. A. Kohn, M. Wanin, J. Arnoult, R. Thomas and L. Backer, "Study of the Origin of Aluminum-Bearing Inclusions in Electric Steels," *Electric Furnace Proceedings*, pp 39-47 (1969).
23. T. E. Brower, J. W. Bain, and B. M. Larsen, "Oxygen in Liquid Open Hearth Steel - Oxidation During Tapping and Ladle Filling," *Transactions AIME*, Vol 188, 1950, pp 851-861.
24. V. Brabie, "Studies and Research on the Formation of Inclusions in Steels, as a Result of Reoxidation during Casting," *Metalurgia* (Bucharest) 1983, 35(10), 493-497.
25. C. Nalbone, "Quality Steel Castings through Enhanced Melting and Pouring Practice," *SFRJ*, No 2, 2-83, pp 21-28.
26. A. Dainton, "Better Quality and Chemistry: A Look at New Developments in Molten Metal Transfer," presented at AFS 89th Casting Congress, Pittsburgh, PA, 4/29 - 5/3/85.
27. M. C. Ashton, "Gating System Design and Bottom-Pour Ladle Practice -Their Interactive Effect-on As-Cast Quality," *Steel Foundry Facts*, pp 1135 (February 1980).
28. John W. Pollard and D. E. Dutcher, "Unusual Ways to Reduce the Cost of Surface Defects. SFSA Research Report 78, May 1973.
29. AFS, *Analysis of Casting Defects*, Chapter 6, "Dirt, Slag and Other Inclusions," pp 16-22.
30. W. Stuart Lyman and F. W. Boulger, "An Investigation of Factors Producing the Cerioxide Defect on Steel Castings: Part II--Controlling the Occurrence of Cerioxide by Gating and Trapping," *SFSA Research Report* 52, July 1962.
31. Raymond Monroe and John Svoboda, "Making Quality Steel Castings; A Review of 20 Years of SFSA Literature," *SFSA Special Report* 23, Published Steel Founders' Society of America, Des Plaines, IL, March 1984.
32. A. Steck, "Gating Systems for Reducing Macroinclusion," *Steel Foundry Facts*, April 1985.

33. P. J. Trojan, P. J. Guichelaar and R.A. Flinn, "An Investigation of Entrapment of Dross and Inclusions using Transparent Whirl Gate Models, *AFS Transactions*, Vol 75, pp 462-469 (1966).
34. A. K. Zaman, "Evaluation of Whirl Runners for Large Steel Castings, " *Steel Foundry Facts* 321, January 1978.

Task 4

WASTE STREAM IDENTIFICATION AND TREATMENT

M.D. McKinley and I.A. Jefcoat

WASTE MANAGEMENT STUDY OF FOUNDRIES' MAJOR WASTE STREAMS

1.0 Background

Metalcasting is one of the most recycle-intensive of all manufacturing industries. Nevertheless, it produces solid, liquid, and volatile wastes. As a result, many of the environmental regulations which have been issued have a substantial impact on the foundry industry. In attempting to comply with these regulations, the industry has seen its costs rise, particularly in comparison with competitors in countries where environmental regulations are less stringent. Indeed, some organizations have found it expedient to move their operations overseas rather than comply with increasingly stringent U. S. environmental laws. Because the foundry industry must meet environmental requirements of the United States and compete internationally, it is in need of a significant effort to develop cost effective technology which will allow it to meet United States environmental regulations.

More stringent environmental emission limits and limits on concentrations of hazardous materials in the workplace make dealing with environmental problems a major expense that is rising each year. In 1989, over 2 percent of the production costs of a casting were a result of compliance and waste disposal costs. For foundries that cast leaded copper-base alloys this amounted to 9 percent. Environmental legislation recently enacted is expected to double the compliance and waste disposal costs by 1993.³ New environmental regulations regarding sand disposal in landfills will significantly increase landfill complexity and costs. The National Pollutant Discharge Elimination System requires permits for storm water discharges. There are also new regulations for underground storage tanks, underground pipelines, and for sludge disposal.

While the regulations mentioned above are important, the Clean Air Act Amendment of 1990 will have the most far-reaching impact on the nation of any recent new environmental legislation. The original Clean Air Act failed to address toxic air emissions in any meaningful way, and EPA promulgated rules for only a few. The amendments, however, cover 189 air toxics, and Maximum Achievable Control Technology (MACT) standards will be applied to source categories which emit 10 tons annually of a single toxic or 25 tons per year of a combination of air toxics. The goal is to have all toxic emissions under controls within ten years.^{6,8} The EPA schedule calls for iron and steel foundry air emission standards to be in place by 1997.

The American Foundrymen's Society (AFS) asked each of the eleven divisions of AFS to have their technical committees identify and prioritize the research needs of the U.S. foundry industry. The recommendations were categorized in two areas: materials and processes. The four process categories were green sand, chemically bound, investment casting, and expendable pattern (Figure 1). In each case, waste identification was a common element, in three of the four areas waste treatment or recycling of waste was listed, and two listed identification of emissions as a priority.

FOUNDRY RESEARCH NEEDS

(Priority per Process)

Process			
Green Sand	Chemically Bound	Investment Casting	Expendable Pattern
Waste Identification	Waste Identification	Core & Shell Removal	Determine Defect Cause
Waste Treatment Technologies	Optimize Reclamation	Waste Identification	Dimensional Control
Reuse Potential	Treatment Technology	Reclamation Potential	Identify Emissions
Penetration Defects	Reuse Potential	Dimensional Control	Waste Identification
Optimize Reclamation	Core Removal Technologies	Delivery System Design	Alternate Treatment
Delivery System Design	Delivery System Design		Delivery System Design
Dimensional Control			

Source: AFS Research - 1991

Figure 1. Foundry Research Needs

The present effort was directed toward the identification and categorization of the origin of waste streams and emissions in the metalcasting industry.

Research on emission control and waste disposal is the number one priority within AFS. The identification of foundry process waste is the first step in developing specific research programs. To this end, AFS conducted an industry survey to determine the top ten foundry waste streams of environmental concern. A copy of the survey document is attached as Figure 2. The top ten areas of environmental control concern to American foundries identified from this survey are given below (in priority order).

1. Sand System Waste
2. Mold and Pouring Emissions
3. Melt Furnace Emissions
4. Shake-Out Emissions
5. Storm Water Runoff
6. Unfired Core Waste
7. Core Room Emissions
8. Cleaning Room Dust
9. Shotblast Dust
10. Emission Control Water

Leading the list is sand system waste. Only recently, as landfills have begun to close down, has the issue of the disposal of spent molding sand been recognized as being a serious problem.

The second area is mold and pouring emissions, many of which come from resin binders in the sand and cores. (Note the importance of core binders as contributors to the waste problems in the top-ten list.) An idea of the complexity of the airborne emission problem from resin binders can be judged from the fact that there are some nineteen different *families* of resin binder systems in commercial use in foundries today.⁹ The airborne products given off when these systems are used to make cores or molds, and when they break down on exposure to molten metal, depend on the temperatures seen by the resins, and on process operating conditions. Important parameters are the pressures generated, and other gas species present, such as atmospheric moisture. No systematic study has been published which defines what these reaction products are, or how to control them.

Another notable item on the list is melt furnace emissions, which are receiving increased attention. Shakeout area emissions are related to the pouring emissions and binder systems, and are increasingly recognized as a problem to be addressed. While stormwater runoff has been largely ignored, the new storm water regulations mentioned above have attracted a lot of industry attention.

The list of top-ten areas of environmental concern show a recognition that elimination or control of air emissions in foundries will necessarily require a high level of attention. The Clean

FIGURE 2

Name _____

Company _____

A. Choose the top 10 areas, in descending order, of major concern to your company.

☐ Sand System Waste	☐ Cooling Water (contact)	☐ Melt Furnace Emissions
☐ Shotblast Dust	☐ Cooling Water	☐ Ladle Emissions
☐ Cleaning Room Dust	☐ (noncontact)	☐ Sand Reclaim Emissions
☐ Spent Furnace Refractory	☐ Emission Control Water	☐ Core Room Emissions
☐ Sand Reclaim Dust	☐ Cutting Oils	☐ Mold and Pouring Emissions
☐ Crucibles/Ladies	☐ Storm Water Runoff	☐ Shake Out Emissions
☐ Slags/Dross	☐ Cleaning Water	☐ Sand Transport & Cooling Emissions
☐ Floor Sweepings	☐ Solvents	
☐ Unfired Core Waste	☐ Off-spec. Binders	
☐ Fired Core Waste	☐ Scrubbing Solutions	☐ Molding Line Emissions
☐ General Refuse	☐ EPC Pattern Coating & Adhesives	☐ Welding & Cutting Emissions
☐ Off-spec. Material	☐ Cleaning Room Emissions	
☐ Spent Packaging/Containers		
☐ Scrap Polystyrene		
☐ General Refuse	☐ PCBs	
☐ Off-spec. Material	☐ Furnace Dust	
☐ Spent Packaging/Containers	☐ Hazardous System Sand Waste	
☐ Scrap Polystyrene & PMMA Patterns		

B. List any additional categories which may require consideration.

C. If specific subcategories can be identified, please include (i.e., CaC_2 desulfurization slag is a subcategory of dross/slag).

D. Do you foresee the top 10 categories changing priority over the next three to five years?

_____ If so, how might they change? _____

Air Act Amendments of 1990 (CAAA) will require this. In the top-ten list, only sand system waste and unfired core waste are not related in some way to air emissions. Dust emissions have received attention in the past, and technology for dealing with them is readily available. Emissions from the melt furnaces, however, have not been dealt with so extensively, and increased attention will be required. By far the largest problem in air emissions is related to air toxics, which are primarily organic compounds emitted during core making, pouring, and shake-out. The nature and amount of these airborne toxics are largely unknown, as are the methods for controlling the emissions. The need for emphasis on addressing air emissions is clear.

A number of strategies for dealing with foundry waste can be contemplated. Clearly, minimization of the waste generated is the first step. Elimination of those processes and products which inherently produce toxic wastes and emissions, or substitution of more benign processes and materials is a further step. Some binder systems which reduce environmental problems are now on the market. Increased use of reclamation and recycling of waste products will be important. Conversion of waste to useful commercial products at the foundry site is another tactic. For the remainder of the waste generated, however, it will be necessary to develop treatment methods which are inexpensive and reliable.

AFS has developed a research plan to address environmental concerns of the metalcasting industry. The research plan outlined by AFS is given in Figure 3. The objective of the program is to define the foundry waste streams and emissions, establish where the streams originate, what they consist of, and then to identify current available technology to minimize, treat, dispose, or reuse the waste.

The first step in this process is to define the foundry waste streams that pose the largest problems. This first phase has already been completed, and the results were given above. The industry survey identified the ten waste streams of most concern to the industry. Interestingly, there was little disagreement among the foundries which responded as to the importance of these specific waste streams.

The second step is to define the nature of the foundry waste streams, establish where the streams originate, and what they consist of. This report covers the research on this aspect of the emission studies.

2.0 Approach

Up to now, foundry waste emission concerns have emphasized sand, water, and particulate emissions. Concerns about emissions of air toxics have largely been focused on occupational health and safety. The Clean Air Act Amendments of 1990 (CAAA) require the control of emissions of toxic and hazardous materials to the air. The scope of a project which dealt with all types of emissions from foundries would be far too large for the current project. Therefore, this project dealt only with air emissions of toxic and hazardous chemicals subject to the CAAA.

FIGURE 3
ENVIRONMENTAL RESEARCH PLAN
By Phase

2/28/91

This report does not address nonattainment area requirements. The preconstruction review requirements for major new sources or major modifications locating in areas designated nonattainment differ from prevention of significant deterioration (PSD) requirements. The emissions control requirement for nonattainment areas, lowest achievable emission rate (LAER), is defined differently than the best available control technology (BACT). This report discusses only the HAP's covered under Title III of the CAAA. Those foundries under LAER requirements will also have to look at the requirements under Title I; SO₂, NO_x, and CO. In addition some states have set lower emission limits for some compounds to trigger MACT than the CAAA. Therefore, a small foundry may easily pass all criteria under Title III, but still have to be concerned about state regulations or Title I.

The U. S. foundry industry is very diverse. A comprehensive study of air emissions from all the different types of foundries and binder systems is beyond the scope possible for this project. Figures 4 and 5 show that grey iron, ductile iron and steel account for about 84 percent of the metal cast in 1990. In addition, EPA has chosen iron and steel foundries to be the first foundry types to come under compliance of the CAAA. Therefore, the emphasis for this project was air emissions from green sand iron and steel foundries. In particular, emphasis has been placed on core making, pouring, and shake-out. Metal preparation and melting have not been considered, as there are a number of current technologies for treating melting effluents (such as baghouses, etc.).

The approach used included a review of available information on emissions. The information sources were the technical literature, suppliers of chemicals to foundries, AFS workshops, technical meetings, and visits to foundries. A questionnaire was developed in the early stages of the project but was not given a general mail-out. This was mainly because of attempts to coordinate this project with EPA's efforts.

2.1 Literature review

A review of the literature for emissions from foundries has focused on binder systems, pyrolysis and thermal decomposition products of binder systems, and air toxics. Binder systems are considered to be the most likely source for the emission of the chemicals on EPA's list of Hazardous Air Pollutants (HAP). The binder starting materials and pyrolysis products all present a potential HAP release. There are very few literature articles on emissions from these binder systems.

2.1.1 Search methodology

Several different approaches were used in order to search for relevant information. They were the following:

FIGURE 4

FOUNDRY WASTE MANAGEMENT PROJECT

TONS OF METAL CAST
United States and Canada

1975

1980

1985

1990

Source: Metal Casting Industry Census Guide
April, 1992

FIGURE 5

FOUNDRY WASTE MANAGEMENT PROJECT **TRENDS IN TONS OF METAL CAST** **United States**

Source: Metal Casting Industry Census Guide
April, 1992

Database of STN International

This major database contains references to most of the scientific and technical literature. Included in the database are Chemical Abstracts, Engineering Index, Government Documents and Patents, both U.S. and foreign work, and foreign language articles as well as English. The search was performed with emphasis on the following keywords: pyrolysis, thermal decomposition, and the specific chemical name (phenol, formaldehyde, etc.).

National Technical Information Service (NTIS)

This database contains U. S. Government Documents. The University has 1980-1989 on CD-ROM in the Engineering Library. Several Articles were found of interest. The references from these articles provided several more sources.

Database of the AFS Library

A search was performed on this database with the assistance of an AFS librarian. This search proved to be very useful in providing articles of interest, which were retrieved from various sources through interlibrary loan and the help of AFS.

Compendex Plus

This database is the CD-ROM equivalent of the Engineering Index. The Engineering Library contains the years 1987-1991 on CD-ROM.

The University of Alabama Library

The University of Alabama is a member of the Association of Research Libraries and has extensive holdings. The card catalog is computerized so that it can be searched for books and journal titles by author, subject, or Library of Congress call number.

These searches led to 38 articles and journals that were relevant to this project. The articles and journals are listed in the bibliography at the end of this report.

2.2 Binder Processes and Potential Emissions

The primary driving force behind this project is the new Clean Air Act Amendments of 1990 (CAAA).³³ This legislation requires more stringent control of the emission of the 189 hazardous air pollutants (HAP'S) listed under Title III of the CAAA. One of the main source for these HAP's from foundries are the binders used in core and mold production. Although not counted as a resin binder, green sand may be another source. All of these sources are discussed below with their potential emissions.

There are three main classes of binder systems: heat activated, no bake, and cold box.³¹ The heat activated class includes several different binder systems. Among these are the hot box, shell, warm box, and core oil.

Hot Box

This process is initiated by blowing a resin and a sand mixture into a heated corebox.^{2,3} The curing process begins immediately upon contact with the heated corebox.^{2,31} Operating temperatures of the box are in the range of 450-550 °F. Emissions occur during the baking of the core and when the core is removed from the box.²

Binders that are in the hot box category include phenolic resins, furan resins, and combinations of the two. These resins can also be modified by the addition of urea. The phenolic resins are phenol formaldehyde polymers. Sometimes urea formaldehyde is added in order to improve the tensile strength. The furan resins are mixtures of furfuryl alcohol and urea formaldehyde polymers.

The chemical reaction for the phenolic resin of this process involves reacting phenol with an excess of formaldehyde and an aqueous weak acid (usually ammonium chloride).¹ The acid provides the hydrogen ions which catalyze the reaction. The resin is allowed to polymerize until the reaction is stopped, still in the liquid state.

The cure time of the resin binding the sand is a function of the temperature of the corebox and the catalyst type.¹⁰ The reaction is an exothermic reaction, therefore, the resin continues to cure even after it is removed from the corebox. Hot box binders have a high hot strength and fewer shakeout problems than other binders.

Hot-box binders decompose during the casting process and emit possible pollutants covered by the CAAA. Formaldehyde is a concern because it is present in excess.^{1,2} Table 1 is a list of possible HAP emissions covered by the CAAA when pouring metal in molds made by the hot box process.^{2,10,12,27,32}

Table 1. Potential HAP Emissions from Hot Box Binders.

Phenols	Formaldehyde
m-Xylene	o-Xylene
Benzene	Toluene
Aniline	Naphthalene
Hydrogen cyanide	Acrolein
Acetaldehyde	Hydrogen sulfide

The laboratory experiments performed by Scott et al yielded information on the amounts of chemicals released during the pouring and cooling process.³² They obtained emissions data for 12 systems: green sand, dry sand, silicate-ester, core oil, alkyd isocyanate, phenolic urethane, phenolic no-bake, low N₂ furan-H₃PO₄, medium N₂ furan TSA, furan hot box, phenolic hot box, and shell (phenolic). The test method used in their laboratory experiments was the quasi-stack method. The hot-box test molds were prepared using an irregular gear pattern designed by AFS Committee 80F. The gear casting with the gating system and riser weighed about 40 Kg and was poured in a mold weighing approximately 100 Kg. The castings were poured with a gray iron

at 2642 °F. The concentrations were measured in samples taken from a constant 1000 L/min flow of gas through the stack. The sand-resin mixture was cured against a heated pattern and then baked to ensure proper curing. Table 2 lists the results from their hot-box experiments.

Shell

As with the hot box process, the shell process begins with the addition of heat³¹. The sand used in the shell process is usually precoated before arriving at the foundry^{10,12}. Therefore, the core making process can be broken down into five steps: blow, invert, drain, cure, and strip.³¹ The operating temperature of the corebox is above 450 °F. The heat transfer must be uniform in order to ensure proper binding of the sand.

The chemistry of the shell process involves the reaction of formaldehyde, an excess amount of phenol, and an acid catalyst.¹ This reaction yields a strong three dimensional polymer network which is then either solvent coated or heat coated with hexamine. Hexamine is the cross linking agent which carries the reaction to completion upon the addition of heat. The cure speed is a function of time and temperature.¹⁰ Some of the advantages of the shell process include indefinite shelf life and the applicability to a wide range of metals.

Table 2. Quantities of Chemicals Released in the Hot Box Process.

<u>Chemical</u>	<u>Concentration (mg/m³) from Hot Box Binders</u>	
	Furan Hot Box	Phenolic Hot Box
Sulfur dioxide	2.8	1.2
Hydrogen sulfide	1.9	0.3
Hydrogen cyanide	110.0	39.0
Ammonia	620.0	360.0
Nitrous oxides	13.0	21.0
Formaldehyde	0.3	0.2
Acrolein	0.4	0.3
Total Aldehydes	<5	9
Total Aromatic Amines	96	42
Benzene	17	33
Toluene	<1	6
m-Xylene	<1	4
o-Xylene	<1	1
Naphthalene	<1	<1
Phenol	0.5	6.7
Bischloromethyl ether	<10.0 ppb	<10.0 ppb

Unlike the hot box, the shell process is rich in phenol.¹ Therefore, a major concern environmentally, is the emission of phenol. Table 3 lists possible emissions covered by the CAAA when pouring metal into molds made by the shell process.^{1,2,12,14}

Table 3. Possible HAP Emissions from Shell Binders.

Phenol	Formaldehyde
Aniline	Benzene
Toluene	m-Xylene
o-Xylene	N,N dimethyl formide
Naphthalene	Acrolein
Acetaldehyde	Hydrogen sulfide

In their laboratory study, Scott et al have reported the amounts of chemicals released from shell process molds during the pouring and cooling process.³² The data obtained are shown in Table 4.

Table 4. Quantities of Chemicals Released in the Shell Process.

<u>Chemical</u>	<u>Concentration (mg/m³)</u>
Sulfur dioxide	30.0
Hydrogen sulfide	0.8
Hydrogen cyanide	90.0
Ammonia	33.0
Nitrous oxides	8.5
Formaldehyde	0.3
Acrolein	0.4
Total Aldehydes	<5
Total Aromatic Amines	20
Benzene	57
Toluene	24
m-Xylene	5
o-Xylene	<1.0
Naphthalene	<<1.0
Phenol	21
Bischloromethyl ether	<10.0 ppb

Moorman et al have reported on the emissions of chemicals from cooling molds in operating foundries.²³ They obtained emission data for four different binder systems: furan (urea-formaldehyde-furfuryl alcohol), green sand with sea coal, urethane (phenolic isocyanate), and phenol-formaldehyde resins in shell molds. The emissions were collected using a train of three components: cyclone, venturi scrubber, and an entrainment separator. Particles were collected in the range of 0.5-10 μ m in diameter. Air entered the cyclone at 100 cfm. The water soluble fraction and particulate fraction were collected and analyzed. Emissions of polycyclic aromatic hydrocarbons and phenols were obtained from areas where shell-sand castings were cooling. Table 5 gives the results for these shell mold tests.

Laboratory work was performed by Emory et al to quantitate potentially hazardous nitrogen-containing compounds in foundry mold effluents.¹⁴ When metal pouring was started, sampling was begun and continued for 30 minutes while the casting solidified and cooled. The binder

systems studied included an alkyd isocyanate, a phenolic urethane, a shell binder, a phenolic no-bake, a nitrogen free furan no-bake, and a furan no-bake. Using an experimental procedure similar to that used by Scott et al,³² they employed the quasi-stack method to collect emissions while the mold was cooling. A constant flow rate of 1000 L/min was maintained through the chimney of the hood. Samples were taken for analysis from the gas flowing through the hood. The pouring temperature was 2650 °F and new sand was used. Their results for shell molds can be found in Table 6.

Table 5. Emissions from Shell Molds.

<u>Particulate Fraction</u>	
Compound	Emission (µg/g particulate)
Acridine	<0.6
Naphthalene	<0.6
Carbazole	<0.6
Phenanthrene	1500
Benzo(a)anthracene	\ 350
Chrysen	/
Benzo(a)pyrene	270
Dibenzo(a,h)anthracene	<0.6
<u>Water Soluble Fraction</u>	
Compound	Emission (µg/g sample)
Phenol	1600
Pentachlorophenone	<2
4-Nitrophenol	1800
2-Nitrophenol	2300
2,4-Dimethylphenol	60

Table 6. Amines Present in Shell Mold Effluent.

Compound	Concentration (mg/m ³)
Aniline	3.1
Triethylamine	<0.2
Morpholine	<0.2
N,N dimethylformamide	0.3
N,N dimethylaniline	<0.2
o-Toluidine	<0.2
2,4-Xylidine	<0.2
o-Anisidine	<0.2
p-Anisidine	<0.2
Mesidine	<0.2

Warm Box

The warm box process uses the same process steps as the hot box but the binders are cured at a lower temperature.³¹ The temperature range for this process is 300-450 °F, with the optimum temperature being 400 °F. This is approximately 100 degrees below that of the hot box.

The ability to cure at low temperatures is due to the catalyst used in the process.¹⁰ The catalyst is copper salts or sulfonic acids. These catalysts dissociate quickly at low temperatures and rapidly cure the cores at low heat. The cure speed can be controlled by the different formulations of the catalyst. Advantages of the warm box are the lower energy cost, a longer bench life, and low gas evolution.^{10,20} They can also be used with a wide variety of metals¹⁰.

As with the hot box, the warm box binders are phenolic resins and furan resins.¹⁰ The furan resin is high in furfuryl alcohol but low in nitrogen and free formaldehyde. These binders can also be modified with the addition of urea formaldehyde or phenolic formaldehyde. Metal pouring with molds made by the warm box process may release phenol and formaldehyde.^{4,27}

Core Oil

This process involves the mixing of core oil and a water activated cereal.³¹ This mixture is blended with sand and then blown into the core box at room temperature. The wet core is then removed and placed into a oven for curing. The catalyst for this reaction is heat. The final strength of the core is a function of oven temperature, drying humidity, and time. Table 7 shows the possible HAP emissions when pouring metal into cores made by this process.³²

Table 7. Possible HAP Emissions from Core Oils.

Phenol	Formaldehyde
Benzene	Toluene
m-Xylene	o-Xylene
Naphthalene	Acrolein
Hydrogen cyanide	Acetaldehyde
Amines (Aniline)	Hydrogen sulfide

Table 8 list the results from the laboratory experiments of Scott et al with molds made by the core oil process.³²

Table 8. Quantities of Chemicals Released in the Core Oil Process.

<u>Chemical</u>	<u>Concentration (mg/m³)</u>
Sulfur dioxide	2.4
Hydrogen sulfide	1.2
Hydrogen cyanide	1.8
Ammonia	0.8
Nitrous oxides	1.7
Formaldehyde	2.0
Acrolein	1.6
Total Aldehydes	16
Total Aromatic Amines	2
Benzene	49
Toluene	10
m-Xylene	5
o-Xylene	6
Naphthalene	<1.0
Phenol	1.2

No Bake

The second group of binders are the no bake (self-setting) binders, which are either acid catalyzed or ester cured.^{1,2,10,31} The difference between these binders and the ones previously mentioned is that they cure at room temperature. Heat is not required in the process. The operating temperatures for this process range from 75-85 °F.¹ The sand, binder, and catalyst are continuously mixed and blown into the corebox. For the best results, the sand mixture should be used in a relatively short time after the mixing of the resin and sand.

The chemistry of the phenolic no-bake binder consists of copolymers of formaldehyde with phenol and/or urea containing varying amounts of furfuryl alcohol.² The formaldehyde is fed at excess during the reaction. The acid catalyst is an organic sulfonic or phosphoric acid, with the organic usually being benzene or toluene.^{1,10} The acid provides the hydrogen ions to catalyze the reaction.¹ The strong acid lowers the activation energy of the binder allowing it to cure at room temperature. The curing time depends on the type of resin, sand chemistry, percent and type of catalyst, and temperature.³¹

The binders used in this process include furan/acid, phenolic/acid, phenolic/ester, silicate/ester, phenolic urethane, and alkyd urethane systems.^{1,2,10,12,31} Once again, modifications can be made to these binders. The furan/acid system consists of furfuryl alcohol and the catalyst.¹⁰ Other chemicals such as urea, formaldehyde, and phenol may be incorporated into the resin along with the furfuryl alcohol. The phenolic/acid system consists of phenol and formaldehyde. The phenolic/ester system contains a phenolic resole, an alkaline catalyzed thermosetting phenol-formaldehyde type resin consisting primarily of partially condensed phenol alcohols, and an ester. The ester causes the resole to polymerize into the binder and also yielding polymerized phenol formaldehyde resin, a metallic salt, and an alcohol as byproducts. The silicate/ester system contains a sodium silicate solution and an ester. The phenolic urethane system is made with

formaldehyde, phenol, xylene, cumene, 1,2,4 trimethylbenzene, methylene phenylene isocyanate, and naphthalene.⁴ The alkyd urethane is composed of lead, cobalt, naphthalene, 1,2,4 trimethylbenzene, and methylene phenylene isocyanate. All these binders are potentially sources of HAP's. Table 9 shows possible HAP emissions when metal pouring into molds from the no-bake systems.^{1,2,14,17,32}

Table 9. Possible HAP Emissions from No-Bake Binders.

Phenols	Formaldehyde
Carbonyl sulfide	Carbon disulfide
Methyl ethyl ketone	Benzene
Toluene	Xylenes
Cresol	Aniline
Naphthalene	Acrolein
Acetaldehyde	Hydrogen cyanide
Hydrogen Sulfide	

Specific quantities of chemical species as reported by Scott et al are given in Table 10³².

Table 10. Quantities of Chemicals Released in the No-Bake Process.

Chemical	Concentration (mg/m ³) by Binder Systems				
	Alkyd Isocyanate	Phenolic Urethane	Phenolic No-Bake	Low N ₂ Furan-H ₃ PO ₄	Med N ₂ Furan-TSA
Sulfur dioxide	1.1	1.4	310.0	15.0	120.0
Hydrogen sulfide	0.2	1.3	30.0	10.0	12.0
Hydrogen cyanide	4.8	24.0	0.6	9.1	15.0
Ammonia	1.0	1.9	0.8	1.0	5.0
Nitrous oxides	9.7	1.0	0.6	0.3	7.7
Formaldehyde	2.9	0.5	0.2	6.6	1.6
Acrolein	2.4	0.7	0.1	0.7	0.4
Total Aldehydes	59.0	<5	63.0	6	420
Total Aromatic Amines	<1	8	<1	2	9
Benzene	146	122	230	16	112
Toluene	42	19	13	3	218
m-Xylene	69	10	2	55	6
o-Xylene	105	3	<1	18	1
Naphthalene	1	<<1	<1	<1	1
Phenol	3.0	89.0	20.0	0.6	2.5
Furfuryl alcohol	--	--	--	1.6	0.2

Moorman et al, in their foundry studies, have reported on the emissions of polycyclic aromatic hydrocarbons and phenols from no-bake resins as shown in Table 11.²³

Table 11. Emissions from No-Bake Molds.

Particulate Fraction

Compound	Emission ($\mu\text{g/g}$ particulate) from Binder Systems.	
	Furan	Urethane
Acridine	<0.6	<0.6
Naphthalene	<0.6	12
Carbazole	<0.6	<0.6
Phenanthrene	31	230
Benzo(a)anthracene	\ <0.6	5.4
Chrysene	/	
Benzo(a)pyrene	<0.6	<0.6
Dibenzo(a,h)anthracene	<0.6	<0.6

Water Soluble Fraction

Compound	Emission ($\mu\text{g/g}$ sample) from Binder System	
	Furan	Urethane
Phenol	2000	50000
Pentachlorophenol	3	<2
4-Nitrophenol	48	420
2-Nitrophenol	<2	<2
2,4-Dimethylphenol	<2	21

Emory et al in their laboratory studies determined the amount of amines present in the mold effluent using the quasi-stack method.¹⁴ The results can be found in Table 12.

Cold Box

The third type of binder is the cold box. The cold box binder systems are relatively new to the foundry industry.⁶ Their acceptance was largely due to the increasing prices of oil and natural gas used in the heat activated systems. The cold box process is distinguished from the other processes by the use of a gas or vaporization catalyst to cure the core.³¹ With the exception of the silicate/ CO_2 system, the cold box system is a four step process: blow, gas, purge, strip. The whole process is a relatively fast operation.

There are several different gasses used in the cold box systems. These include amines, sulfur dioxide, and carbon dioxide.^{10,31} An example of the chemistry of the amine gassed process is a two part resin.¹ The first part consists of a phenol formaldehyde Novalak resin and the second part a partially polymerized diisocyanate based on diphenylmethane diisocyanate. The reaction is catalyzed by a tertiary amine, usually either triethylamine, or dimethylethylamine. In the presence of the catalysts, parts I and II form a solid thermoset urethane binder, which binds the sand together.¹⁰ If the proper amounts are not added, then the curing will not be complete.

Therefore, overgassing has become a general way of practice. Advantages of the cold box system include an increase in productivity and a reduced machinery maintenance cost.⁶

Table 12. Amines Present in No-Bake Mold Effluent.

Compound	Concentration (mg/m ³) from Binder System				
	Alkyd Isocyanate	Phenolic Urethane	Phenolic No-Bake	Furan No-Bake	Nitrogen Free Furan No-Bake
Aniline	4.5	2.8	<0.2	4.9	<0.2
Triethylamine	<0.2	<0.2	<0.2	<0.2	<0.2
Morpholine	<0.2	<0.2	<0.2	<0.2	<0.2
N,N dimethylformamide	<0.2	<0.2	<0.2	<0.2	<0.2
N,N dimethylaniline	<0.2	<0.2	<0.2	<0.2	<0.2
o-Toluidine	<0.2	<0.2	<0.2	<0.2	<0.2
2,4-Xylidine	<0.2	<0.2	<0.2	<0.2	<0.2
o-Anisidine	<0.2	<0.2	<0.2	<0.2	<0.2
p-Anisidine	<0.2	<0.2	<0.2	<0.2	<0.2
Mesidine	<0.2	<0.2	<0.2	<0.2	<0.2

The binders in the cold box system include phenolic/urethane/amine, phenolic ester, furan/SO₂, epoxy/SO₂, free radical curing (FRC)/SO₂, and silicate/CO₂.^{10,31} The phenolic/urethane/amine system is composed of a phenolic formaldehyde Novalak resin reacted with diphenylmethane diisocyanate.^{1,10} The catalyst of the reaction can be either triethylamine or dimethylamine. The phenolic/ester binder consists of a liquid phenolic resole and a volatile ester.¹⁰ The phenolic resole is an alkaline liquid containing: less than 0.5% free formaldehyde, less than 2.0% free phenol, and a significant portion of an inorganic compound. The ester is methyl formate.

The furan/SO₂ system is made up of a furan based resin, an organic peroxide (methyl ethyl ketone peroxide (MEKP)), and sulfur dioxide.⁶ The MEKP and SO₂ acting together work as the catalyst. The epoxy/SO₂ system contains cumene hydroperoxide, and isopropylbenzene as the first part of the binder.²⁴ The second part consists of bis(2-ethylhexyl)adipate, naphthalene, and 1,2,4 trimethyl benzene. The silicate/CO₂ system is composed of sodium silicate and carbon dioxide.¹⁰ The FRC (Free Radical Curing)/SO₂ process consists of a part A and a part B. Part A is an epoxy resin blended with an organic hydroperoxide and solvents and part B is an acrylic or vinyl-ester component with an epoxy resin. Table 13 gives a list of possible HAPs found in the cold box process.^{2,5,12,4}

Table 13. Possible HAP Emissions from Cold Box Binders.

Phenols	Formaldehyde
Naphthalene	Hydrogen Cyanide
Cresol	Isocyanates (MDI)
Aniline	Triethylamine
Benzene	

Laboratory studies by Archibald and Warren showed quantities of chemicals released during the pouring and cooling of the metal castings in molds made by the Ashland process, the FRC process, the SO₂ process, and the phenolic ester process.⁵ Hood stack studies similar to those of Scott et al³² were made on the molds to measure the releases of the thermal decomposition products. All the molds were poured within twenty-four hours of making the mold. The experiment used an irregular gear pattern developed by AFS. The metal used was a class 30 gray iron poured at 2600 °F. The results were reported in mg emission/g binder over a one hour sampling period, except where noted. Samples were taken over 15-minute intervals, except for the SO₂ process where only one sample over 30 minutes was used. Table 14 list the results of these experiments for these gas-cured binder systems.

Table 14. Quantities of Decomposition Products Released for Four Cold Box Binders.

<u>Binder Process</u>	<u>Chemical</u>	<u>Range (mg emission/g binder)</u>
Phenolic Urethane (Ashland Process)	Formaldehyde	0.051
	Phenol	11.74
	Aromatic hydrocarbons	17.22
	Aromatic isocyanates	0.195
FRC	Acrylic acid	1.51
	Hydroxyethyl acrylate	1.09
	Phenol	14.17
	Sulfur dioxide	0.54
	Aromatic hydrocarbons	26.8
Sulfur Dioxide (30 min test)	Sulfur dioxide	9.6
	Aromatic hydrocarbons	2.85
Phenolic Ester	Formaldehyde	1.86
	Phenol	1.88
	Aromatic hydrocarbons	6.21

Green Sand

The most common system used in the production of molds is green sand, which is packed into a mold with no curing. Some properties of the sand are it must be able to pack tightly, deform slightly without cracking, withstand the pressure of the molten metal, must be flowable, and must not melt or fuse to the casting at high temperatures.³¹ Generally green sand is mixed with different additives. These are carbons, cereals, starches, celluloses, clays, chemicals, refractories, and water.¹⁸ The green sand additives potentially release HAPs to the atmosphere. Table 15 is a list of potential HAPs released by green sand during pouring and cooling.

Table 15. Possible HAP Releases from the Use of Green Sand.

Phenols	Benzene
Toluene	Formaldehyde
m-Xylene	o-Xylene
Naphthalene	Acrolein
Acetaldehyde	Amines (Aniline)
Hydrogen sulfide	

Scott et al determined the amounts of chemicals released during the pouring and cooling process for green sand.³² Table 16 lists the results from this experiment.

Table 16. Quantities of Chemicals Released in the Green Sand Process.

<u>Chemical</u>	<u>Concentration (mg/m³)</u>
Sulfur dioxide	12.0
Hydrogen sulfide	39.5
Hydrogen cyanide	5.6
Ammonia	3.1
Nitrous oxides	26.7
Formaldehyde	0.2
Acrolein	0.1
Total Aldehydes	3
Total Aromatic Amines	1
Benzene	29
Toluene	3
m-Xylene	<1
o-Xylene	<1
Naphthalene	<1
Phenol	6.2

The amounts of polycyclic aromatic hydrocarbons and phenols released from green sand molds during the cooling process as reported by Moorman et al are given in Table 17.²³

Table 17. Emissions from Green Sand Molds.

<u>Particulate Fraction</u> <u>Compound</u>	<u>Emission (µg/g particulate)</u>
Acridine	<0.6
Naphthalene	<0.6
Carbazole	<0.6
Phenanthrene	7200
Benzo(a)anthracene	\ 1100
Chrysene	/
Benzo(a)pyrene	230
Dibenzo(a,h)anthracene	<0.6

Water Soluble Fraction

<u>Compound</u>	<u>Emission (ug/g sample)</u>
Phenol	1000
Pentachlorophenol	<2
4-Nitrophenol	<2
2-Nitrophenol	<2
2,4-Dimethylphenol	<2

A more detailed list of HAP emissions can be found in the next section of this report.

Along with the HAP emissions from these processes are other emissions. Table 18 lists some other typical emissions found when pouring metal into molds made with binders from these processes.^{1,2,5,10,12,14,17,4,27,32}

Table 18. Non HAP Emissions from Binders.

Heat Activated	Ethyl Alcohol
	Carbon Monoxide
	Carbon Dioxide
	Furfuryl Alcohol
	Ammonia
	Sulfur Dioxide
	Nitrous Oxides
No-Bake	Sulfur Dioxide
	Furans
	Acetone
	Nitrous Oxides
Cold Box	Carbon Monoxide
	Sulfur Dioxide
	Methyl Formate

FOUNDRY EMISSION INVENTORY

The total air emissions from a foundry were determined in a case study done by Euvrard and Jackson.¹⁵ The foundry studied was a medium sized gray and ductile iron foundry, with two cupolas melting approximately 17,000 tons of metal a year. The plant used a green sand molding system and a variety of oil, hot box, and cold box resins. Resins used for the cores included oil, phenolic isocyanate, phenolic ester, and furan hot box.

The air emissions were divided into metals, semi-volatiles, and volatile organic compounds and were reported in tons per year. Table 19 shows all air emissions converted to tons of emission per ton of metal poured. Emissions of 25 tons per year of a combination of the HAP

Table 19. Total Air Emissions from an Iron Foundry

<u>Air Pollutant Emissions</u>		<u>PLANT TOTAL</u> (tons emission/ton metal poured)
METALS		
	Aluminum	4.4900e-05
*	Antimony	1.4176e-06
*	Arsenic	4.8824e-07
	Barium	4.8235e-07
*	Beryllium	5.8824e-09
*	Cadmium	7.6471e-08
*	Chromium	1.1647e-06
*	Cobalt	1.0000e-07
	Copper	9.5000e-06
	Iron	6.6826e-04
*	Lead	6.8176e-06
	Magnesium	5.3935e-05
*	Manganese	3.5552e-04
*	Mercury	<1.6471e-07
	Molybdenum	2.2941e-07
*	Nickel	4.1765e-07
*	Selenium	1.6471e-07
	Silver	7.6471e-08
	Tin	7.7706e-06
	Titanium	9.0588e-07
	Zinc	9.7412e-06
	TOTAL METALS	1.1621e-03
	TOTAL CAAA METAL HAPs	3.6634e-04
	PARTICULATE	6.5067e-03
*	HYDROGEN CHLORIDE	2.5465e-05
	SULFUR OXIDES	
	Sulfur dioxide	6.9676e-05
	Sulfur trioxide	2.7841e-05
	Sulfuric acid	1.8008e-04
	TOTAL SULFUR OXIDES	2.7759e-04
	OXIDES OF NITROGEN	1.5081e-04
	CARBON MONOXIDE	4.0428e-03
	SEMI-VOLATILE ORGANIC COMPOUNDS	
*	Acenaphthylene **	1.1765e-08
*	Acenaphthene **	4.8824e-08
*	Benzo (a) anthracene **	1.1765e-09
*	Bis (2-ethylhexyl) phthalate	9.3294e-07
*	Dibutylphthalate	1.9941e-07
	Diethylphthalate	4.7941e-07
	Di-n-octylphthalate	6.4706e-09

Table 19, Continued. Total Air Emissions from an Iron Foundry

<u>Air Pollutant Emissions</u>		<u>PLANT TOTAL</u>
		<u>(tons emission/ton metal poured)</u>
*	Fluoranthene **	1.7647e-09
*	Fluorene **	5.1765e-08
*	Naphthalene	1.4824e-06
*	Phenanthrene **	6.8235e-08
*	Pyrene **	1.7647e-09
	2,4-Dimethylphenol	1.6106e-06
*	Phenol	1.0541e-06
*	Cresols	1.8976e-06
*	Methylnaphthalenes **	1.1229e-06
	TOTAL SEMI-VOLATILES	8.9712e-06
	TOTAL CAAA SEMI-VOLATILE HAPs	6.8747e-06
VOLATILE ORGANIC COMPOUNDS		
	Acetone	2.1439e-05
*	Benzene	8.2353e-09
*	Bromoform	2.4882e-07
*	1,3-Butadiene	6.5235e-07
*	2-Butanone (MEK)	2.1871e-06
*	Carbon Disulfide	1.2353e-08
*	Chlorobenzene	5.8824e-10
*	Chloroform	1.5276e-06
*	Chloromethane (Methyl Chloride)	5.8824e-10
*	1,2-Dichloroethane (EDC)	4.1765e-08
	1,1-Dichloroethane	6.4353e-07
*	Dichloromethane	2.8824e-08
	Ethyl Butyl Cellusolve	<1.1318e-06
*	Ethylbenzene	1.4941e-07
*	Formaldehyde	<2.7059e-08
	2-Hexanone	3.0000e-08
*	4-Methyl-2-Pentanone (MIBK)	5.1176e-07
*	Styrene	7.0647e-07
*	Tetrachloroethene (PCE)	2.7912e-05
*	Toluene	9.7588e-06
*	1,1,1-Trichloroethane (TCA)	4.0588e-08
*	Trichloroethene (TCE)	1.0588e-07
	Trichlorofluoromethane (F-11)	2.2471e-07
	Trichlorotrifluoroethane (F-113)	3.7412e-07
*	Vinyl Acetate	9.1418e-06
*	Xylenes	9.8616e-05
	TOTAL VOLATILES	1.7552e-04
	TOTAL CAAA VOLATILE HAPs	1.5168e-04
	FACILITY TOTAL CAAA HAPs	5.5036e-04

* Denotes CAAA HAP
 ** Denotes Polycyclic Organic Matter

compounds will trigger MACT. Table 20 reports the amount of metal to be poured to trigger MACT based on a combination of HAP component emissions.

Once again, these are total foundry air emissions and not process specific. However, it was determined that 90% of the HAP metals came from over the cupolas, 54% of the semi-volatiles and 24% of the volatiles came from the shakeout area, and 16% of the organics, semi-volatile and volatile were from pouring and cooling.

Table 20. Summary of CAAA HAP Emissions from Foundry Audit.

Air Pollution Emissions	PLANT TOTAL	AMOUNT OF METAL POURED TO TRIGGER	
	(Tons emission/ ton metal poured)	MACT (tons)	
TOTAL CAAA METALS HAPs	3.663e-04	6.824e+04	
TOTAL CAAA SEMI-VOLATILES HAPs	6.875e-06	3.637e+06	
TOTAL CAAA VOLATILE HAPs	1.517e-04	1.648e+05	
FACILITY TOTAL CAAA HAPs	5.248e-04	4.542e+04	

2.3 Development of Emission Factors

The emissions of HAP's from iron and steel foundries can generally be classified as metals or organics.

2.3.1 Metals

Emissions from melting furnaces are primarily volatile metals, which are generally controlled by particulate emission control devices. These emissions depend upon the type of scrap melted and on the type of melting furnace. The rate of metal emissions from electric and induction furnaces would be expected to be lower than from cupolas, for example. Many cupolas have particulate control devices on them, which reduces the net emission of metals. Any polymers, especially vinyl polymers, in the scrap may generate organic emissions, but the levels of organic emissions to be expected have not been quantified. Afterburners to control CO emissions in cupolas may also give sufficient control of many organic compound emissions. A study of emissions from melting operations was beyond the scope of the present study. Metal emissions from core and mold making, and shakeout are considered to be insignificant. Metal emissions from pouring depends on the alloy poured and the pouring temperature and are not included in this study.

2.3.2 Organic Compound Emissions

The potential emissions of HAP's from production of cores and molds are generally volatile organic compounds that result from unreacted components of the resin, solvents, or catalysts.

Potential HAP emissions from pouring and shakeout are pyrolysis and oxidation products from the binder resins. The compounds that potentially could be emitted in these operations are shown in Table 21, which contains the 189 HAP's included in the CAAA. Entries in the table have been coded with EPA's suggested code on their proposed foundry industry questionnaire:

- A = specific HAP is known to be emitted
- B = specific HAP is known NOT to be emitted
- C = no reason or data to assume the HAP is emitted
- D = specific HAP has been reported in the literature in trace amounts

Forty-seven HAP's have been identified in foundry air emissions, but many of these are at very low levels. Excluding metals, there are 38 potential HAP's emitted, but of these only 16 have been identified in this study as being potentially emitted in any significant quantity in foundry operations. These HAP's have been identified by type, but quantitative data on levels of emissions are very scarce and generally not available. This will be discussed in more detail later.

Table 22 (3 pages) lists the binder systems reviewed in this study, along with the chemical ingredients, approximate use level, and known HAP emissions from core making, pouring, and shakeout. Binder systems not included in this study were oil/urethane or alkyd/urethane binders, which are declining in popularity and are known to contain the HAP's cobalt and lead.

The previous lists of HAP's are inclusive of emissions which may occur in several different locations in a foundry. It probably will be necessary to pinpoint more accurately which HAP's are emitted from each area of the plant. Therefore, some discussion will be made of the potential emissions from several areas of the plant.

Core and Mold Making Emissions

Actual published quantitative emission data taken in core rooms were not found. Emissions of HAP's in core and mold making up to now have been of concern mainly for occupational health and safety. The main reason for needing to know the level of emissions has been to determine ventilation requirements. Mosher⁴ recently has compiled data from suppliers and manufacturers of binder chemicals to determine the fate of the ingredients put into the coremaking process. This document was prepared to assist foundries in filling out the EPA form R on emissions. The fate of the chemical ingredients was categorized as percent that was reacted and no longer existed after coremaking, percent unchanged in the process and remaining in the core, and percent evaporated to give an airborne emission. Therefore, these data can be used to give estimates of emissions from core and mold preparation areas. For example, Tables 23 through 25 show sample calculations of the amount of core sand usage that would result in 10 tons/year of emissions in core making for naphthalene, formaldehyde, and methanol evaporation emissions from three of the common binder systems that would be expected in the core room, when the binders are used at typical binder/sand ratios.

TABLE 21
POTENTIAL EMISSIONS OF HAP'S FROM FOUNDRIES

CAS Number	Chemical	Code	CAS Number	Chemical	Code
75070	acetaldehyde	C	110543	hexane	C
60355	acetamide	C	302012	hydrazine	C
73054	acetanilide	C	7647010	hydrochloric acid	C
98882	acetophenone	C	7664383	hydrogen fluoride	C
53883	2-acetylaminofluorene	C	7783084	hydrogen sulfide	C
107028	acrolein	C	123319	hydroquinone	C
79081	acrylamide	C	78581	isophorone	C
79107	acrylic acid	C	58898	isodane (all isomers)	C
107131	acrylonitrile	C	106316	maleic anhydride	C
107051	allyl chloride	C	675361	methanol	C
92871	4-aminobiphenyl	C	72436	methoxychlor	C
62533	aniline	C	74838	methyl bromide (bromomethane)	C
80040	o-anisidine	C	74873	methyl chloride (chloromethane)	C
1332214	asbestos	C	71558	methyl chloroform	C
71432	benzene (including gasoline)	C	78933	methyl ethyl ketone (2-butanone)	C
92875	benzidine	C	60344	methyl hydrazine	C
98077	benzotrifluoride	C	74884	methyl iodide (iodomethane)	C
100447	benzyl chloride	C	108101	methyl isobutyl ketone (hexane)	C
92524	biphenyl	C	624838	methyl isocyanate	C
117817	bis(2-ethylhexyl) phthalate (DEHP)	C	80626	methyl methacrylate	C
542881	bis(chloromethyl)ether	C	1634044	methyl-tert-butyl ether	C
73252	bromoform	C	101144	4,4-methylene bis	C
108880	1,3-butadiene	C	75082	methylene chloride	C
158827	calcium cyanamide	C	101688	MDI	C
105802	caprolactam	C	101779	4,4-methylenedianiline	C
133082	captan	C	91203	naphthalene	C
63252	carbaryl	C	98853	nitrobenzene	C
75150	carbon disulfide	C	92933	o-nitrophenyl	C
56235	carbon tetrachloride	C	100027	4-nitrophenol	C
463581	carbonyl sulfide	C	79468	2-nitropropane	C
120808	catechol	C	684835	n-nitroso-n-methylurea	C
133804	chloramben	C	67759	n-nitrosodimethylamine	C
57748	chlorane	C	58882	n-nitrosomorpholine	C
7782505	chlorine	C	56382	parathion	C
79118	chloroacetic acid	C	82688	pentachloronitrobenzene	C
532274	2-chloroacetophenone	C	87865	pentachlorophenol	C
108907	chlorobenzene	C	108952	phenol	C
510156	chlorobenzilate	C	106503	p-phenylenediamine	C
67883	chloroform	C	75445	phosgene	C
107302	chloromethyl methyl ether	C	7803512	phosphine	C
128988	chloroprene	C	7723140	phosphorus	C
1319773	cresols/cresylic acid	C	85448	phthalic anhydride	C
95487	cresol	C	1336383	polychlorinated biphenyls	C
108384	m-cresol	C	1120714	1,3-propane sultone	C
108445	p-cresol	C	57578	beta-propiolactone	C
98628	cumene	C	123386	propionaldehyde	C
94757	2,4-D salts and esters	C	114281	propoxur (Baygon)	C
3647644	DOE	C	78875	propylene dichloride	C
334883	dioxomethane	C	75588	propylene oxide	C
132848	dibenzofuran	C	75554	propylene imine	C
98128	1,2-dibromo-3-chloropropane	C	91225	quinoline	C
84742	diethylphthalate	C	108514	quinone	C
106467	1,4-dichlorobenzene(p)	C	100425	styrene	C
91941	3,3'-dichlorobenzidine	C	98083	styrene oxide	C
111444	dichloroethyl ether	C	1748016	2,3,7,8-tetrachloro-dibenzo-p-dioxin	C
542736	1,3-dichloropropane	C	78345	1,1,2,2-tetrachloroethane	C
62737	dichlorvos (dichlorovos)	C	127184	tetrachloroethylene	C
111422	diethanolamine	C	7550450	titanium tetrachloride	C
121887	N,N-dimethylaniline	C	108883	toluene	C
91887	N,N-diethylaniline	C	95807	2,4-toluene diamine	C
84673	diethyl sulfate	C	584848	2,4-toluene diisocyanate	C
119804	3,3'-dimethoxybenzidine	C	95534	o-toluidine	C
80117	dimethylaminobenzene	C	8001352	toxaphene (chlorinatedcamphene)	C
119837	3,3'-dimethylbenzidine	C	120821	1,2,4-trichlorobenzene	C
78447	dimethylcarbamoyl chloride	C	79005	1,1,2-trichloroethane	C
68122	dimethylformamide	C	79016	trichloroethylene	C
57147	1,1-dimethyl hydrazine	C	95854	2,4,5-trichlorophenol	C
131113	dimethyl phthalate	C	88082	2,4,6-trichlorophenol	C
77781	dimethyl sulfate	C	121448	triethylamine	C
534521	4,6-dinitro-o-cresol and salts	C	1562086	trifluralin	C
51285	2,4-dinitrophenol	C	540841	2,2,4-trimethylpentane	C
121142	2,4-dinitrotoluene	C	108054	vinyl acetate	C
123811	1,4-dioxane (1,4-dithylenesoxol)	C	583802	vinyl bromide	C
122887	1,2-diphenylhydrazine	C	75014	vinyl chloride	C
106886	epichlorohydrin	C	75354	vinylidene chloride	C
106887	1,2-epoxybutane	C	1330207	xylene	C
140885	ethyl acrylate	C	95476	o-xylenes	C
100414	ethylbenzene	C	108383	m-xylenes	C
51796	ethyl carbamate (urethane)	C	106423	p-xylenes	C
75003	ethyl chloride (chloroethane)	C	0	antimony compounds	C
108934	ethylene dibromide	C	0	arsenic compounds	C
107082	ethylene dichloride	C	0	beryllium compounds	C
107211	ethylene glycol	C	0	cadmium compounds	C
151564	ethylenimine (aziridine)	C	0	chromium compounds	C
75218	ethylene oxide	C	0	cobalt compounds	C
98457	ethylene thiourea	C	0	coke oven emissions	C
75343	ethylenedichloride	C	0	cyanide compounds	C
50000	formaldehyde	C	0	glycol ethers	C
78448	heptachlor	C	0	lead compounds	C
118741	hexachlorobenzene	C	0	manganese compounds	C
87883	hexachlorobutadiene	C	0	mercury compounds	C
77474	hexachlorocyclopentadiene	C	0	fine mineral fibers	C
67721	hexachloroethane	C	0	nickel compounds	C
822080	hexamethylene diisocyanate	C	0	polycyclic organic matter	C
680318	hexamethylphosphoramide	C	0	radionuclides (including radon)	C
			0	selenium compounds	C

TABLE 22
WASTE MANAGEMENT STUDIES OF FOUNDRIES
MAJOR WASTE STREAMS PROCESS: COREMAKING

Binder System	Type	Major Reactant Chemicals	Use Level (sand basis)	POTENTIAL HAP' PRODUCTS		
				COREMAKING	POURING	SHAKEOUT
<u>Cold Box</u>	Phenolic Urethane	phenolics isocyanates triethylamine	0.4-1.2% 0.4-1.2% 0.1%	formaldehyde MDI phenol triethylamine	benzene cresole/cresylic acid formaldehyde MDI naphthalene phenol toluene polycyclic- organic matter cyanide compounds	benzene cresole/cresylic acid formaldehyde MDI naphthalene phenol toluene polycyclic- organic matter cyanide compounds
	Phenolic Ester	phenolic resins methyl formate	1-2% 0.75-1.5%	formaldehyde phenol	benzene cresole/cresylic acid formaldehyde naphthalene phenol toluene polycyclic- organic matter	benzene cresole/cresylic acid formaldehyde naphthalene phenol toluene polycyclic- organic matter
	Silicate- CO ₂	sodium silicate CO ₂	1.5-4.0%			

Binder System	Type	Major Reactant Chemicals	Use Level (sand basis)	POTENTIAL HAP' PRODUCTS		
				COREMAKING	POURING	SHAKEOUT
Heat Activated	Shell (Resin Coated sand)	phenolic resin hexamethyl-tetramine	4-5%	formaldehyde methanol phenol	benzene cresole/cresylic acid formaldehyde phenol toluene polycyclic-organic matter	benzene cresole/cresylic acid formaldehyde phenol toluene polycyclic-organic matter
	Phenolic Hot Box	phenolic resin acid chloride salt	1.5-2.0%	formaldehyde phenol	benzene cresole/cresylic acid formaldehyde naphthalene phenol toluene polycyclic-organic matter cyanide compounds	benzene cresole/cresylic acid formaldehyde naphthalene phenol toluene polycyclic-organic matter cyanide compounds
No Bake	Furan/Acid	furfuryl alcohol benzene-sulfonic-acid	0.9-2.0% 0.3-0.9%	benzene methanol phenol toluene	benzene cresole/cresylic acid formaldehyde phenol toluene polycyclic-organic matter cyanide compounds	benzene cresole/cresylic acid formaldehyde phenol toluene polycyclic-organic matter cyanide compounds

Binder System	Type	Major Reactant Chemicals	Use Level (sand basis)	POTENTIAL HAP ¹ PRODUCTS		
				COREMAKING	POURING	SHAKEOUT
No Bake (Cont'd)	Phenolic/ acid	phenolic resin sulfonic-type acid catalyst	1.5-2.0% 0.3-0.9%	formaldehyde methanol phenol toluene	benzene cresole/cresylic acid formaldehyde phenol toluene polycyclic-organic matter	benzene cresole/cresylic acid formaldehyde phenol toluene polycyclic-organic matter
	Phenolic/ Ester	phenolic resins esters	1.5-2.0% 0.3-0.5%	formaldehyde phenol	benzene cresole/cresylic acid formaldehyde naphthalene phenol toluene polycyclic- organic matter	benzene cresole/cresylic acid formaldehyde naphthalene phenol toluene polycyclic- organic matter
	Phenolic Urethane	phenolic resin isocyanates amine catalyst	1-2% " 0.1%	formaldehyde MDI phenol	benzene cresole/cresylic acid formaldehyde naphthalene phenol toluene polycyclic- organic matter cyanide compounds	benzene cresole/cresylic acid formaldehyde naphthalene phenol toluene polycyclic- organic matter cyanide compounds

¹HAP = hazardous air pollutant

Table 23. Estimated Naphthalene Emissions from Phenolic Urethane Cold Box Binder
Sample Calculation 1

Binder System: Phenolic Urethane Cold Box

Source of Data: UA/AFS Mosher

Chemical: Naphthalene

Assumptions:

Concentration in Binder: 6.04%

Use Level: 0.8%

Evaporation Rate: 50%

No Air Capture or Control Devices

Pounds of Binder Needed to Generate 10 Tons/Year Emissions in Coremaking Operations:

$$\frac{20,000 \text{ lb/yr emissions}}{\text{Concentration in Binder} * \text{Evaporation Rate}} =$$

$$20,000 / (0.0604 * 0.5) = 662,252 \text{ pounds of binder} = 331 \text{ tons of binder}$$

Pounds of Core Sand Needed at Above Binder Use Rate to Generate 10 Tons/Year Emissions in Coremaking Operations:

$$662,252 / 0.008 = 82,781,500 \text{ pounds of core sand} \\ = 41,391 \text{ tons of core sand}$$

Table 24. Estimated Formaldehyde Emissions from Furan No Bake Binder
Sample Calculation 2

Binder System: Furan No Bake

Source of Data: UA/AFS Mosher

Chemical: Formaldehyde

Assumptions:

Concentration in Binder: 1.70%

Use Level (Core Sand Basis): 1.5%

Evaporation Rate: 10%

No Air Capture or Control Devices

Pounds of Binder Needed to Generate 10 Tons/Year Emissions in Coremaking Operations:

$$20,000 / (0.017 * 0.1) = 11,764,706 \text{ pounds of binder} = 5882 \text{ tons of binder}$$

Pounds of Core Sand Needed at Above Binder Use Rate to Generate 10 Tons/Year Emissions in Coremaking Operations:

$$11,764,706 / 0.015 = 784,313,733 \text{ pounds of core sand} \\ = 392,157 \text{ tons of core sand}$$

Table 25. Estimated Methanol Emissions from Phenolic No Bake - Acid Binder
Sample Calculation 3

Binder System: Phenolic No Bake - Acid

Source of Data: UA/AFS Mosher

Chemical: Methanol

Assumptions:

Concentration in Binder: 4.00%

Use Level: 0.6%

Evaporation Rate: 50%

No Air Capture or Control Devices

Pounds of Binder Needed to Generate 10 Tons/Year Emissions in Coremaking Operations:

$$20,000 / (0.04 \times 0.5) = 1,000,000 \text{ pounds of binder} = 500 \text{ tons of binder}$$

Pounds of Core Sand Needed at Above Binder Use Rate to Generate 10 Tons/Year Emissions in Coremaking Operations:

$$1,000,000 / 0.006 = 166,666,667 \text{ pounds of core sand} = 83,333 \text{ tons of core sand}$$

Pouring and Cooling Emissions

Laboratory data on emissions from pouring and cooling for one hour for most common binder systems have been reported. Although the studies were made for workplace health and safety considerations, quantities of the major organic compounds emitted can be calculated from the data. The experiments were made to give a comparison among binder systems, and no parameter studies were made. The experimental conditions were well presented by Scott, Bates and Jamesl.³² The casting was an irregular gear, which weighed approximately 40 kg with the gating system and riser. The sand weighed approximately 100 kg to give a sand-to-metal ratio of 2.5, except for the shell mold which had a sand-to-metal ratio of 0.9. The pouring temperature was 1450 °C. Emissions data were reported in concentrations (ppm), but with the specified gas flow rate of 1000 L/min through the stack the mass of emissions of each component can be calculated. They made measurements on 10 hot-box and no-bake binders, as well as for green sand and dry sand. Emory et al¹⁴ used an identical setup to study nitrogen compound emissions from three hot-box and three no-bake binder systems. A third set of experiments, again using the same setup, was made by Archibald and Warren⁵ on four cold-box binder systems. Their results were given in terms of milligrams of emission per gram of binder resin in the mold.

Tables 26 and 27 contain emission factors calculated from the data of Scott et al³² and Archibald and Warren.⁵ The factors are in terms of tons of emissions per ton of metal poured, and tons of emissions per ton of binder used. These factors should be used with a great deal of caution. First, the work of Scott et al³² was published in 1977. The binders in use at that time are probably not the same as the binders carrying the same name today, and the normal usage level

Table 26. HAP Emissions per Ton of Metal Poured for Common Binder Systems.

Binder System	EMISSIONS, ton/ton metal poured					
	Acrolein	Ammonia	Formaldehyde	Hydrogen Sulfide	Hydrogen Cyanide	Nitrogen Oxides
1. Alkyd Isocyanate	3.60e-06	1.50e-06	4.35e-06	3.00e-07	7.20e-06	1.46e-05
2. Core Oil	2.40e-06	1.20e-06	3.00e-06	1.80e-06	2.70e-06	2.55e-06
3. Dry Sand	1.05e-06	1.95e-05	7.50e-07	4.35e-05	3.00e-06	7.65e-06
4. Furan Hot Box	6.00e-07	9.45e-04	4.50e-07	2.85e-06	1.65e-04	1.95e-05
5. Green Sand	1.50e-07	4.65e-06	3.00e-07	5.93e-05	8.40e-06	4.01e-05
6. Low N2 Furan	1.05e-06	1.50e-06	9.90e-06	1.50e-05	1.37e-05	4.50e-07
7. Med. N2 Furan	6.00e-07	7.50e-06	2.40e-06	1.80e-05	2.25e-05	1.16e-05
8. Phenolic Hot Box	4.50e-07	5.40e-04	3.00e-07	4.50e-07	5.85e-05	3.15e-05
9. Phenolic No-Bake	1.50e-07	1.20e-06	3.00e-07	4.50e-05	9.00e-07	9.00e-07
10. Phenolic Urethane	1.05e-06	2.85e-06	7.50e-07	1.95e-06	3.60e-05	1.50e-06
11. Shell	1.60e-06	1.32e-04	1.20e-06	3.20e-06	3.60e-04	3.40e-05
12. Silicate-Ester	4.50e-07	6.00e-07	2.70e-06	3.15e-06	2.85e-06	4.50e-07
13. Ashland Process	NR	NR	1.91e-06	NR	NR	NR
14. Phenolic Ester	NR	NR	9.30e-05	NR	NR	NR
15. FRC Process	NR	NR	NR	NR	NR	NR
16. SO2 Process	NR	NR	NR	NR	NR	NR

Table 26, Continued. HAP Emissions per Ton of Metal Poured for Common Binder Systems
EMISSIONS, ton/ton metal poured

Binder System HAPs	Phenol	Sulfur Dioxide	Total Aldehydes	Benzene	Other Aromatics	Total
1. Alkyd Isocyanate	4.50e-06	1.65e-06	8.85e-05	2.19e-04	3.26e-04	6.71e-04
2. Core Oil	1.80e-06	3.60e-06	2.40e-05	7.35e-05	3.30e-05	1.50e-04
3. Dry Sand	6.00e-06	7.65e-05	1.20e-05	4.35e-05	2.25e-05	2.36e-04
4. Furan Hot Box	7.50e-07	4.20e-06	7.50e-06	2.55e-05	6.00e-06	1.18e-03
5. Green Sand	9.30e-06	1.80e-05	4.50e-06	4.35e-05	9.00e-06	1.97e-04
6. Low N2 Furan	9.00e-07	2.25e-05	9.00e-06	2.40e-05	1.16e-04	2.13e-04
7. Med. N2 Furan	3.75e-06	1.80e-04	6.30e-04	1.68e-04	3.39e-04	1.38e-03
8. Phenolic Hot Box	1.01e-05	1.80e-06	1.35e-05	4.95e-05	1.80e-05	7.24e-04
9. Phenolic No-Bake	3.00e-05	4.65e-04	9.45e-05	3.45e-04	2.55e-05	1.01e-03
10. Phenolic Urethane	1.34e-04	2.10e-06	7.50e-06	1.83e-04	4.95e-05	4.20e-04
11. Shell	8.40e-05	1.20e-04	2.00e-05	2.28e-04	1.24e-04	1.11e-03
12. Silicate-Ester	4.35e-06	3.90e-06	2.10e-05	2.25e-05	9.00e-06	7.10e-05
13. Ashland Process	4.40e-04	NR	NR	NR	6.46e-04	1.09e-03
14. Phenolic Ester	9.40e-05	NR	NR	NR	3.11e-04	4.98e-04
15. FRC Process	4.25e-04	1.62e-05	NR	NR	8.04e-04	1.25e-03
16. SO2 Process	NR	3.60e-04	NR	NR	1.07e-04	4.67e-04

*NR Not Reported

Table 27. HAP Emissions per Ton of Resin Used for Common Binder Systems.

EMISSIONS, ton/ton resin

Binder System	Acrolein	Ammonia	Formaldehyde	Hydrogen Sulfide	Hydrogen Cyanide	Nitrogen Oxides
1. Alkyd Isocyanate	7.62e-05	3.17e-05	9.21e-05	6.35e-06	1.52e-04	3.08e-04
2. Core Oil	2.40e-05	1.20e-05	3.00e-05	1.80e-05	2.70e-05	2.55e-05
3. Dry Sand	2.43e-05	4.51e-04	1.73e-05	1.01e-03	6.94e-05	1.77e-04
4. Furan Hot Box	1.00e-05	1.58e-02	7.50e-06	4.75e-05	2.75e-03	3.25e-04
5. Green Sand	4.62e-06	1.43e-04	9.23e-06	1.82e-03	2.58e-04	1.23e-03
6. Low N2 Furan	2.15e-05	3.08e-05	2.03e-04	3.08e-04	2.80e-04	9.23e-06
7. Med. N2 Furan	1.23e-05	1.54e-04	4.92e-05	3.69e-04	4.62e-04	2.37e-04
8. Phenolic Hot Box	7.50e-06	9.00e-03	5.00e-06	7.50e-06	9.75e-04	5.25e-04
9. Phenolic No-Bake	3.85e-06	3.08e-05	7.69e-06	1.15e-03	2.31e-05	2.31e-05
10. Phenolic Urethane	2.80e-05	7.60e-05	2.00e-05	5.20e-05	9.60e-04	4.00e-05
11. Shell	6.00e-06	4.95e-04	4.50e-06	1.20e-05	1.35e-03	1.28e-04
12. Silicate-Ester	5.45e-06	7.27e-06	3.27e-05	3.82e-05	3.45e-05	5.45e-06
13. Ashland Process	NR	NR	5.10e-05	NR	NR	NR
14. Phenolic Ester Process	NR	NR	1.86e-03	NR	NR	NR
15. FRC Process	NR	NR	NR	NR	NR	NR
16. SO2 Process	NR	NR	NR	NR	NR	NR

Table 27, Continued. HAP Emissions per Ton of Resin Used for Common Binder Systems

EMISSIONS, ton/ton resin

Binder System	Phenol	Sulfur Dioxide	Total Aldehydes	Benzene	Other Aromatics	Total HAPs
1. Alkyd Isocyanate	9.52e-05	3.49e-05	1.87e-03	4.63e-03	6.89e-03	1.42e-02
2. Core Oil	1.80e-05	3.60e-05	2.40e-04	7.35e-04	3.30e-04	1.50e-03
3. Dry Sand	1.39e-04	1.77e-03	2.77e-04	1.01e-03	5.20e-04	5.46e-03
4. Furan Hot Box	1.25e-05	7.00e-05	1.25e-04	4.25e-04	1.00e-04	1.96e-02
5. Green Sand	2.86e-04	5.54e-04	1.38e-04	1.34e-03	2.77e-04	6.06e-03
6. Low N2 Furan	1.85e-05	4.62e-04	1.85e-04	4.92e-04	2.37e-03	4.38e-03
7. Med. N2 Furan	7.69e-05	3.69e-03	1.29e-02	3.45e-03	6.95e-03	2.84e-02
8. Phenolic Hot Box	1.68e-04	3.00e-05	2.25e-04	8.25e-04	3.00e-04	1.21e-02
9. Phenolic No-Bake	7.69e-04	1.19e-02	2.42e-03	8.85e-03	6.54e-04	2.59e-02
10. Phenolic Urethane	3.56e-03	5.60e-05	2.00e-04	4.88e-03	1.32e-03	1.12e-02
11. Shell	3.15e-04	4.50e-04	7.50e-05	8.55e-04	4.65e-04	4.16e-03
12. Silicate-Ester	5.27e-05	4.73e-05	2.55e-04	2.73e-04	1.09e-04	8.60e-04
13. Ashland Process	1.174e-02	NR	NR	NR	1.72e-02	2.90e-02
14. Phenolic Ester	1.880e-03	NR	NR	NR	6.21e-03	9.95e-03
15. FRC Process	1.417e-02	5.400e-04	NR	NR	2.68e-02	4.15e-02
16. SO2 Process	NR	9.600e-03	NR	NR	2.85e-03	1.25e-02

* NR Not Reported

in a mold may also be quite different. The operating parameters were not varied in either of these studies. If the sand-to-metal ratios are different, the part being cast has a very different configuration, or the metal temperature is different, the effects of these variable changes on the emission factors are unknown.

Shakeout

No emission factors were developed for shakeout. There were no adequate data in the literature for making estimates of shakeout emission. Obviously operating parameters such as metal temperature, cooling time, and sand-to-metal temperature will have an effect on shakeout emissions.

2.4 Treatment Technologies

2.4.1 Survey of Currently Available Technologies

In order to assess the current commercial availability of pollution control equipment, a letter was sent to each of 99 air pollution control equipment suppliers listed in the Foundry Management & Technology, October, 1992 WHERE-TO-BUY Directory Section. In the letter, the project was identified and information requested on equipment recommended for control of potential air pollutants from coremaking, pouring and shakeout, and sand reclamation processes. Specific requests were made for methods used for sizing equipment, operating parameters, and other factors of importance. Some 26 responses were received, with the majority offering air filtration and gas sampling equipment or services (Table 28). This information was reviewed in preparation of this report.

Table 28. Response to Survey on Current HAP Control Technology Recovery Technology Area.

	Particulates	Gas	Hoods	Other
Number of Responses	13	4	2	7*

*3 responses dealt with sand reclamation processes

2.4.2 Treatment Equipment and Processes

In the past several decades, industry has directed its attention toward the protection of the environment. There are five control strategies followed in order to reduce and/or eliminate pollutant emissions. They include elimination of the operation entirely or in part, recycling, modification of the operation, relocation of the operation, applications of control technologies, and combinations of the above. This section deals solely with the use of control technologies.

Before selecting air pollution control equipment, several environmental, engineering, and economic factors must be considered. They are as follows:

Environmental, Economic and Engineering Factors

1. Equipment location
2. Available space
3. Ambient conditions
4. Availability of adequate utilities
5. Maximum allowable emissions
6. Aesthetic considerations
7. Contribution of air pollution control systems to wastewater and solid waste.
8. Contribution of air pollution control system to plant noise level.

ENGINEERING

1. Contaminant characteristics
2. Gas stream characteristics
3. Design and performance characteristics of the particular control system.

ECONOMICS

1. Capital cost
2. Operating cost
3. Expected equipment lifetime and salvage value

The following section gives descriptions of several different control systems. The first section deals with control of gaseous pollutants and the second with the control of particulates.

2.4.3 Treatment Processes

The objective in any treatment process is to bring the gas or liquid containing the particulates or chemical species in contact with a medium (air, water, etc.) so as to remove these species. Gas-liquid contacting processes that involve several components in the gas phase, similar to the foundry emissions, include transfer of one or more species from the gas to a liquid (absorption or scrubbing) or vice-versa (stripping). Some important aspects concerning the behavior of gas-liquid systems and relevant terms used to explain the state of such systems are noted below:

1. The gas in equilibrium with a liquid must be saturated with that liquid.

2. A limited number of intensive system variables may be arbitrarily specified (Gibb's Phase Rule) but the remaining variables must then be evaluated using equilibrium relationships for the distribution of components between the two phases.
3. The partial pressure of a vapor at equilibrium in a gas mixture containing one or more condensable components cannot exceed their respective pure component vapor pressures at the system temperature. Any attempt to increase the partial pressure of the component (by adding more vapor to the gas phase or increasing the total pressure) would lead to condensation of that component.

The techniques available for treating foundry emissions are abundant and the criteria that are important for such an operation should be based on the following:

1. Particle size distribution (including shape and density).
2. Efficiency of the equipment and emission reductions required.
3. Allowable pressure drop vs. required flow rate of gas processed.
4. Capital and operating costs of equipment.
5. Ease of treatment of dirty liquid or solids generated

Among the various collection devices such as spray towers, condensers, cyclone scrubbers, and electrostatic precipitators that are available - a venturi scrubber proves to be a good choice for the treatment of foundry emissions. Inertial impact is the primary collection mechanism for this type of removal. Water is injected upstream of the venturi throat and the curtain of water is broken up by the gas stream into drops which collect the dust. Venturi scrubbers are considered to be highly efficient for small particles similar to foundry emissions (between 0.001 to 100 microns) and there is no particle reentrainment. In spite of its higher efficiency scrubbers do not function well where plume rise is important since a wet plume has little buoyancy.

Absorption

Absorption is a process which removes one or more components from a gas stream by treatment with a liquid.⁷ The necessary condition for the removal of components from a gas stream is the solubility of these components in the absorbing liquid. The two most commonly used absorbers are packed and plate towers. In packed towers, the gas moves up through the packing while the liquid flows down the tower. Plate towers, on the other hand, use trays for the liquid to flow across and then down to the next tray, while the gas moves up through perforations in the tray. The design of these towers must be based on the principles of diffusion, equilibrium, and mass transfer.⁷ The main objective of the design is to provide a large interfacial area to bring the gas into contact with the liquid.

The efficiency of the tower depends on several factors including a) solubility of the component in a given solvent, b) concentration, c) temperature, d) flow rates of the gas and liquid streams, e) constant surface area, and f) efficiency of solvent regeneration (if the solvent is recycled).²⁸ Under ideal conditions, efficiencies of 99+ % can be obtained with absorption.

Absorbers are commonly used for inorganic vapors.²⁸ If used for organic vapors one may be faced with the following problems. First, the solvent for a particular component may be hard to find or identify. The component must be soluble in the solvent and the solvent should be easily regenerated for recycling. Second, the effluent must be disposed of in an environmentally safe way. Finally, the outlet gas concentrations normally will be small which may lead to unrealistic tower heights, contact times, and high liquid-gas flow rates.²⁸

This report will not go into a discussion of design equations. They can be found in mass transfer books such as Treybal, *Mass Transfer Operations*; and Henley & Seader, *Equilibrium-Stage Separation Operations in Chemical Engineering*.

The following table is a list of some advantages and disadvantages of absorption towers.⁷

Advantages

1. Relatively low pressure drop.
2. Standardization in fiberglass-reinforced plastic (FRP) construction permits operation in highly corrosive atmospheres.
3. Capable of achieving relatively high mass-transfer efficiencies.
4. Increasing the height and/or type of packing or number of plates can improve mass transfer without purchasing a new piece of equipment.
5. Relatively low capital cost.
6. Relatively small space requirements.
7. Ability to collect particulates as well as gases.

Disadvantages

1. May create liquid disposal problem.
2. Product collected wet.
3. Particulates deposition may cause plugging of the bed or plates.
4. When FRP construction is used, it is sensitive to temperature.
5. Relatively high maintenance costs.

Adsorption

Adsorption is a process in which certain components of a gas are transferred to the surface of a solid adsorbent. Adsorption is useful in air pollution control because it concentrates gaseous pollutants, thus facilitating their disposal.³⁵ It is used for industrial applications such as odor control, or recovery of volatile solvents.¹¹

There are two types of adsorption, physical and chemical. Physical adsorption is the result of intermolecular forces of attraction between the solid and the substance being adsorbed.³⁷ This process is reversible, which allows recovery of the adsorbed material. When the attractive forces between the solid and the gas are stronger than those between the molecules of the gas itself, the gas will condense on the surface of the solid. This process is accompanied by the release of heat, which usually is larger than the latent heat of vaporization of the sorbed material. The

forces holding the sorbed material to the solid can be overcome by the addition of heat or lowering the pressure, allowing regeneration of the adsorbent.

Chemical adsorption is the result of chemical interaction between the gas and solid.³⁷ Chemisorption is characterized by the following characteristics: a) energy released is greater than that of physical adsorption, b) the process is irreversible, c) the rate increases with a rise in temperature, d) it is more highly selective than physical adsorption, e) the capacity of the adsorbent is limited to that of the active sites on its surface. Chemical adsorption is not a feasible process if the recovery of the material is desired or if the adsorbent is to be regenerated for re-use.

There are several different solid adsorbents. The most widely used are activated carbon and molecular sieves. Descriptions and physical properties of different adsorbents can be found in Buonicore & Davis, Air Pollution Engineering Manual; Cooper & Alley, Air Pollution Control A Design Approach, and Rao, Environmental Pollution Control Engineering.

Adsorption takes place in fixed, moving, and fluidized beds.⁷ A fixed bed adsorber is fitted with perforated screens to support the adsorbent.²⁹ The moving bed adsorbers move the adsorbent in and out of the adsorption zone. Finally, the fluidized bed adsorbers contain a number of shallow fluidized beds of activated adsorbent. Design equations for these different beds can be found in mass transfer books, such as Treybal, Mass Transfer Operations and Sherwood, Pigford and Wilke, Mass Transfer.

The following is a list of advantages and disadvantages of the adsorption process:⁷

Advantages

1. Recovery of the sorbed material may be possible.
2. Excellent control and response to process changes.
3. No chemical disposal problem when pollutant is recovered and returned to the process.
4. Capability of systems to provide fully automatic, unattended operation.
5. Capability to reduce gaseous vapor contaminants from process streams to extremely low levels.

Disadvantages

1. Product recovery may require an exotic, expensive distillation (or extraction) scheme.
2. Adsorbent progressively deteriorates in capacity as the number of cycles increases.
3. Adsorbent regeneration requires a steam or vacuum source.
4. Relatively high capital cost.
5. Prefiltering of gas stream may be required to remove any particulate capable of plugging the adsorbent bed.
6. Cooling of the gas stream may be required to get the usual range of operation (less than 120° F).
7. Relatively high steam requirements to desorb high molecular-weight hydrocarbons.
8. Generally applicable to the removal of small amounts of pollutants.

Combustion

Combustion is a process in which organics are converted to carbon dioxide and water by rapid oxidation. Combustion, also known as incineration, can be used for odor control, and to destroy toxic compounds.¹¹ This process can achieve 95 to 99 percent efficiencies.²⁸ There are three combustion processes used to destroy organic contaminants: 1) flaring, 2) thermal incineration, 3) catalytic incineration.²⁶

Time, temperature, and turbulence, the three T's, govern the speed and completeness of combustion.²⁶ The oxygen must come into intimate contact with the combustible material at a sufficient temperature for a sufficient length of time for the reaction to be completed. Incomplete reactions may result in the formation of aldehydes, organic acids, and carbon monoxide.

Flares and thermal incineration are characterized by a flame, while catalytic incineration is flameless. In catalytic incineration, a metallic catalyst is used to produce oxidation.

Flares are usually applied when the heating value of the gases cannot be recovered economically.²⁸ They are commonly used to control process upsets and accidental releases. They are most widely used to dispose of hydrocarbons.²⁶ There are three common types of flares: 1) elevated 2) ground level 3) burning pits.²⁹

Thermal incineration is used for a wide but low range of organic vapor concentrations.⁷ They consist of burners, which ignite the fuel and organic vapor, and a chamber, which provides appropriate residence time for the oxidation process. The concentration of gas to be treated must be below the lower explosive limit. The feed is usually preheated since the reaction occurs at elevated temperatures. Following is a list of some operating ranges: Temperature-1200 to 1500°F; Time-0.2 to 1.0 seconds; and gas velocity-10 to 50 ft/s. High velocities are needed to prevent settling of particulates (if any) and minimize dangers of flashback and fire hazards. The advantage of thermal incinerators is that energy can usually be recovered in some form.

In catalytic incineration, the waste stream passes over a catalyst bed.²⁶ For simple reactions, the effect of the presence of a catalyst is to 1) increase the reaction rate, 2) permit the reaction to occur, and 3) reduce the reactor volume. Conditions for operation are lower than those of thermal incineration. Gas is delivered at a velocity between 10 to 30 ft/s and a much lower temperature, between 650 to 800 °F. Catalytic incineration is more sensitive to pollutant characteristics. The design is generally less expensive than thermal incinerators.²⁸ Commonly, metals from the platinum family are used for the catalyst due to their ability to combust at low temperatures.²⁶

Following is a list of advantages and disadvantages of combustion processes.⁷

Advantages

1. Simplicity of operation
2. Capability to provide steam generation or heat recovery in other forms.
3. Capability for high destruction efficiency of organic contaminants.

Disadvantages

1. Relatively high operating cost.
2. Potential for flashback and subsequent explosion hazard.
3. Catalyst poisoning.
4. Incomplete combustion can create potentially worse pollution problems (NO_x, SO_x).

Condensation

Condensation is a process which changes a vapor into a liquid. It is frequently applied as a preliminary air pollution control device to remove concentrated vapors from a gas stream before the gas reaches more expensive equipment, such as an absorber.²⁸ Condensation is accomplished by either lowering the temperature or increasing the pressure. However, increasing the pressure is often economically infeasible. Efficiencies of 50 to 90 percent can be reached using condensation,²⁸ however, the effectiveness depends directly upon the vapor pressure or volatility of the compounds being condensed.

Metallurgical dusts and fumes have a range of particle diameters from 0.001 to 100 microns. Particulate controls are used in many foundries, and condensible vapor components may condense on solid particles and be trapped in these collection devices. Therefore, particulate collection may reduce somewhat the emissions of low-volatility HAP's. When considering the level of emissions from an air pollution control device, one should remember that the partial pressure of a component in a gas stream cannot exceed the vapor pressure of that component. Thus, if a gas stream is cooled, some of the less volatile components may condense.

There are two common types of condensers used for air pollution control: contact and surface.²⁶ Contact condensers bring the gas stream into direct contact with the cooling fluid, where the vapors condense and mix with the coolant. Three common types of contact condensers are spray, jet, and barometric, which are usually more flexible and have better efficiencies than surface condensers. They also have the following advantages: 1) they can be used to produce a vacuum, therefore, creating a draft to remove odorous vapors, 2) they are usually simpler and less expensive than surface condensers, and 3) they usually have considerable odor-removing capacity. However, the principle disadvantage is their large water requirement.

Surface condensers are used for recovery, control and/or removal of trace impurities or contaminants.²⁶ In the surface-type condenser the vapor does not contact the coolant. The coolant is placed in the tubes while the vapor condenses in the shell portion of the condenser. Three types of surface condensers are the tube-and-shell, fin fan, and tubular. The advantages of the surface condenser are as follows: salable condensate can be recovered; water, used as the coolant, can be reused; and surface condensers require less water and produce 10 to 20 times less condensate. On the other hand, they are more expensive and require more maintenance than the contact condensers.

Design equations can be found in Kern, *Process Heat Transfer*, and Buonicore & Davis, *Air Pollution Engineering Manual*.

The following is a list of advantages and disadvantages of the use of a condenser.⁷

Advantages

1. Pure product recovery (in the case of surface condensers).
2. Water used in surface condensers does not contact the contaminated gas stream and can be used after cooling.

Disadvantages

1. Relatively low removal efficiencies for gaseous contaminants.
2. Coolant requirements may be extremely expensive.

Estimation of Vapor Pressure:

Because the effectiveness of condensation for removing components from an air stream is directly related to the volatility of the compounds, calculations of vapor pressures were made for compounds of interest. The vapor pressures of the various chemical emissions from Foundry Molds were estimated at two temperatures (100 and 200°F) by using an integrated form of the Clausius-Clapeyron equation. These temperatures were chosen because they should cover the range of expected temperatures for particulate treatment devices which treat ambient air from the various parts of the foundry. Each species of the emissions has an appropriate form of equation which estimates vapor pressure that agrees well with the observed vapor pressures in literature. The following are the three forms of expressions used from *The Properties of Gases & Liquids* by Reid et al:

$$\ln(P_{vp}/P_c) = (1-x)^{-1} [Ax + Bx^{1.5} + Cx^3 + Dx^6] \quad (1)$$

$$\ln P_{vp} = A - \frac{B}{T} + C \ln T \quad (2)$$

$$\text{where } x = 1 - T/T_c$$

$$\ln P_{vp} = A - \frac{B}{[T+C]} \quad (3)$$

where

P_{vp} = Vapor pressure, in bars

P_c = Critical pressure, in bars

T_c = Critical temperature, in degrees Kelvin

T = Temperature, in degrees Kelvin

A,B,C,& D = Constants

Listed below are the equations used for each of the chemical species.

<u>Equation 1</u>		<u>Equation 2</u>	<u>Equation 3</u>
1. Benzene	6. Acetaldehyde	11. Ammonia	16. Acrolein
2. Toluene	7. n-Butyraldehyde	12. Hydrogen Sulfide	17. Valeraldehyde
3. m-Xylene	8. Propionaldehyde	13. Hydrogen Cyanide	
4. o-Xylene	9. Phenol	14. Sulfur Dioxide	
5. Naphthalene	10. Formaldehyde	15. Nitrogen Oxides	

Table 29. Pure Component Vapor Pressures and Equilibrium Mole Fractions at 100°F[1] and 200°F[2]

Component	Vapor[1] (bar)	Vapor[2] (bar)	Molfr[1]	Molfr[2]
1. Ammonia	46.997	141.790	4.638e-04	1.399e-03
2. Hydrogen Sulfide	58.668	134.395	5.790e-04	1.326e-03
3. Hydrogen Cyanide	8.315	43.630	8.207e-05	4.306e-04
4. Sulfur Dioxide	22.765	78.244	2.247e-04	7.722e-04
5. Nitrogen Oxides	380.074	486.480	3.751e-03	4.801e-03
6. Total Aldehydes	3.788	24.360	3.738e-05	2.404e-04
8. Acrolein	3.800	24.370	3.750e-05	2.405e-04
9. Formaldehyde	7.743	29.939	7.641e-05	2.955e-04
10. Phenol	0.002	0.041	1.550e-08	4.011e-07
11. Benzene	0.222	1.494	2.189e-06	1.474e-05
12. Toluene	0.071	0.601	6.999e-07	5.936e-06
13. m-Xylene	0.022	0.247	2.218e-07	2.435e-06
14. o-Xylene	0.018	0.209	1.796e-07	2.061e-06

While condensation has not been widely used as an air pollution control method in the metal casting industry, other equipment such as venturi scrubbers and bag houses are common. Compounds which are emitted in hot operations, such as pouring, cooling, and shakeout will condense to form a smoke or fume that may be trapped in a bag-house or scrubber. The data on equilibrium partial pressures presented in Table 29 can be used to estimate the emissions of condensible compounds from particulate collection devices. If the mole fraction of a component is less than the listed values, the component will not condense. If, however, the mole fraction of a component exceeds the values listed, the component will condense and will be collected in a particulate collection device if the condensate has a large enough particle size. It is very common for condensate to collect on solid particles, so that the chance of collection of a fume in conjunction with other particulates is enhanced.

Cyclone Separators

Cyclone separators are used for the control of medium-sized and coarse particulates.⁷ They have a low purchase cost, no moving parts, and can be made to withstand harsh conditions.¹¹ The efficiency of a cyclone is not as high as other particulate collection devices.⁷ For this reason, cyclones are usually used as a precleaner for other particulate control devices.

Gas enters the cyclone near the top, then it is forced in a downward spiral because of its shape and tangential entry.¹¹ As the gas spirals down, centrifugal force and inertial forces cause the particles to move outward, collide with the wall and slide down to be collected. Near the bottom, the gas reverses its downward spiral and moves up in a tighter spiral and exits out the top of the cyclone. There are three categories of cyclones: high efficiency, conventional, and high throughput.

The efficiency depends on the particle size and cyclone design.¹¹ Efficiency may be 98% for particles greater than 5 microns but drops off to 90% for particles greater than 15 to 20 microns. As the efficiency of the cyclone increases so does the operating cost due to a high pressure drop. When the gas flow is high, several cyclones may be used in series or parallel.¹¹ Using them in series will increase the overall efficiency, but there will be a significant pressure drop. Cyclone separator design equations can be found in Buonicore and Davis, *Air Pollution Engineering Manual*; and Cooper and Alley, *Air Pollution Control A Design Approach*.

The following are the advantages and disadvantages of cyclones.⁷

Advantages

1. Low cost of construction
2. Relatively simple equipment with few maintenance problems.
3. Relatively low operating pressure drop in the range of approximately 2 to 6 inches water column.
4. Temperature and pressure limitations imposed only by the materials of construction used.
5. Dry collection and disposal.
6. Relatively small space requirements.

Disadvantages

1. Relatively low overall particulate collection efficiencies.
2. Inability to handle tacky materials.
3. Operating cost increase with increasing efficiency.

Fabric Filtration

One of the most frequently used technologies for airborne particulate control is fabric filtration or baghouses. They operate by pumping the dirty gas into the baghouse, where the particulates accumulate on the bags. The dust is allowed to build up on the bags until the pressure drop begins to become excessive, then the bags are cleaned. The build up of the cake is usually what determines the efficiency of the process.

Baghouses are least efficient for collecting particulates between 0.1 to 0.3 μm in diameter;²⁸ however, particles larger or smaller than this can be collected with an efficiency of 99% or greater. The efficiency is largely insensitive to the physical characteristics of the gas and dust, and, depending on the fabric cleaning method, to the inlet dust loading.

There are three types of baghouses: 1.) reverse-air, 2.) shaker, and 3.) pulse-jet.¹¹ The reverse air baghouse feeds the gas/dust stream up through the bottom of the bags, in which the dusts collect on the inside of the bags. The dust builds up until the pressure drop gets too high, and then the clean gas flow is reversed back through the bags. This reversal knocks the filter cake off the bags and the solid collects in the bottom in the hopper. They are usually constructed with several different bag compartments to allow continuous running while some of the bags are being cleaned. The reverse air cleaning process is gentle, therefore, the bags have a long life span.

Shaker baghouses operate in the same way as the reverse air type. The difference comes from the manner in which they are cleaned. The filter cake on the inside of the bags is mechanically shaken off the bags. The shaking motion can be vertical, horizontal, or a combination of both.⁷ The one condition that absolutely has to be met during cleaning is that there be no positive direction flow. For this reason, as with the reverse air baghouses, they are designed with several compartments to allow a continuous operation during cleaning. The shaking of the bags tend to decrease their life span.

The third type of baghouse, pulse jet, employs high pressure compressed air to back flush the bags.⁷ This method creates a shock wave, that travels down the bag knocking dust off. This cleaning technique is fast, only lasting a fraction of a second. Therefore, this process does not require that the baghouse be divided into separate compartments. Another difference between the pulse jet and the others is that the bags are closed at the bottom and open at top, hence, the dust collects on the outside of the bags. Internal frames, called cages, support the bags to prevent them from collapsing while they are in use. Once again the pulse jet action is harsher on the bags, shortening their life span.

The design equations for baghouses can be found in Buonicore and Davis, *Air Pollution Engineering Manual*, and Cooper and Alley, *Air Pollution Control A Design Approach*.

The following is a list of the advantages and disadvantages of baghouses.⁷

Advantages

1. Extremely high collection efficiency on both coarse and fine (submicron) particulates.
2. Relatively insensitive to gas stream fluctuation. Efficiency and pressure drop are relatively unaffected by large changes in inlet dust loadings for continuously cleaned filters.
3. Filter outlet air may be recirculated within the plant in many cases (for energy conservation).
4. Collected material is recovered dry for subsequent processing or disposal.

5. No problems with liquid waste disposal, water pollution, or liquid freezing.
6. Corrosion and rusting of components are usually not problems.
7. There is no hazard of high voltage, simplifying maintenance and repair and permitting collection of flammable dusts.
8. Use of selected fibrous or granular filter aids (precoating) permits the high-efficiency collection of submicron smokes and gaseous contaminants.
9. Filter collectors are available in a large number of configurations, resulting in a range of dimensions and inlet and outlet flange locations to suit installation requirements.
10. Relatively simple operation.

Disadvantages

1. Temperatures much in excess of 550 °F require special refractory mineral or metallic fabrics that are still in the development stage and can be very expensive.
2. Certain dusts may require fabric treatments to reduce dust seeping or, in other cases, assist in the removal of the collected dust.
3. Concentrations of some dusts in the collector may represent a fire or explosion hazard of a spark or flame is admitted by accident. Fabrics can burn if readily oxidizable dust is being collected.
4. Relatively high maintenance requirements (bag replacement, etc.).
5. Fabric life may be shortened by elevated temperatures and in the presence of acid or alkaline particulate or gas constituents.
6. Hygroscopic materials, condensation of moisture, or tarry adhesive components may cause crusty caking or plugging of the fabric or require special additives.
7. Replacement of fabric may require respiratory protection for maintenance personnel.
8. Medium pressure-drop requirements, typically in the range of 4 to 10 inches water column.

Electrostatic Precipitators (ESP)

ESP's induce a charge on the particle in the gas stream that causes the particles to accumulate on collector plates. Once collected on the plates, the particulates are knocked off and transferred to a hopper. They are less sensitive to the size of the particles but very sensitive to aerosol density and electrical resistivity of the particle.²⁸ Drift velocity of the particle is influence by this resistivity. The overall efficiency will experience a decrease if there is a low drift velocity due to a high resistivity.

The operation of an ESP consists of forcing the particle through a corona to give them an electric charge.⁷ A corona is an action in which the voltage applied to the electrodes cause the gas between the electrodes to break down electrically. Then an electric field, caused by high voltage electrodes, force the particle to the collector plates. There are five common type of ESP's: 1.) plate-wire, 2.) flat-plate, 3.) tubular, 4.) wet, and 5.) two-stage.

In plate-wire ESP's, the gas flows between parallel plates of sheet metal and high voltage electrodes, passing each wire in sequence as it flows through the unit.⁷ The units may be tall, however, they also allow many flow lanes to operate and are able to handle large volumes of

gasses. The electrodes are commonly given a negative polarity because a negative corona supports a higher voltage than a positive corona before sparking. A charging zone is established by the ions, generated in the corona, following electric field lines from the wires to the collecting plates.

Flat-plate ESPs operate on the same principles as plate-wire ESPs.⁷ The difference is that they use flat plates instead of wires. They are able to increase the average electric field, however, they are not able to generate coronas. Therefore, the coronas are generated using electrodes placed ahead of and sometimes behind the flat plate collecting zones.

Tubular ESPs have the electrodes running along the axis of the tube.⁷ The tubes can be formed as circular, square, or hexagonal honeycombs, with the gas flowing either upward or downward. The high voltage electrodes operate at one voltage for the entire length of the tube and the current varies along length as the particulates are removed from the system.

Wet ESPs are any of the above configurations with wet walls instead of dry.⁷ Water may be applied intermittently or continuously to wash the walls. The advantages of a wet ESP are there are no back coronas or problems with reentrainment when knocking the particulates off the wall.

A two-stage ESP is a series device while those described above are parallel in nature.⁷ The discharge electrode precedes the collector electrodes, and in indoor applications is operated with a positive polarity to limit ozone production. They are usually used for gas flows of 50,000 cfm and less. Two-stage ESPs are considered a separate and unique device as compared to large high gas volume single stage ESPs.

The design procedure and equations for an ESP can be found in Buonicore and Davis, *Air Pollution Engineering Manual*, and Cooper and Alley, *Air Pollution Control A Design Approach*.

The advantages and disadvantages of ESPs are listed below.⁷

Advantages

1. Extremely high particulate collection efficiencies can be attained.
2. Dry collection and disposal.
3. Low pressure drop
4. Designed for continuous operation with minimum maintenance requirements.
5. Relatively low operating costs.
6. Capable of operation under high pressure (to 150 psi) or vacuum conditions.
7. Capable of operation at high temperatures (to 1300 °F)
8. Relatively large gas flow rates can be effectively handled.

Disadvantages

1. High capital cost.

2. Very sensitive to fluctuations in gas stream conditions (flow rates, temperatures, particulate and gas composition and particulate loadings).
3. Certain particulates are difficult to collect due to extremely high or low resistivity characteristics.
4. Relatively large space requirements for installation.
5. Explosion hazard when treating combustible gases and/or collecting combustible particulates.
6. Special precautions required to safeguard personnel from the high voltage.
7. Ozone is produced by the negatively charged electrode during gas ionization.
8. Relatively sophisticated maintenance personnel required.

Wet Scrubbers

Wet scrubbers remove particulates from a gas stream by trapping the particles in liquid droplets and then separating the droplets from the gas stream.⁷ They can be used for the following conditions: 1.) contaminant cannot be removed easily in a dry form, 2.) soluble gases are present, 3.) soluble or wettable particulates are present, 4.) contaminant will undergo some subsequent wet process, 5.) pollution control equipment must be compact, 6.) contaminants more safely handled wet than dry. The particulates are captured in the liquid droplets by one of the following mechanisms: impaction, interception, and diffusion.

The goal of the scrubber is to cause the particle to become trapped in a water droplet and then be removed from the gas stream.⁷ The size of the particle removed is determined by the size of the liquid droplets. The smaller particles will be trapped in the smaller droplets. If the droplets are densely packed, there will be higher probability of capturing the particles. The scrubber must be designed properly to ensure that the droplets are densely packed with the proper droplet sizes. A successful scrubber will be able to create and control droplet dispersion effectively. Commonly, there are five types of wet scrubbers in use: 1.) venturi, 2.) mechanically aided, 3.) pump aided, 4.) wetted filter type, and 5.) tray or sieve.

Venturi scrubbers consist of a converging section, throat, and diverging section.⁷ The scrubbing liquid can be injected in a variety of ways including at the throat zone, at the gas inlet, and upward against the gas flow. They are usually considered to be a high energy particulate control device. They operate by converting the static pressure to kinetic energy in order to shear the scrubbing liquid into fine droplets.

Mechanically aided scrubbers create droplet dispersion by the use of a whirling mechanical device (usually a fan wheel or disk).⁷ The scrubbing liquid is injected into the mechanical device and mechanical energy is added to the system to break the liquid into fine droplets. Typically, the scrubber itself uses lower fan energy but the collection energy comes from a supplemental, device equipment. Therefore, the entire system would have to be considered in deciding the energy requirements.

Pump aided scrubbers introduce the liquid in a variety of ways including countercurrent to the gas, in the same direction as the gas, and at an angle.⁷ They use atomized sprays to control the

dispersion of the droplets. The energy input comes from the pressurized liquid stream and they are considered more efficient than fan aided scrubbers. Some different types of pump aided scrubbers are spray chambers, cyclone spray chambers, and orifice scrubbers.¹¹

Wetted filter scrubbers force the liquid and gas to go through small openings where a filtration process occurs.⁷ The particulates temporarily stick to the filter. These type scrubbers are best suited for low particulate loadings.

Tray or sieve scrubbers accelerate the gas stream through small orifices on the tray.⁷ The kinetic energy is used to create a froth in the liquid and the particulate is injected into the liquid stream.

Once again, design equations can be found in Buonicore and Davis, *Air Pollution Engineering Manual*; and Cooper and Alley, *Air Pollution Control A Design Approach*.

The following are the advantages and disadvantages of wet scrubbers.⁷

Advantages

1. No secondary dust sources.
2. Relatively small space requirements.
3. Abilities to collect gases as well as particulates.
4. Ability to handle high-temperature, high-humidity gas streams.
5. Low capital cost (if wastewater treatment system is not required).
6. For some processes, the gas stream is already at high pressures (so pressure drop considerations may not be significant).
7. Ability to achieve high collection efficiencies on fine particulates (however, at the expense of pressure drop).

Disadvantages

1. May create water disposal problem.
2. Product is collected wet.
3. Corrosion problems are more severe than with dry systems.
4. Steam plume opacity and/or droplet entrainment may be objectionable.
5. Pressure drop and horsepower requirements may be high.
6. Solids build up at the wet-dry interface may be a problem.
7. Relatively high maintenance costs.

2.5 *Field Information on Potential Air Emissions of Hap's from Iron and Steel Foundry Binders and Other Chemicals*

Potential air emissions of HAP's from binders and other chemicals used in iron and steel foundries were assessed from information obtained from the technical literature, suppliers, MSDS's, foundry contacts, and from AFS educational workshops.

SUPPLIER CONTACTS

Suppliers of chemicals to foundries were contacted by form letter and asked to submit information on binder chemical emissions. Phone calls to four major binder manufacturers also yielded applicable information. Material Safety Data Sheets (MSDS) were obtained from these manufacturers. One supplier provided information by binder type and process, while another provided information with only by binder type. Two other suppliers did not respond. Several iron foundries were also contacted for information but only a few responded.

WORKSHOPS

One of the investigators attended an AFS workshop on coremaking at the AFS training center in Chicago in April, 1992. The workshop provided valuable information from the instructors and attendees. Notes taken from the school were used to make a chart with several different binders and their emissions. Much of this information was included in the binder process descriptions discussed above.

FOUNDRY VISITS

Visits have been made to six major foundries in Alabama to discuss current process information and extent of data available on air emissions of hazardous air pollutants from coremaking, pouring, and shakeout operations.

2.6 *Other Activities*

USEPA COORDINATION

Several trips have been made to Durham, NC to coordinate activities with USEPA's Office of Air Quality Planning and Standards. James H. Maysilles, the EPA Project Officer, was our designated contact for the project. The EPA contractor for developing the Background Information Document is Research Triangle Institute, also in Durham.

QUESTIONNAIRE DEVELOPMENT

A questionnaire was developed to help foundries to begin to assess air emission potentials for the different processes. Worksheets were prepared for scrap pretreatment, melt furnace, core room, molding, pouring, shakeout, and sand reclaiming. The questionnaire was tested on several foundries in Alabama, but contact with USEPA's Office of Air Quality Planning and Standards indicated that their screening information request (the "short form"), and maximum achievable control technology (MACT) standards development information request (the "long form"), were to be issued shortly. To prevent confusion between the documents, we suspended work on our

version and concentrated on coordinating our efforts with the USEPA in developing the questionnaire and in helping the foundryman understand and fill out the required forms, which were mailed in September or October, 1993. Our notes to support the completion of the forms, the forms themselves, and our original questionnaire draft are included in the appendix of this report.

PAPERS AND PRESENTATIONS

The following presentations have been made in conjunction with this project:

Jim Maysilles and Marvin D. McKinley, "Filling out EPA's Air Toxics Request Form", Proceedings, American Foundrymen's Society 5th Annual Environmental Affairs Conference, Dearborn, MI, 1992.

Marvin D. McKinley, "EPA's Information Request for Hazardous Air Pollutants", CMI Course No. 8-207-Environmental Paperwork (32-93), Des Plaines, IL, November 1992.

Marvin D. McKinley, Irvin A. Jefcoat, William J. Herz, and Chris Frederick, "Air Emissions from Foundries: A Survey of Currently Available Information from the Literature, Suppliers, and Foundrymen", Presented at the 97th Casting Congress & CASTEXPO '93, Chicago, IL, April, 1993. Paper has been accepted for publication in AFS Transactions.

William J. Herz, "Filling out EPA's Hazardous Air Pollutants (HAP) Information Request Form" Alabama Cast Metals Association Conference, Joe Wheeler State Park, Alabama, August 28, 1992

2.7 Conclusions

The data in the literature on organic HAP emissions are of two types: (1) identification of chemical types and their concentrations in the workplace needed for worker health and safety, and (2) emissions during pouring and cooling. There are no emission data reported for shakeout. The pouring and cooling emissions were made for a single type of casting using the same metal-to-sand ratio and gray iron. Most data were reported either as concentrations in the gas or as milligrams of HAP per gram of binder resin. Emission factors were calculated from the literature data in terms of tons emission per ton of resin or per ton of metal poured for 16 binder systems from pouring and cooling, but much of the data were taken a long time ago and do not reflect improvements in binders or current usage levels. Even though some of the data may be out of date, they are the only published data available. It is clear that many small and medium-sized foundries will not have emissions at levels which will trigger MACT. The numbers presented here can be viewed as "worst-case" for purposes of estimating the impact of the CAAA on a particular foundry. While these emission factors allow calculation of order of magnitude estimates of emissions, they do not give the effect of parameters on the emission level. It is not clear that reporting the data as either ton HAP/ton of resin or ton HAP/ton of metal poured is valid if the sand-to-metal ratio changes. There are no data at different metal temperatures, so that

emission factors based on this literature cannot be used for steel casting. Since shakeout may occur at a different part of the plant, and because pyrolysis products may be trapped in the sand before shakeout, the effect of cooling time on shakeout emissions is needed. It is apparent that additional research is needed to determine the important parameters that control HAP emissions.

While laboratory data on emissions are needed for parameter studies, these data must be supplemented by plant measurements for validation. A research program which includes both laboratory data and plant testing is needed.

Treatment technologies currently available for reducing HAP emissions were briefly covered in this report. There is a conflict between control of concentration of HAP's in the ambient air in the foundry for worker health and safety and the effective collection and treatment of emissions to the air. For worker health and safety, a large volume of air is normally pulled through the plant. This large volume of air makes concentrations low and amount of gas to be treated high, which is detrimental to gas treatment for HAP emission control. It appears that most small and medium foundries will emit HAP's at a level below the threshold amounts specified by the CAAA. The large foundries, however, appear to be likely to exceed the thresholds. It appears that the first approach to emission control should be reduction of emissions through process and binder changes, and that controls to capture emissions other than particulate controls may be prohibitively expensive.

2.8 Bibliography

1. Ambidge, P., "Foundry atmosphere pollutants related to the chemistry of organic sand binders," BCIRA Journal, BCIRA Report 1673, Sept. 1986, pp 345-351.
2. Ambidge, P., Biggins, P., "Environmental problems arising from the use of chemicals in moulding materials," BCIRA Journal, BCIRA Report 1631, July 1985, pp 296-308.
3. American Foundrymen's Society, Inc., Foundry Industry Research Plan - 1991.
4. American Foundrymen's Society and Casting Industry Suppliers Association, Form R: Reporting of Binder Chemicals Used in Foundries", 1992.
5. Archibald, J., Warren, D., "Productivity and ecology considerations of gas cured binder systems," The World Foundry Congress, Dusseldorf, Germany, May 19-23, 1989.
6. Broome, A., "Cold Box Core and Mould Making Using the Furan SO₂ Process," *Castings*, vol 30, N 3-4, Mar/Apr 1984, pp 26-33.
7. Buonicore, A. and Davis, W. (ed), *Air Pollution Engineering Manual*. Van Nostrand Reinhold, New York, 1992.
8. Burditt, M. F., Carey, P. R., "Mold and Core Binders Keep Pace with Industry Demands," *Modern Casting*, vol 78, N 6, June 1988, pp 20-24.
9. Carey, P., "Today's Resin Binder Processes for Coremaking", *Foundry M & T*, November, 1990, p. 32.

10. Chemically Bonded Cores & Molds (an operators manual for the use of chemically bonded, self setting sand mixtures). American Foundrymen's Society Inc., Illinois, 1987.
11. Cooper, C. and Alley, F., *Air Pollution Control A Design Approach*, Waveland Press Inc., Illinois, 1986.
12. Eftax, D., "Air Sampling For Organic Binder System Emissions," *Modern Casting*. Sept. 1980, pp 49-53.
13. Eklund, G., "Foundry environment with ester-hardening phenolic binders," *Gjuteriet*. vol 78, N 11, 1988 pp 7-8. (Translated from Swedish. BCIRA T 1710.)
14. Emory, M., Goodman, P., James, R., and Scott, W., "Nitrogen containing compounds in foundry mold emissions," *Industrial Hygiene Association Journal*, vol 39, July 1978, pp 527-533.
15. Euvrard, Roy and Jackson, Barry, "Case Study: Air Audit at a Medium Size Gray Iron Foundry", Proceedings, American Foundrymen's Society Environmental Affairs Conference, Dearborn, Michigan, August, 1992.
16. Gshwandtner, G., Fairchild, S., and McCrillis, R., "Air Toxic Emissions from Iron Foundries," Air & Waste Management Association. 84th Annual Meeting & Exhibition, Vancouver, British Columbia, June 16-21, 1991.
17. Gshwandtner, G., Fairchild, S., Emission Factors for Iron Foundries--Criteria and Toxic Pollutants. EPA-600/2-90-044 (NTIS PB 90-266743), U. S. Environmental Protection Agency, Research Triangle Park, North Carolina, Aug. 1990.
18. Green Sand Additives (Properties, Applications, and Effects of Misuse, including indicative Test Results). American Foundrymen's Society Inc., Illinois, 1987.
19. Henley, E. and Scader, J., *Equilibrium-Stage Separation Operations in Chemical Engineering*, John Wiley & Sons, New York, 1981.
20. Kolb, L., "The Warm-Box Process: An Energy Saving and Environmentally Acceptable Development in Core Production," *Giessereitechnik*, vol 28, N 12, 1982, pp 382-384. (Translated from German. BCIRA T 1648.)
21. Marchello, J., Control of Air Pollution Sources. Marcel Dekker Inc., New York, 1976.
22. Moorman, W., James, R., and Palmer, W., "Analysis of Emissions Collected from Four Types of Iron Casting Molds," *American Industrial Hygiene Association Journal* vol 46, Dec. 1985, pp 724-730.
23. Moorman, W., Palmer, W., Garner, F. and Mulligan, L., "Carcinogenic Potential of Foundry Pyrolysis Effluents," *AFS Transactions* vol 93, Paper 85-05, 1985, pp 23-28.
24. Moorman, W., Palmer, W. and Scholz, R., "Carcinogenic Potential of Condensed Pyrolysis Effluents from Iron Foundry Casting Operations: A Preliminary Report," *AFS Transactions*, vol 88, Paper 80-65, 1980, pp 745-750.
25. Moore, J. J., and Mason, R., "An examination of the gas evolution characteristics of various synthetic core binders," *British Foundryman*, vol 74, N 9, Sept. 1981, pp 189-195.
26. Perry, R., Green, D. and Maloney, J. (eds), *Perry's Chemical Engineering Handbook*, 6th ed., McGraw-Hill, New York, 1984.
27. Personal Communication, "Hazardous Air Pollutants Present in Foundry Resin Systems," David Hortsman, Delta Resins & Refractories, 1992.

28. Purcell, R., and Sharcef, G., *Handbook of Control Technologies for Hazardous Air Pollutants*, Hemisphere Publishing Corporation, New York, 1986.
29. Radian Corporation, "Final Report: Control Techniques For Volatile Organic Emissions From Stationary Sources," Radian DCN 77-200-187-23-08, EPA Contract No. 68-02-2608, Task 12 and 23, Texas, 1978.
30. Rao, C., *Environmental Pollution Control Engineering*, John Wiley & Sons, New York, 1991.
31. "Sand/Binders/Sand Preparation/Core Making," *Foundry Management & Technology*, vol 119, N 12, Dec. 1991, pp D1-D13.
32. Scott, W., Bates, C., and James, R., "Chemical Emissions from Foundry Molds," *AFS Transactions*, vol 85, 1977, pp 203-208.
33. Smith, V., "Foundries and the Clean Air Act-several unanswered questions," *Foundry Management & Technology*, Feb. 1991, pp 16-18.
34. Southern Research Institute, "Binder Decomposition During Pouring and Solidification of Foundry Castings, Part II: Particulate Emissions from Foundry Molds," *AFS International Cast Metals Journal*, June 1979, pp 14-15.
35. Stern, A., *Air Pollution*, 3rd ed., vol IV, Academic Press, New York, 1977.
36. Thomas Register of American Manufacturers. 82nd ed., Thomas Publishing Co., New York, 1992.
37. Treybal, R., *Mass Transfer Operations*, 3rd ed., McGraw- Hill, New York, 1987.
38. Wallace, D., and Cowherd Jr., C., Fugitive Emissions from Iron Foundries. EPA-600/7-79-195, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, Aug. 1979

APPENDIX

VENDORS OF AIR EMISSION CONTROL EQUIPMENT

Listed under the same headings as found in the Thomas Register of American Manufacturers, 82nd Edition, Thomas Publishing Co., New York, 1992

ABSORBERS: GAS

1. Analytichem International Inc.--Harbor City, CA
2. Adsorbents & Dessicants Corp. of America--Los Angeles, CA
3. Divesified Vacuum Technology, Inc.--Colorado Springs, CO
4. Ultrapure Systems Inc.--Colorado Springs, CO
5. Micrographic Technology, Inc.--Denver, CO
6. Entroler, Inc.--New Haven, CT
7. ABB/ASEA Brown Boveri Inc.--Stamford, CT
8. Patterson Process Equipment Div., Patterson Pump Co.--Toccoa, GA
9. Flex-Kleen Corporation--Chicago, IL
10. Trema North America Inc.--Reisterstown, MD
11. Sphinx Adsorbents Inc.--Springfield, MA
12. Monroe Environmental Corp.--Monroe, MI
13. Iroquis Industries Inc.--Muskegon, MI
14. Missouri Boiler & Tank Co.--St. Louis, MO
15. Sigri Corporation--Bedminster, NJ
16. RaySolv Inc.--Bound Brook, NJ
17. Advanced Industrial Technology Corp.--Lodi, NJ
18. Ambient Engineering Inc.--Matawan, NJ
19. Allied Group--Mendham, NJ
20. Hydronics Engineering Corp.--Midland Park, NJ
21. York, Otto H., Co. Inc.--Parsippany, NJ
22. Ergenics Inc.--Ringwood, NJ
23. Croll-Reynolds Co. Inc.--Westfield, NJ (908-232-4200)
24. Buffalo Forge Co., Machine Tool Div.--Buffalo, NY
25. Clean Gas Systems Inc.--Farmingdale, NY (516-756-2474 Ext. 91)
26. Ducon Environmental Systems--Farmingdale, NY
27. Emtrol Corp.--Hauppauge, NY (516-582-9700)
28. Zelcron Industries Inc. C/O Ducon Environmental Systems--Melville, NY (800-394-4990)
29. Chemipulp/Jenssen Div.--Watertown, NY
30. Harrison Plastic Systems--Aurora, OH
31. Midwest Filtration Co.--Hamilton, OH
32. Nutter Engineering Div., Patterson-Kelley--Tulsa, OK
33. Air Products & Chemicals--Allentown, PA
34. GE Company, GE Environmental Services--Lebanon, PA
35. CTC Industrial Servics, Inc.--Memphis, TN
36. BS & B Engineering Co., Inc.--Houston, TX
37. Ershings, Inc.--Bellingham, WA

TOWERS: ABSORPTION

1. Ecodyne Cooling Tower Services--Santa Rosa, CA
2. Monroe Environmental Corp.--Monroe, MI
3. Duall Div. Met-Pro Corporation--Owosso, MI
4. Anel Industries, Inc.--Winona, MI
5. Pullman Power Products Corp.--Kansas City, MO

6. Missouri Boiler & Tank Co.--St. Louis, MO
7. Sigri Corporation--Bedminster, NJ
8. North American Pollution Control Systems Inc.--Linden, NJ (800-752-0237)
9. Advanced Industrial Technology Corp.--Lodi, NJ
10. Ambient Engineering, Inc.--Matawan, NJ
11. Hydronics Engineering Corp.--Midland Park, NJ
12. Belco Technologies Corp.--Parispany, NJ
13. York, Otto H., Co., Inc.--Parispany, NJ
14. Croll-Reynolds Co., Inc.--Westfield, NJ (908-232-4200)
15. Mixing Equipment Co., Inc.--Rochester, NY
16. Corflex International Inc.--Warren, OH
17. Sentinel Process Systems Inc.--Hatboro, PA
18. Smith Industries, Inc.--Houston, TX

TOWERS: PACKED

1. Jagger Aerospace Engineering--Costa Mesa, CA
2. Bohn Fiberglass Industries, Inc.--Louisville, KY
3. Fisher-Klosterman, Inc.--Louisville, KY
4. Vendome Copper & Brass Works, Inc.--Louisville, KY
5. Trema North America, Inc.--Registerstown, MD (800-833-2925)
6. Process Systems International, Inc.--Westborough, MA
7. Monroe Environmental Corp.--Monroe, MI
8. Duall Div. Met-Pro Corporation--Owosso, MI
9. Viron International--Owosso, MI
10. Hydro Group Inc.--Bridgewater, NJ
11. Delta Cooling Towers, Inc.--Fairfield, NJ
12. Advanced Industrial Technology Inc.--Lodi, NJ
13. Ambient Engineering, Inc.--Matawan, NJ
14. Hydronics Engineering Corp.--Midland Park, NJ
15. York, Otto H., Co., Inc.--Parispany, NJ
16. Research-Cottrell Companies--Somerville, NJ (908-685-4000)
17. Croll-Reynolds Co., Inc.--Westfield, NJ (908-232-4200)
18. Beltran Associates, Inc.--Brooklyn, NY (718-338-3311)
19. Clean Gas Systems Inc.--Farmingdale, NY
20. Ducon Environmental Systems--Farmingdale, NY
21. Zelcron Industries Inc. C/O Ducon Environmental Systems Div.--Melville, NY (800-394-4990)
22. Swemco, Inc.--New York, NY
23. Fabrication Engineering Service Company, Inc.--Charlotte, NC
24. Air Plastics, Inc.--Cincinnati, OH
25. Sentinel Process Systems, Inc.--Hatboro, PA
26. Luftrol, Inc.--Warminster, PA
27. Chemco Engineering Inc.--Belton, TX
28. Smith Industries, Inc.--Houston, TX
29. ECO Equipment FEP Inc.--PQ, Anjou, Canada

SCRUBBERS: AIR

1. Zurn Industries Inc., Air Systems Div. Air Quality Control Products-Clarage Fans--Birmingham, AL (205-853-4112)
2. Beco Corporation--Benton, AR
3. Tigg Corp.--Heber Springs, AR (800-925-0011)
4. Advance Fiberglass, Inc.--Little Rock, AR (800-342-7367)

5. Jaeger Aerospace Engineering-- Costa Mesa, CA
6. ACME Fibergalss, Inc.-- Hayward, CA (510-538-3440)
7. Air Chem Systems Inc.-- Huntington Beach, CA
8. Campbell, J.A., Company-- Long Beach, CA (310-424-0455)
9. Joy Technologies, Inc., Western Precipitation Div.--Monrovia, CA
10. Calvert Environmental-- San Diego, CA (619-272-0050)
11. Aqua Craft, Inc.-- San Francisco, CA (415-637-0322)
12. Environmental Corrections, Inc.-- Sun Valley, CA
13. TFI International-- Commerce City, CO
14. Air Sentry, Inc.-- Denver, CO (800-878-7897)
15. Interel Corp.-- Englewood, CO (303-773-0753 Ext.300)
16. Quality Plating Services, Inc.-- Bristol, CT (203-582-7518)
17. M & S Engineering & Mfg. Co., Inc.-- Broad Brook, CT
18. Entoleter, Inc.-- New Haven, CT (203-787-3575)
19. ABB/ASEA Brown Bovcri, Inc.-- Stamford, CT (800-626-4999)
20. Industrial Plastic Systems, Inc.-- Lakeland, FL (813-646-8551)
21. Andersen 2000, Inc.-- Peachtree City, GA (800-241-5424)
22. Savage Industries-- Tucker, GA
23. Amcrex, Inc.-- Woodstock, GA (404-928-0970)
24. Advanced Air Technology, Inc.-- Arlington Heights, IL (708-394-9553 Ext.23)
25. Bact Engineering Inc.-- Arlington Heights, IL
26. Flex-Kleen Corporation-- Chicago, IL (312-648-5300)
27. Bisco Enterprise-- Franklin Park, IL (708-671-4466)
28. Nokorrode, Inc.-- Mundelein, IL
29. Quad Environmental Technologies Corp.-- Northbrook, IL
30. ARI Technologies, Inc.-- Palatine, IL (708-359-7810)
31. Amquip Inc.-- Hammond, IN
32. Snodgrass, Brad, Inc.-- Indianapolis, IN
33. AAF/Snydergeneral Corp.-- Louisville, KY (502-637-0011)
34. Fisher-Klosterman, Inc.-- Louisville, KY (502-776-1505)
35. Vanaire-- Louisville, KY (502-491-3553)
36. Precision Industries Inc.-- Baton Rouge, LA
37. Environmental Elements Corp.-- Baltimore, MD
38. Danzer Metal Works Co., The-- Hagerstown, MD
39. Trema North America, Inc.-- Reisterstown, MD (800-833-2925)
40. Telpac Company, Ltd.-- Boston, MA (617-523-0948)
41. Koby Incorporated-- Marlboro, MA (508-481-8348)
42. Utilities Supply Co.-- Medford, MA (800-343-7555)
43. Jet Air Technologies, A Div. of B & U Corp.-- Adrian, MI (517-263-0113)
44. Clarkson Controls & Equipment Co.-- Detroit, MI (313-255-9110)
45. Uni-Wash, Incorporated-- Harbor Springs, MI (616-347-5005 Ext.20)
46. CMI-Schneible-- Holly, MI (313-634-8211)
47. Centri-Spray Corp.-- Livonia, MI
48. Haden Management Corp.-- Madison Heights, MI
49. Haden Schweitzer Corp.-- Madison Heights, MI
50. Monroe Environmental Corp.-- Monroe, MI (800-922-7707)
51. Monroe Welding & Engineering Co.-- Monroe, MI
52. Duall Div. Met-Pro Corporation-- Owosso, MI
53. Tri-Mer Corp.-- Owosso, MI (517-723-7838 Ext.77)
54. Viron International-- Owosso, MI (517-723-8255 Ext.224)
55. Beckert & Hiester Inc.-- Saginaw, MI (800-332-4031 Ext.12)
56. CIL Incineration Systems, Inc.-- Blaine, MN

57. Atlas Incinerators, Inc.-- Minneapolis, MN
58. Ancl Industries, Inc.-- Winona, MS
59. Monsanto Enviro-Chem Systems Inc.-- St. Louis, MO
60. Willow Springs Mfg., Ltd.-- Willow Springs, MO (417-469-2792)
61. Bio Plex Environmental Inc.-- Englewood Cliffs, NJ (800-947-0025)
62. Eastern Cyclone Industries, Inc.-- Fairfield, NJ
63. DR Technology, Inc.-- Freehold, NJ
64. Environmental Dynamics Corp.-- Kresson, NJ (609-768-1100)]
65. North American Pollution Control Systems, Inc.-- Linden, NJ (800-752-0237)
66. Advanced Industrial Technology Corp.-- Lodi, NJ
67. Ambient Engineering Inc.-- Matawan, NJ (908-566-6866)
68. Hydronics Engineering Corp.-- Midland Park, NJ
69. Bioclimatic, Inc.-- Moorestown, NJ (800-962-5594)
70. Mikropul Environmental Systems-- Morris Plains, NJ (201-606-5900)
71. Belco Technologies Corp.-- Parsippany, NJ
72. Sonic Environmental Systems-- Parsippany, NJ (201-882-9288)
73. York, Otto H., Co., Inc. (World Headquarters)-- Parsippany, NJ
74. Research-Cottrell Companies-- Somerville, NJ (908-685-4000)
75. Omni Coil, Inc.-- Southampton, NJ
76. Omni Fabricators Inc.-- Southampton, NJ (609-859-3900)
77. Aer-X-Dust Corp.-- Tennent, NJ
78. Airpol, Inc.-- Teterboro, NJ (201-288-7070)
79. Advanced Oxidation Systems, Inc.-- Wayne, NJ (201-628-0309)
80. Croll-Reynolds Co., Inc.-- Westfield, NJ (908-232-4200)
81. C O H Norcarb Inc.-- Brewster, NY
82. Ward Automation Inc.-- Buffalo, NY
83. Clean Gas Systems Inc.-- Farmingdale, NY (516-756-2474 Ext.91)
84. Ducon Environmental Sytems-- Farmingdale, NY (516-420-4900)
85. Heat Systems Inc.-- Farmingdale, NY (800-645-9846)
86. Emtrol Corp.-- Hauppauge, NY (516-582-9700)
87. Zelcron Industries Inc. c/o Ducon Environmental Systems Div.-- Melville, NY (800-394-4990)
88. Swemco, Inc.-- New York, NY (212-645-0440)
89. KCH Services, Inc. Dept. N-- Forest City, NC
90. Harrison Plastic Systems-- Aurora, OH
91. Ceilcote, Air Pollution Control Div. Master Builders Inc.--Brrca, OH (216-243-0700)
92. Air Plastics, Inc.-- Cincinnati, OH
93. Effox, Inc.-- Cincinnati, OH
94. Kleinfeldt, R.F., Co., Inc.-- Cincinnati, OH
95. Aquatech Inc.-- Cleveland, OH
96. Sly W.W., Mfg. Co.-- Cleveland, OH (216-238-2000)
97. Barnebey & Sutcliffe Corp.-- Columbus, OH (614-258-9501)
98. R. L. Industries, Inc.-- Fairfield, OH (800-846-2735)
99. Volk Environmental Technology-- Mansfield, OH
100. Volk, Mike, Co., Inc.-- Mansfield, OH
101. ACDC Inc.-- Milford, OH (513-248-1820)
102. Vorti-Siv Div. of M M Industries, Inc.-- Salem, OH
103. Apacs, Inc.-- Sylvania, OH
104. Ecolotreat Process Equipment Corp.-- Toledo, OH (419-729-5443)
105. U.S. Waste Control-- Ardmore, OK (800-546-2182)
106. Custom Fiberglass Mfg.-- Oklahoma City, OK
107. Tech-Mark Inc./Enviro-Pak Div.-- Clackamas, OR
108. Ketema Inc., Schutte & Koerting Div.-- Bensalem, PA

109. Ceco Filters, Inc.-- Conshohocken, PA (215-825-8585)
110. C & E Plastics-- Georgetown, PA
111. GE Company, GE Environmental Services, Inc.-- Lebanon, PA
112. Jones & Hunt, Inc.-- Orwigsburg, PA
113. Pennsylvania Engineering Corp., Engineering Construction Div.-- Pittsburgh, PA
114. Wheelabrator Air Pollution Control-- Pittsburgh, PA (800-394-0992)
115. Global Environmental Corp.-- Plumsteadville, PA (800-220-1533)
116. Plastic Ducting Systems, Inc.-- Pottstown, PA (800-457-0405)
117. E S T Corp.-- Quakertown, PA (215-538-7000)
118. Luftrol, Inc.-- Warminster, PA
119. Hansen Engineering, Inc.-- West Alexander, PA (412-484-7551)
120. Augusta Fiberglass, Inc.-- Blackville, SC (803-284-2246)
121. Spartan Tanks, Inc.-- Spartanburg, SC
122. ABB Environmental Systems (Industrial), Knoxville, TN
123. Chemco Engineering, Inc.-- Belton, TX (817-771-1966)
124. CJM Custom Steel Fabrication Environmental Tech.-- Denton, TX (800-548-2182)
125. Dyna-Therm Corp.-- Houston, TX (713-444-9759)
126. Winston Mfg. Corp.-- Longview, TX
127. Unisorb Corp.-- South Houston, TX (713-943-3753)
128. Centrifix Corp.-- Woodlands, TX (713-363-4868)
129. Tri Dim Filter Corp.-- Louisa, VA (703-967-2600)
130. GPI Corp.-- Schofield, WI (715-359-6123 Ext.25)
131. Vaportek, Inc.-- Sussex, WI

SCRUBBERS: FUME

1. Tigg Corp.-- Heber Springs, AR (800-925-0011)
2. Pardce Engineering-- Berkeley, CA (510-845-4516)
3. Jaeger Aerospace Engineering-- Costa Mesa, CA
4. Gold Shield-- Fontana, CA
5. ACME Fiberglass, Inc.-- Hayward, CA (510-538-3440)
6. Joy Technologies, Inc., Western Precipitation Div.--Monrovia, CA
7. Paramount Fabricators-- Rancho Cucamonga, CA
8. Calvert Environmental-- San Diego, CA (619-272-0050)
9. Environmental Corrections, Inc.-- Sun Valley, CA
10. TFI International-- Commerce City, CO
11. Interel Corp.-- Englewood, CO (303-773-0753 Ext.300)
12. M & S Engineering & Mfg. Co., Inc.-- Broad Brook, CT
13. Entoleter, Inc.-- New Haven, CT (203-787-3575)
14. Spatz Fiberglass Products, Inc.-- New Castle, DE
15. Industrial Plastic Systems, Inc.-- Lakeland, FL (813-646-8551)
16. Daniel & Jones Sheet Metal, Inc.-- Tampa, FL
17. Advanced Air Technology, Inc.-- Arlington Heights, IL (708-394-9553 Ext.23)
18. Brule, C.E. & E., Inc.-- Blue Island, IL (708-388-7900)
19. Cyclone Blow Pipe Co.-- Chicago, IL
20. Fiberbasin, Inc.-- Chicago, IL (312-622-4343)
21. Flex-Kleen Corporation-- Chicago, IL (312-648-5300)
22. Nokorode, Inc.-- Mundelein, IL
23. ARI Technologies, Inc.-- Palatine, IL (708-359-7810)
24. Snodgrass, Brad, Inc.-- Indianapolis, IN
25. AAF/Snydergeneral Corp.-- Louisville, KY (502-637-0011)
26. Vanair-- Louisville, KY (502-491-3553)
27. Precision Industries Inc.-- Baton Rouge, LA

28. Environmental Elements Corp.-- Baltimore, MD
29. Danzer Metal Works Co., The-- Hagerstown, MD
30. Trema North America, Inc.-- Reisterstown, MD (800-833-2925)
31. Telpac Company, Ltd.-- Boston, MA (617-523-0948)
32. IPF Inc.-- Canton, MA
33. Euro-Matic Ltd. c/o Leomass Ltd.-- Leominster, MA (508-537-8274)
34. Walbert Plastics, Inc.-- Lowell, MA
35. Utilities Supply Co.-- Medford, MA (800-343-7555)
36. Koch Process Systems, Inc.-- Westborough, MA
37. Jet Air Technologies, A Div. of B & U Corp.-- Adrian, MI (517-263-0113)
38. Clarkson Controls & Equipment Co.-- Detroit, MI (313-255-9110)
39. Savard Corporation-- Detroit, MI (313-931-6880)
40. Haden Schweitzer Corp.-- Madison Heights, MI
41. Monroe Environmental Corp.-- Monroe, MI (800-922-7707)
42. Duall Div. Met-Pro Corporation-- Owosso, MI
43. Tri-Mer Corp.-- Owosso, MI (517-723-7838 Ext.77)
44. Viron International-- Owosso, MI (517-723-8255 Ext.224)
45. Beckert & Hiester Inc.-- Saginaw, MI (800-332-4031 Ext.12)
46. Air Engineering Co.-- Warren, MI (800-594-5110)
47. CIL Incineration Systems, Inc.-- Blaine, MN
48. Atlas Incinerators, Inc.-- Minneapolis, MN
49. Anel Industries, Inc.-- Winona, MS
50. Labconco Corp.-- Kansas City, MO
51. Monsanto Enviro-Chem Systems Inc.-- St. Louis, MO
52. Plastic Engineered Products, Inc.-- Branchburg, NJ (908-534-6111)
53. Environmental Dynamics Corp.-- Kresson, NJ (609-768-1100)
54. North American Pollution Control Systems, Inc.-- Linden, NJ (800-752-0237)
55. Advanced Industrial Technology Corp.-- Lodi, NJ
56. Ambient Engineering Inc.-- Matawan, NJ (908-566-6866)
57. Hydronics Engineering Corp.-- Midland Park, NJ
60. FRP Corp.-- Millburn, NJ
61. Bioclimatic, Inc.-- Moorestown, NJ (800-962-5594)
62. Mikropul Environmental Systems-- Morris Plains, NJ (201-606-5900)
63. Belco Technologies Corp.-- Parsippany, NJ
64. Sonic Environmental Systems-- Parsippany, NJ (201-882-9288)
65. York, Otto H., Co., Inc. (World Headquarters)-- Parsippany, NJ (800-524-1543)
66. Hollow Shapes, Inc.-- Pompton Plains, NJ
67. Omni Coil, Inc.-- Southampton, NJ
68. Omni Fabricators Inc.-- Southampton, NJ (609-859-3900)
69. Acr-X-Dust Corp.-- Tennent, NJ
70. Airpol, Inc.-- Teterboro, NJ (201-288-7070)
71. Plastinetics Inc.-- Towaco, NJ (800-627-7473)
72. Advanced Oxidation Systems, Inc.-- Wayne, NJ (201-628-0309)
73. Croll-Reynolds Co., Inc.-- Westfield, NJ (908-232-4200)
74. C O H Norcarb Inc.-- Brewster, NY
75. Beltran Associates, Inc.-- Brooklyn, NY (718-338-3311)
76. Cortech Plastics Inc.-- Buffalo, NY
77. Brucar Process Systems, Inc.-- Deer Park, NY
78. Primary Plastics Inc.-- Endwell, NY
79. Clean Gas Systems Inc.-- Farmingdale, NY (516-756-2474 Ext.91)
80. Ducon Environmental Sytems-- Farmingdale, NY (516-420-4900)
81. Heat Systems Inc.-- Farmingdale, NY (800-645-9846)

82. Emtrol Corp.-- Hauppauge, NY (516-582-9700)
83. Leroy Plastics, Inc.-- Leroy, NY (716-768-8159)
84. Descon International Inc.-- Lindenhurst, NY (516-226-7766)
85. Zelcron Industries Inc. c/o Ducon Environmental Systems Div.-- Melville, NY (800-394-4990)
86. M.K. Plastics Corp.-- Mooers, NY (518-236-7949)
87. Bayfield Enterprises Inc.-- New York, NY (212-684-3589)
88. Swemco, Inc.-- New York, NY (212-645-0440)
89. Burgess-Manning, Inc., Sub. of Nitram Energy, Inc.--Orchard-Park, NY
90. PKG Equipment Inc.-- Rochester, NY (716-436-4650)
91. KCH Services, Inc. Dept. N-- Forest City, NC
92. Filtajet Dust Control Dept. T-- Salisbury, NC
93. Kar-Del Plastics, Inc.-- Ashland, OH
94. Harrison Plastic Systems-- Aurora, OH
95. Magnum Plastics, Inc.-- Aurora, OH (216-562-9200)
96. Ceilcote, Air Pollution Control Div. Master Builders Inc.--Berea, OH (216-243-0700)
97. United States Manufacturers Resource of Pro-Fab Mfg. Inc.--Bedford, OH (216-232-3584)
98. Interstate Plastics Div. of Westerman, Inc.-- Bremen, OH
99. Protectoplas Co.-- Burton, OH
100. Air Plastics, Inc.-- Cincinnati, OH
101. Effox, Inc.-- Cincinnati, OH
102. Kleinfeldt, R.F., Co., Inc.-- Cincinnati, OH
103. Sly W.W., Mfg. Co.-- Cleveland, OH (216-238-2000)
104. R. L. Industries, Inc.-- Fairfield, OH (800-846-2735)
105. Harrison Machine & Plastics Corp.-- Hiram, OH
106. United States Plastic Corp.-- Lima, OH (419-228-2242)
107. Volk Environmental Technology-- Mansfield, OH
108. Vanguard Plastics-- Mantua, OH
109. ACDC Inc.-- Milford, OH (513-248-1820)
110. Process Environmental Systems, Inc.-- North Ridgeville, OH
111. Vorti-Siv Div. of M M Industries, Inc.-- Salem, OH
112. Ecolotreat Process Equipment Corp.-- Toledo, OH (419-729-5443)
113. Neundorfer Inc.-- Willoughby, OH
114. Ketema Inc., Schutte & Koerting Div.-- Bensalem, PA
115. Ceco Filters, Inc.-- Conshohocken, PA (215-825-8585)
116. C & E Plastics-- Georgetown, PA
117. Met-Pro Corp. Systems Division-- Harleysville, PA
118. Goodhart Sons, Inc.-- Lancaster, PA (717-656-2404)
119. GE Company, GE Environmental Services, Inc.-- Lebanon, PA
120. Keystone Metal & Machine Co., Inc.-- Millersville, PA (717-464-2204)
121. Beco Engineering Co.-- Oakmont, PA
122. Jones & Hunt, Inc.-- Orwigsburg, PA
123. Pennsylvania Engineering Corp., Engineering Construction Div.-- Pittsburgh, PA
124. Wheelabrator Air Pollution Control-- Pittsburgh, PA (800-394-0992)
125. Global Environmental Corp.-- Plumsteadville, PA (800-220-1533)
126. Plastic Ducting Systems, Inc.-- Pottstown, PA (800-457-0405)
127. Luftrol, Inc.-- Warminster, PA
127. Hansen Engineering, Inc.-- West Alexander, PA (412-484-7551)
129. Ambi, Inc.-- Lincoln, RI
130. Plasfab, Inc.-- Warwick, RI
131. Augusta Fiberglass, Inc.-- Blackville, SC (803-284-2246)
132. Spartan Tanks, Inc.-- Spartanburg, SC
133. Chemco Engineering, Inc.-- Belton, TX (817-771-1966)567

134. CJM Custom Steel Fabrication Environmental Tech.-- Denton, TX (800-548-2182)
135. Corr Tech, Inc.-- Houston, TX (800-752-7054)
136. Dyna-Therm Corp.-- Houston, TX (713-444-9759)
137. Emissions Technology, Inc.-- Houston, TX (713-448-0135)
138. I.C.P. Industries, Inc.-- Houston, TX (713-641-6401)
139. Process Specialties, Inc.-- Houston, TX (713-448-7177)
140. Unisorb Corp.-- South Houston, TX (713-943-3753)
141. Centrifix Corp.-- Woodlands, TX (713-363-4868)
142. Tri Dim Filter Corp.-- Louisa, VA (703-967-2600)
143. Precisionceering Ltd.-- Scarborough, ON Canada
144. AC Plastiques Canada, Inc.-- Les Cedres, PQ Canada

SCRUBBERS: GAS

1. Zurn Industries Inc., Air Systems Div. Air Quality Control Products-Clarage Fans-- Birmingham, AL (205-853-4112)
2. Tigg Corp.-- Heber Springs, AR (800-925-0011)
3. Jaeger Aerospace Engineering-- Costa Mesa, CA
4. ACME Fibergalss, Inc.-- Hayward, CA (510-538-3440)
5. Cryogenic Industries Inc.-- Irvine, CA (714-261-1219)
6. Campbell, J.A., Company-- Long Beach, CA (310-424-0455)
7. Virotrol, Inc.-- Loomis, CA
8. Joy Technologies, Inc., Western Precipitation Div.--Monrovia, CA
9. Cryoquip Inc.-- Murrieta, CA
10. Delatech Inc.-- Napa, CA
11. Calvert Environmental-- San Diego, CA (619-272-0050)
12. Aqua Craft, Inc.-- San Francisco, CA (415-637-0322)
13. Stearns Catalytic World Corp.-- Denver, CO
14. Entoleter, Inc.-- New Haven, CT (203-787-3575)
15. ABB/ASEA Brown Boveri, Inc.-- Stamford, CT (800-626-4999)
16. Industrial Gas Systems-- Palm Coast, FL (904-445-4200)
17. Wittemann-Hasselberg, Division of Wittemann Company, Inc., The-- Palm Coast, FL (904-445-4200)
18. Warren Engineering-- Atlanta, GA (404-843-8333)
19. Tampella Power Corp. Dept HG-- Marietta, GA (800-394-8871)
20. Thyssen Rheinstahl Technik Co. Dept. TRTCO-- Marietta, GA
21. Andersen 2000, Inc.-- Peachtree City, GA (800-241-5424)
22. Amerex, Inc.-- Woodstock, GA (404-928-0970)
23. Buchbinder-- Alsip, IL
24. Advanced Air Technology, Inc.-- Arlington Heights, IL (708-394-9553 Ext.23)
25. Fiberbasin, Inc.-- Chicago, IL (312-622-4343)
26. Flex-Kleen Corporation-- Chicago, IL (312-648-5300)
27. Amquip Inc.-- Hammond, IN
28. AAF/Snydergeneral Corp.-- Louisville, KY (502-637-0011)
29. Fisher-Klosterman, Inc.-- Louisville, KY (502-776-1505)
30. Vanaire-- Louisville, KY (502-491-3553)
31. Precision Industries Inc.-- Baton Rouge, LA
32. Danzer Metal Works Co., The-- Hagerstown, MD
33. Telpac Company, Ltd.-- Boston, MA (617-523-0948)
34. Koch Process Systems, Inc.-- Westborough, MA
35. Monroe Environmental Corp.-- Monroe, MI (800-922-7707)
36. Duall Div. Met-Pro Corporation-- Owosso, MI
37. Tri-Mer Corp.-- Owosso, MI (517-723-7838 Ext.77)
38. Ancl Industries, Inc.-- Winona, MS

39. Monsanto Enviro-Chem Systems Inc.-- St. Louis, MO
40. Willow Springs Mfg., Ltd.-- Willow Springs, MO (417-469-2792)
41. Sigri Corporation-- Bedminster, NJ (908-231-3100)
42. Spectra Gases, Inc.-- Irvington, NJ (800-932-0624)
43. North American Pollution Control Systems, Inc.-- Linden, NJ (800-752-0237)
44. Advanced Industrial Technology Corp.-- Lodi, NJ (201-265-1414)
45. S & S Industrial Corp.-- Marlton, NJ
46. Ambient Engineering Inc.-- Matawan, NJ (908-566-6866)
47. Hydronics Engineering Corp.-- Midland Park, NJ
48. Bioclimatic, Inc.-- Moorestown, NJ (800-962-5594)
49. Mikropul Environmental Systems-- Morris Plains, NJ (201-606-5900)
50. Sonic Environmental Systems-- Parsippany, NJ (201-882-9288)
51. York, Otto H., Co., Inc. (World Headquarters)-- Parsippany, NJ
52. Research-Cottrell Companies-- Somerville, NJ (908-685-4000)
53. Omni Coil, Inc.-- Southampton, NJ
54. Omni Fabricators Inc.-- Southampton, NJ (609-859-3900)
55. Acr-X-Dust Corp.-- Tennent, NJ
56. Airpol, Inc.-- Teterboro, NJ (201-288-7070)
57. Advanced Oxidation Systems, Inc.-- Wayne, NJ (201-628-0309)
58. Croll-Reynolds Co., Inc.-- Westfield, NJ (908-232-4200)
59. Perkins, P.W., Co., Inc.-- Woodstown, NJ (609-769-3525)
60. C O H Norcarb Inc.-- Brewster, NY
61. Beltran Associates, Inc.-- Brooklyn, NY (718-338-3311)
62. Arrow Tank Co., Inc.-- Buffalo, NY
63. Cortech Plastics Inc.-- Buffalo, NY
64. Metal Cladding, Inc.-- Buffalo, NY
65. Clean Gas Systems Inc.-- Farmingdale, NY (516-756-2474 Ext.91)
66. Ducon Environmental Systems-- Farmingdale, NY (516-420-4900)
67. Heat Systems Inc.-- Farmingdale, NY (800-645-9846)
68. Emtrol Corp.-- Hauppauge, NY (516-582-9700)
69. Rosenwach Tank Co., Inc.-- Long Island City, NY
70. Zelcron Industries Inc. c/o Ducon Environmental Systems Div.-- Melville, NY (800-394-4990)
71. Pyro Industries Inc.-- Mincola, NY
72. Swemco, Inc.-- New York, NY (212-645-0440)
73. Burgess-Manning, Inc., Sub. of Ntram Energy, Inc.-- Orchard Park, NY
74. Chemipulp/Jenssen Div.-- Watertown, NY
75. KCH Services, Inc. Dept. N-- Forest City, NC
76. Harrison Plastic Systems-- Aurora, OH
77. Babcock & Wilcox, Power Generation Group, Customer Parts & Service Dept. TR-- Barberton, OH (800-354-4400)
78. Air Plastics, Inc.-- Cincinnati, OH
79. Effox, Inc.-- Cincinnati, OH
80. Sly W.W., Mfg. Co.-- Cleveland, OH (216-238-2000)
81. Volk Environmental Technology-- Mansfield, OH
82. ACDC Inc.-- Milford, OH (513-248-1820)
83. Vorti-Siv Div. of M M Industries, Inc.-- Salem, OH
84. Nutter Engineering Div., Patterson-Kelly-- Tulsa, OK
85. Filter Fab Mfg. Corp.-- Aliquippa, PA (412-375-6927)
86. Ketema Inc., Schutte & Koerting Div.-- Bensalem, PA
87. Kinney, S.P., Engineers, Inc.-- Carnegie, PA (412-276-4600)
88. Ceco Filters, Inc.-- Conshohocken, PA (215-825-8585)
89. GE Company, GE Environmental Services, Inc.-- Lebanon, PA

90. Matheson Instruments-- Montgomeryville, PA (800-732-0340)
91. Jones & Hunt, Inc.-- Orwigsburg, PA
92. Hall-Woolford Tank Co., Inc.-- Philadelphia, PA
93. Pennsylvania Engineering Corp., Engineering Construction Div.-- Pittsburgh, PA
94. Wheelabrator Air Pollution Control-- Pittsburgh, PA (800-394-0992)
95. Global Environmental Corp.-- Plumsteadville, PA (800-220-1533)
96. E S T Corp.-- Quakertown, PA (215-538-7000)
97. Luftrol, Inc.-- Warminster, PA
98. ACS Industries, Inc.-- Woonsocket, RI (800-343-2257)
99. Spartan Tanks, Inc.-- Spartanburg, SC
100. ABB Environmental Systems (Industrial), Knoxville, TN
101. Peerless Mfg. Co.-- Dallas, TX
102. BS & S Engineering Co., Inc.-- Houston, TX
103. Dyna-Therm Corp.-- Houston, TX (713-444-9759)
104. Emissions Technology, Inc.-- Houston, TX (713-448-0135)
105. Keco Research & Development, Inc.-- Houston, TX
106. Process Specialties, Inc.-- Houston, TX (713-448-7177)
107. Smith Industries, Inc.-- Houston, TX
108. King Tool Co.-- Longview, TX
109. PPC Industries-- Longview, TX
110. Winston Mfg. Corp.-- Longview, TX
111. Unisorb Corp.-- South Houston, TX (713-943-3753)
112. Centrifix Corp.-- Woodlands, TX (713-363-4868)
113. Tri Dim Filter Corp.-- Louisa, VA (703-967-2600)
114. GPI Corp.-- Schofield, WI (715-359-6123 Ext.25)
115. Wells-Hall Fabrication & Construction, Ltd.-- Edmonton, AB Canada

ADSORBERS

1. Tigg Corp.-- Heber Springs, AR (800-925-0011)
2. Active-Carb-- Canoga Park, CA (800-424-2049)
3. Adsorbents & Desiccants Corp. of America-- Los Angeles, CA (800-228-4124)
4. Anderson Industrial Products, Inc.-- East Berlin, CT (203-828-9262)
5. Solvay Performance Chemicals Inc.-- Greenwich, CT (203-629-7900)
6. Pneumatic Products Corp.-- Ocala, FL (904-237-1220 Ext. 320)
7. Trema North America, Inc.-- Reisterstown, MD (800-833-2925)
8. Magic Sorb.-- Danvers, MA
9. Remedial Systems Inc.-- Foxboro, MA (800-394-5622)
10. Koby Incorporated-- Marlboro, MA (508-481-8348)
11. Sphinx Adsorbents, Inc.-- Springfield, MA (413-736-5020)
12. D-Mark, Inc.-- Mount Clemens, MI (800-343-3610)
13. Southeastern Fibers, Inc.-- St. Paul, MN (800-833-2472)
14. Adsorption Systems, Inc.-- Millburn, NJ (201-762-6304)
15. Allied-Signal, Inc.-- Morristown, NJ (210-455-2000)
16. Glenro, Inc.-- Paterson, NJ (800-922-0106)
17. Chromex Corp, Interflo Div.-- Brooklyn, NY (800-468-3735)
18. Mystic Display Co., Inc.-- Brooklyn, NY (800-334-7954)
19. Airtek-- Buffalo, NY (716-692-6111)
20. Multiform Dessicants, Inc.-- Buffalo, NY (716-883-8900)
21. Clean Gas Systems Inc.-- Farmingdale, NY (516-756-2474 Ext. 91)
22. Ducon Environmental Systems-- Farmingdale, NY (516-420-4900)
23. Zelcron Industries Inc. c/o Ducon Environmental Div.--Melville, NY (800-394-4990)
24. Flanders Filters Inc.-- Washington, NC (919-945-8081)

25. Andersons Industrial Products Div.-- Maumee, OH (419-893-5050)
26. General Air Div. Zurn Industries, Inc.-- Erie, PA (814-453-3651)
27. Met-Pro Corp., Systems Division-- Harleysville, PA
28. Calgon Carbon Corp.-- Pittsburgh, PA (800-422-7266)
29. Parker Systems, Inc.-- Norfolk, VA (800-666-0006)
30. North Valley Industries Inc.-- Omak, WA
31. Drummond Welding & Steel Works Ltd.-- PQ Longueuil, Canada

ADSORBERS: ACTIVATED CARBON

1. Tigg Corp.-- Heber Springs, AR (800-925-0011)
2. Magic Sorb-- Danvers, MA
3. Prekins, P.W., Co., Inc.-- Woodstown, NJ (609-769-3525)

COMBUSTION

FLARES: WASTE GAS

1. Hirt Combustion Engineers-- Montebello, CA (213-728-9164)
2. Sur-Lite Corp.-- Santa Fe Springs, CA (310-693-0796)
3. Camden Architectural Metals, Inc.-- Glassboro, NJ
4. Pilgrim Steel Co.-- Glassboro, NJ
5. Almetek Industries, Inc.-- Hackettstown, NJ
6. Flaregas Corp.-- Spring Valley, NY
7. LFG Specialties Inc.-- Cleveland, OH (216-891-0305)
8. It-McGill Pollution Control Systems, Inc.-- Tulsa, Ok (916-748-0700)
9. Zecco, Inc.-- Tulsa, OK (918-258-8551)
10. Zink, Inc.-- Tulsa, OK
11. Chesmont Engineering Co., Inc.-- Eagle, PA (215-458-8057)
12. NAO, Inc.-- Philadelphia, PA (800-523-3495)
13. Flare Industries Inc.-- Austin, TX
14. Allied Flare, Inc.-- Houston, TX (713-332-1000)
15. Kaldair Inc., Div. of BP America-- Houston, TX (800-526-3247)
16. Stackmatch Flare Ignition, Inc.-- Plano, TX (800-623-9260)

INCINERATOR SYSTEMS

1. BDP Thermal Systems Inc.-- San Carlos, CA (800-222-5575)
2. Consertherm Systems, Inc., Enercon Systems, Inc.-- South Windsor, CA (203-289-9330)
3. Andersen 2000, Inc.-- Peachtree City, GA (800-241-5424)
4. CIL Incineration Systems, Inc.-- Blaine, MN (612-784-6052)
5. Thermal Process Construction Co., Inc.-- Dover, NJ (201-361-5900)
6. Joy Energy Systems, Inc., A Joy Technologies Co.--Charlotte, NC (704-587-8000)
7. Enercon Systems Inc.-- Elyria, OH (216-323-7080)
8. It-McGill Pollution Control Systems Inc.-- Tulsa, OK (918-748-0700)
9. Zecco, Inc.-- Tulsa, OK (918-258-8551)
10. T-Thermal-- Conshohocken, PA (215-828-5400)
11. Seco/Warwick Corp.-- Meadville, PA (814-724-1400)
12. Vulcan Iron Works, Inc.-- Wilkes-Barre, PA (717-822-2161)
13. National Incinerator, Inc.-- Corsicana, TX (903-872-4651)
14. Noell, Inc.-- Herndon, VA (703-793-6500)

INCINERATORS

1. Consolidated Engineering Co.-- Kennesaw, GA (800-486-6836)
2. Brule, C.E. & E., Inc.-- Blue Island, IL (708-388-7900)
3. Detrick, M.H. Co.-- Mokena, IL (800-835-3751)
4. Thermal Process Construction Co., Inc.-- Dover, NJ (201-361-5900)
5. JWP Air Technologies-- Mountainside, NJ (908-789-2700)
6. Sonic Environmental Systems-- Parsippany, NJ (201-882-9288)
7. Stelter & Brinck, Inc.-- Harrison, OH (800-568-9703)
8. T-Thermal-- Conshohocken, PA (215-828-5400)
9. NAO, Inc.-- Philadelphia, PA (800-523-3495)
10. International Waste Energy Systems, A Div. of ICF Kaiser Engineers-- Pittsburgh, PA (412-281-5222)
11. Process Combustion Corp.-- Pittsburgh, PA (412-655-0955)
12. Finch Mfg. Co.-- West Pittston, PA (717-655-2277)
13. Pennram Products Division-- Williamsport, PA (717-368-1033)
14. AKI Systems, Inc.-- Tomball, TX (713-351-7945)
15. Epcon Industrial Systems, Inc.-- Woodlands, TX (800-447-7872)
16. International Waste Industries-- Vienna, VA (703-556-4100)
17. Cleaver Brooks Div. of Aqua-Chem Inc.-- Milwaukee, WI (414-962-0100)

INCINERATORS: CATALYTIC

1. Etter Engineering Co., Inc.-- Cheshire, CT
2. CVM Corp.-- Wilmington, DE (302-654-7070)
3. Catalytic Products International-- Lake Zurich, IL (708-438-0334)
4. Dedert Corp.-- Olympia Fields, IL (708-747-7000)
5. ARI Technologies, Inc.-- Palatine, IL (708-359-7810)
6. Gancia-Cote & Co.-- Detroit, MI
7. Moco Thermal Industries-- Romulus, MI (313-728-6800)
8. Glenro, Inc.-- Paterson, NJ (800-922-0106)
9. Corbett Industries, Inc.-- Waldwick, NJ (201-445-6311)
10. CSM Environmental Systems, Inc.-- Brooklyn, NY (718-522-7000)
11. Camet Co.-- Hiram, OH (216-569-3245)
12. Johnson Matthey, Environmental Products Div.-- Wayne, PA (215-341-8535)
13. AKI Systems, Inc., An Astrotech International Co.-- Tomball, TX (713-351-7945)
14. Catalytic Combustion Corp.-- Bloomer, WI (715-568-2882)
15. Thermo Electron Wisconsin, Inc.-- Kaukauna, WI (414-766-7200)
16. Anguil Environmental Systems, Inc.-- Milwaukee, WI
17. Patterson Industries (Canada) Ltd.-- On, Scarborough, Canada (800-336-1110 Ext. 1078)

INCINERATORS: FUME

1. Coen Co., Inc.-- Burlingame, CA
2. Smith Environmental Corp.-- Duarte, CA
3. H E M C Environmental Management-- Irvine, CA (714-727-1217)
4. Hirt Combustion Engineers-- Montebello, CA (213-728-9164)
5. Smith Engineering Co.-- Ontario, CA
6. Keith Co., Inc.-- Pico Rivera, CA
7. Bayco Div. of V.S.B.-- Sacramento, CA (916-924-8061)
8. "Burney" The Burner-- San Bernardino, CA
9. Alzeta Corp.-- Santa Clara, CA (408-727-8282)
10. Sur-Lite Corp.-- Santa Fe Springs, CA (310-693-0796)
11. In-Process Technology, Inc.-- Sunnyvale, CA (408-745-1066)
12. Marquardt Environmental Systems-- Van Nuys, CA
13. Interel Corp.-- Englewood, CO (303-733-0753 Ext.300)

14. M & S Engineering Mfg. Co., Inc.-- Broad Brook, CT
15. ABB/ASEA Brown Boveri, Inc.-- Stamford, CT (800-626-4999)
16. Peabody Engineering Corp.-- Stamford, CT
17. CVM Corp.-- Wilmington, DE (302-654-7070)
18. Simonds Mfg. Corp.-- Auburndale, FL
19. Industrial Equipment & Engineering Co.-- Orlando, FL
20. International Incinerators-- Columbus, GA
21. Consolidated Engineering Co.-- Kennesaw, GA (800-486-6836)
22. Brule, C.E. & E., Inc.-- Blue Island, IL (708-388-7900)
23. Eisenmann Corporation-- Crystal Lake, IL (815-456-4100)
24. Basic Environmental Engineering, Inc.-- Glen Ellyn, IL
25. Enders-Process Equipment Corp.-- Glen Ellyn, IL (708-469-3787)
26. Catalytic Products International-- Lake Zurich, IL (708-438-0334)
27. Dedert Corp.-- Olympia Fields, IL (708-747-7000)
28. ARI Technologies, Inc.-- Palatine, IL (708-359-7810)
29. Kelair Products Inc.-- Spring Grove, IL (815-675-2728)
30. Precision Quincy Corp.-- Woodstock, IL (815-338-2675)
31. Combustion Systems, Inc.-- Camby, IN
32. Koch, George, Sons, Inc.-- Evansville, IN (812-426-9600)
33. Precision Industries Inc.-- Baton Rouge, LA
34. F & E Stokers, Inc., Stokers Div.-- Baltimore, MD
35. Wolverine Corporation-- Merrimac, MA (508-346-4541)
36. Wickberg, B.G., Co., Inc.-- North Quincy, MA (617-328-9200)
37. Process Heating Corp.-- Shrewsbury, MA (508-842-5200)
38. Ferrara, N., Inc.-- Somersct, MA (508-679-2440)
39. Airtech Systems Corp.-- Stoughton, MA (617-344-0467)
40. Clarkson Controls & Equipment Co.-- Detroit, MI (313-255-9110)
41. Gancia-Cote & Co.-- Detroit, MI
42. Jensen Oven Co., Inc.-- Farmington, MI (800-783-OVEN)
43. Haden Management Corp.-- Madison Heights, MI
44. Hade-Schwiter Corp.-- Madison Heights, MI
45. Bigelow-Liptak Corp.-- Plymouth, MI
46. Durr Industries Inc.-- Plymouth, MI (313-459-6800)
47. Moco Thermal Industries-- Romulus, MI (313-728-6800)
48. Euthenergy Systems, Inc.-- Sanford, MI
49. Combustion Technologies, Inc.-- Troy, MI
50. CIL Incineration Systems Inc.-- Blaine, MN
51. North Atlantic Technologies, Inc.-- Bloomington, MN (612-888-8553)
52. Atlas Incinerators, Inc.-- Minncapolis, MN
53. Johnston Mfg. Co.-- Minncapolis, MN
54. North Country Welding-- Mora, MN (612-679-5142)
55. Finishing Technologies, Inc.-- Chesterfield, MO
56. BBC Industries, Inc.-- Fenton, MO
57. Thermal Process Construction Co., Inc.-- Dover, NJ (201-361-5900)
58. North American Pollution Control-- Linden, NJ (800-752-0237)
59. Van-Packer Co.-- Manahawkin, NJ (609-597-8080)
60. REECO (Regenerative Environmental Equipment Co., Inc.-- Morris Plains, NJ (201-538-8585)
61. JWP Air Technologies-- Mountainside, NJ (908-789-2700)
62. Somerset Technologies, Inc.-- New Brunswick, NJ
63. Glenro, Inc.-- Paterson, NJ (800-922-0106)
64. HED Industries, Inc.-- Ringoes, NJ
65. Pereny Equipment Div., HED Industries, Inc.-- Ringoes, NJ

66. Airpol, Inc.-- Teterboro, NJ (201-288-7070)
67. Corbett Industries, Inc.-- Waldwick, NJ (201-445-6311)
68. Ducon Environmental Systems--Farmingdale, NY (516-420-4900)
69. Zelcra Industries Inc. C/O Ducon Environmental Systems Div.--Melville, NY (800-394-4990)
70. Hones, Charles A., Inc.-- North Amityville, NY
71. Flaregas Corp.-- Spring Valley, NY
72. Classic Systems Inc. Dept T-- Statesville, NY
73. Feco Environmental, Div of Feco Engineered Systems, Inc.--Cleveland, OH (216-441-2400)
74. LFG Specialties Inc.-- Cleveland, OH (216-891-0305)
75. Enercon Systems Inc.-- Elyria, OH (216-323-7080)
76. Stelter & Brinck, Inc.-- Harrison, OH (800-568-9703)
77. Camet Co.-- Hiram, OH (216-569-3245)
78. Surface Combustion Inc.-- Maumee, OH (800-537-8980)
79. GLA Finishing Systems-- North Ridgeville, OH
80. It-McGill Pollution Control Systems, Inc.-- Tulsa, Ok (916-748-0700)
81. Thermoflux, Inc.-- Tulsa, OK
82. Zecco, Inc.-- Tulsa, OK (918-258-8551)
83. Zink, John, Co.-- Tulsa, OK
84. Klecnair Products Co., Inc.-- Clackamas, OR
85. Therm Tec Inc.-- Tualatin, OR
86. Advanced Valve Design-- Allentown, PA (800-394-5457)
87. Sela Fluid Processing Corp.-- Blue Bell, PA
88. T-Thermal-- Conshohocken, PA (215-828-5400)
89. Kennedy Van Saun Corp.-- Danville, PA
90. Chesmont Engineering Co., Inc.-- Eagle, PA (215-458-8057)
91. Crouse Group-- Linfield, PA
92. Thermal Transfer Corp.-- Monroeville, PA (412-351-3013)
93. NAO, Inc.-- Philadelphia, PA (800-523-3495)
94. Energy Conversion Technology Corp.-- Pittsburgh, PA (412-831-3501)
95. Process Combustion Corp.-- Pittsburgh, PA (412-655-0955)
96. Global Environmental Corp.-- Plumsteadville, PA (800-220-1533)
97. American International Co.-- Wayne, PA (215-964-9192)
98. Johnson Matthey, Environmental Products Div.-- Wayne, PA (215-341-8535)
99. Vulcan Iron Works, Inc.-- Wilkes-Barre, PA (717-822-2161)
100. Stahl Inc. Farrier Products Div.-- York, PA (717-854-0431)
101. Heatec Inc.-- Chattanooga, TN (615-821-5200)
102. Howell Engineering Corp.-- Houston, TX
103. Incinerator International Inc.-- Houston, TX
104. Omega Conversion Inc.-- Houston, TX
105. AKI Systems, Inc.-- Tomball, TX (713-351-7945)
106. Epcon Industrial Systems, Inc.-- Woodlands, TX (800-447-
107. Des Champs Laboratories Inc.-- Natural Bridge, VA (703-291- 1111)
108. Consumat Systems, Inc.-- Richmond, VA
109. International Waste Industries-- Vienna, VA (703-556-4100)
110. Lundberg, A.H. Associates, Inc.-- Bellevue, WA
111. Advanced Combustion System, Inc.-- Bellingham, WA
112. Catalytic Combustion Corp.-- Bloomer, WI (715-568-2882 Ext.22)
113. Thermo Electron Wisconsin, Inc.-- Kaukauna, WI (414-766-7200)
114. Anquil Environmental Systems-- Milwaukee, WI

INCINERATION: VOLATILE ORGANIC COMPOUNDS

1. Hirt Combustion Engineers-- Montebello, CA (213-728-9164)
2. Alzeta Corp.-- Santa Clara, CA (408-727-8282)
3. In-Process Technology, Inc.-- Sunnyvale, CA (408-745-1066)
4. Marquardt Environmental Systems-- Van Nuys, CA
5. Intercel Corp.-- Englewood, CO (303-733-0753 Ext.300)
6. ABB/ASEA Brown Boveri, Inc.-- Stamford, CT (800-626-4999)
7. CVM Corp.-- Wilmington, DE (302-654-7070)
8. Consolidated Engineering Co.-- Kennesaw, GA (800-486-6836)
9. Enders-Process Equipment Corp.-- Glen Ellyn, IL (708-469-3787)
10. Dedert Corp.-- Olympia Fields, IL (708-747-7000)
11. Wolverine Corporation-- Merrimac, MA (508-346-4541)
12. Wickberg, B.G., Co., Inc.-- North Quincy, MA (617-328-9200)
13. Ferrara, N., Inc.-- Somerset, MA (508-679-2440)
14. Airtech Systems Corp.-- Stoughton, MA (617-344-0467)
15. Jensen Oven Co., Inc.-- Farmington, MI (800-783-OVEN)
16. Thermal Process Construction Co., Inc.-- Dover, NJ (201-361-5900)
17. North American Pollution Control-- Linden, NJ (800-752-0237)
18. REECO (Regenerative Environmental Equipment Co., Inc.--Morris Plains, NJ (201-538-8585)
19. JWP Air Technologies-- Mountainside, NJ (908-789-2700)
20. Glenro, Inc.-- Paterson, NJ (800-922-0106)
21. Corbett Industries, Inc.-- Waldwick, NJ (201-445-6311)
22. Feco Environmental, Div of Feco Engineered Systems, Inc.--Cleveland, OH (216-441-2400)
23. Surface Combustion Inc.-- Maumee, OH (800-537-8980)
24. It-McGill Pollution Control Systems, Inc.-- Tulsa, OK (916-748-0700)
25. Kleenair Products Co., Inc.-- Clackamas, OR
26. Advanced Valve Design-- Allentown, PA (800-394-5457)
27. Selas Fluid Processing Corp.-- Blue Bell, PA
28. T-Thermal-- Conshohocken, PA (215-828-5400)
29. Chesmont Engineering Co., Inc.-- Eagle, PA (215-458-8057)
30. Seco/Warwick Corp.-- Meadville, PA (814-724-1400)
31. Briskel Industries, Inc.-- Philadelphia, PA
32. NAO, Inc.-- Philadelphia, PA (800-523-3495)
33. Global Environmental Corp.-- Plumsteadville, PA (800-220-1533)
34. Finch Mfg. Co.-- West Pittston, PA (717-655-2277)
35. Howell Engineering Corp.-- Houston, TX
36. AKI Systems, Inc.-- Tomball, TX (713-351-7945)
37. Advanced Combustion System, Inc.-- Bellingham, WA
38. Allis Mineral Sytems, Inc.-- Milwaukee, WI (414-475-3000)
39. Anquil Environmental Systems-- Milwaukee, WI

CONDENSERS: GAS

1. Johansing Iron Works-- Alameda, CA
2. Associated Vacuum Technology, Inc.-- Covina, CA
3. REPCO Engineering, Inc.-- Montebello, CA (310-725-3973)
4. Wiegmann & Rose, Sub. of Xchanger Mfg. Corp.-- Richmond, CA
5. Turbotec Products Inc., Div. of Thermodynetics-- Windsor, CA (800-394-1633)
6. Kennedy Tank & Mfg. Co., Inc.-- Indianapolis, IN
7. Holt Corp.-- Saugus, MA (617-233-8808)
8. Super Radiator Coils-- Minneapolis, MN (612-922-3330)
9. Heatcraft Inc.-- Grenada, MS
10. Atlantic Detroit Diesel Allison Inc.-- Lodi, NJ

11. Edwards Engineering Corp.-- Pompton Plains, NJ (800-526-5201)
12. M. P. Tube Works, Inc.-- Roselle, NJ (908-241-1500)
13. Omni Coil, Inc.-- Southampton, NJ (609-859-3955)
14. Omni Fabricators, Inc.-- Southampton, NJ (609-859-3900)
15. Croll-Reynolds Co., Inc.-- Westfield, NJ (908-232-4200)
16. Enerfin Inc.-- Albany, NY
17. Rubican Industries Corp.-- Brooklyn, NY
18. Bos-Hatten, Inc.-- Buffalo, NY (716-662-6540)
19. Doyle & Roth Mfg. Co., Inc.-- New York, NY (212-269-7840)
20. Gaston County Fabrication-- Stanley, NC (704-822-5000)
21. Ambassador Heat Transfer Co.-- Cincinnati, OH
22. Unifin International Div. of Keeprite Inc.-- Cincinnati, OH (519-451-0230)
23. Unifin International Div. of Keeprite Inc., U.S. Sales Headquarters-- Cincinnati, OH (800-336-1110 Ext. 1071)
24. Heat Exchange Applied Technology, A Div. of Voss Industries, Inc.-- Cleveland, OH (216-241-4328)
25. Ecodyne MRM, Inc.-- Massillon, OH
26. Waste Heat Technologies, Inc.-- Wadsworth, OH
27. Stokes Vacuum, Inc.-- Philadelphia, PA
28. Struthers Walls Corp.-- Warren, PA
29. Frick Co.-- Waynesboro, PA
30. F.E.S., Inc.-- York, PA
31. Refrigeration Valve & System Corp.-- Bryan, TX
32. Process Specialties, Inc.-- Houston, TX (713-448-7177)
33. Super Radiator Coils (Richmond Virginia Div.)-- Richmond, VA (804-794-2887)
34. Chil-Con Products Ltd.-- Brnatford, ON Canada
35. Enerfin Inc.-- Boucherville, PQ Canada (514-449-3430)

CONDENSERS: VAPOR

1. Johansing Iron Works-- Alameda, CA
2. Associated Vacuum Technology, Inc.-- Covina, CA
3. REPCO Engineering, Inc.-- Montebello, CA (310-725-3973)
4. Energy Research & Generation Inc.-- Oakland, CA
5. Wiegmann & Rose, Sub. of Xchanger Mfg. Corp.-- Richmond, CA
6. Turbotec Products Inc., Div. of Thermodynamics-- Windsor, CA (800-394-1633)
7. Bailey Refrigeration Co., Inc.-- North Miami, FL
8. Ahlstrom Machinery, Inc.-- Roswell, GA (404-640-2500)
9. Superior Welding Co.-- Decatur, IL
10. Penberthy Inc., A Sub. of Stanwhich Industries, Inc.-- Prophetstown, IL (815-537-2311)
11. Kennedy Tank & Mfg. Co., Inc.-- Indianapolis, IN
12. Lectrodryer Div., Ajax Magnethermic Corp.-- Richmond, KY (606-624-2091)
13. Bailey Refrigeration Co., Inc.-- New Orleans, LA
14. Schmidt-Bretten, Inc.-- Detroit, MI (313-863-0150)
15. Koolant Koolers, Inc.-- Kalamazoo, MI
16. Super Radiator Coils-- Minneapolis, MN (612-922-3330)
17. Heatcraft Inc.-- Grenada, MS
18. Metro Mfg., Inc.-- St. Louis, MO
19. Missouri Boiler & Tank Co.-- St. Louis, MO
20. Nooter Corporation-- St. Louis, MO (314-621-6000)
21. Stemmerich, Inc.-- St. Louis, MO (800-325-9528)
22. Bailey Refrigeration Co., Inc.-- Avenel, NJ
23. Atlas Industrial Mfg. Co.-- Clifton, NJ
24. Foster Wheeler Corp.-- Clinton, NJ
25. Jaygo Inc.-- Mahwah, NJ

26. Armstrong & Sons, Inc.-- Manasquan, NJ
27. Edwards Engineering Corp.-- Pompton Plains, NJ (800-526-5201)
28. Rosenblad Corporation-- Princeton, NJ
29. M. P. Tube Works, Inc.-- Roselle, NJ (908-241-1500)
30. Omni Coil, Inc.-- Southampton, NJ (609-859-3955)
31. Omni Fabricators, Inc.-- Southampton, NJ (609-859-3900)
32. RAS Process Equipment, Inc.-- Trenton, NJ (609-396-9566)
33. Allmark Equipment Co., Inc.-- Wayne, NJ
34. Croll-Reynolds Co., Inc.-- Westfield, NJ (908-232-4200)
35. Calyxes Corp.-- Albuquerque, NM
36. Graham Mfg. Co., Inc.-- Batavia, NY
37. Alstrom Corporation-- Bronx, NY
38. Yula Corporation-- Bronx, NY (212-991-0900)
39. Rubican Industries Corp.-- Brooklyn, NY
40. Bos-Hauten, Inc.-- Buffalo, NY (716-662-6540)
41. Niagra Blower Co.-- Buffalo, NY (800-426-5169)
42. REPCO Inc.-- Islip, NY (516-277-3323 Ext. 20)
43. Doyle & Roth Mfg. Co., Inc.-- New York, NY (212-269-7840)
44. FTS Systems, Inc.-- Stone Ridge, NY (914-687-0071)
45. Ambassador Heat Transfer Co.-- Cincinnati, OH
46. Central Fabricators, Inc.-- Cincinnati, OH
47. Ellis & Waus Company-- Cincinnati, OH (513-752-9000)
48. Heat Exchange Applied Technology, A Div. of Voss Industries, Inc.-- Cleveland, OH (216-241-4328)
49. Ecodyne MRM, Inc.-- Massillon, OH
50. Waste Heat Technologies, Inc.-- Wadsworth, OH
51. G.E.A. Rainey Corp.-- Catoosa, OK
52. Harris Thermal Transfer Products, Inc.-- Newberg, OR
53. Industrial Process Equipment Corp.-- Arnold, PA
54. Ketema Inc., Schutte & Koerting Div.-- Bensalem, PA
55. Joy Power Products, Inc.-- Easton, PA (215-250-1000)
56. Sentinel Process System, Inc.-- Hatboro, PA
57. Baeuerle & Morris, Inc.-- King of Prussia, PA
58. Stokes Vacuum, Inc.-- Philadelphia, PA
59. Resorcon, Inc., A Niagara Blower Co.-- Pittsburgh, PA (412-825-8400)
60. Harris Tube Pulling & Mfg. Inc.-- Ooltewah, TN (615-238-4814)
61. Krueger Engineering & Mfg. Co., Inc.-- Houston, TX
62. Process Specialties, Inc.-- Houston, TX (713-448-7177)
63. Straus Systems Inc.-- Houston, TX
64. Super Radiator Coils (Richmond Virginia Div.)-- Richmond, VA (804-794-2887)
65. Perfex Industrial Products-- Milwaukee, WI (414-546-2880)
66. Modine Mfg. Co., Standard Industrial Products-- Racine, WI

BAGHOUSES

1. Zum Industries Inc., Air Systems Div. Air Quality Control Products-Clarage Fans-- Birmingham, AL (205-853-4112)
2. Beco Corporation-- Benton, AR
3. Global Manufacturing Inc.-- Little Rock, AR (501-374-7416)
4. Pacific Engineering Systems Co.-- Anaheim, CA
5. Murphy-Rodgers, Inc.-- Huntington Park, CA
6. Food Engineering Service-- Irwindale, CA
7. Wire Technology Corp.-- Los Angeles, CA
8. PSP Industries-- Milpitas, CA

9. Joy Technologies, Inc., Western Precipitation Div.-- Monrovia, CA
10. Air Sentry, Inc.-- Denver, CO (800-878-7897)
11. Interel Corp.-- Englewood, CO (303-733-0753 Ext.300)
12. Warwick Mfg. & Equipment Co.-- Bridgeport, CT
13. GE Company-- Fairfield, CT (800-626-2004)
14. National Filter Media Corp.-- Hamden, CT
15. ABB/ASEA Brown Boveri, Inc.-- Stamford, CT (800-626-4999)
16. DuPont Filtration Systems-- Wilmington, DE (800-453-8527)
17. AFL Industries, Inc.-- Riviera Beach, FL (407-844-5200)
18. Advanced Metal & Welding Corp.-- Atlanta, GA
19. Transac, Inc.-- Macon, GA (800-841-4982)
20. Amerex, Inc.-- Woodstock, GA (404-928-0970)
21. Dustvent, Inc.-- Addison, IL
22. Flex-Kleen Corporation-- Chicago, IL (312-648-5300)
23. Great Lakes Filter, Filpaco Div.-- Chicago, IL (312-722-2200)
24. Meyer, Wm. W., & Sons, Inc.-- Skokie, IL (708-673-0312)
25. Turn Key Engineering Inc.-- Vincennes, IN (800-878-8534)
26. Deter Company, Inc.-- Burgin, KY (606-748-5262)
27. AAF/Snydergeneral Corp.-- Louisville, KY (502-637-0011)
28. Fisher-Klosterman, Inc.-- Louisville, KY (502-776-1505)
29. Dixie Air Engineering Co.-- Baltimore, MD
30. Dovco Industrial Fabrication, Inc.-- Baltimore, MD
31. Environmental Elements Corp.-- Baltimore, MD
32. Trema North America, Inc.-- Reisterstown, MD (800-833-2925)
33. Alpha Environmental Services, Inc.-- Boston, MA (617-787-0282)
34. Wickberg, B.G., Co., Inc.-- North Quincy, MA (617-328-9200)
35. Aget Mfg. Company-- Adrian, MI (800-832-2438 Ext. 99)
36. Great Lakes Filter, Div of Acme Mills Co.-- Detroit, MI (313-894-1950)
37. Forrest Brothers Inc.-- Gaylord, MI (517-732-8220)
38. Specified Design Corp.-- Grand Blanc, MI
39. Duall Div. Met-Pro Corporation--Owosso, MI
40. Beckert & Hiester Inc.-- Saginaw, MI (800-332-4031 Ext. 12)
41. Filco Filtration Systems, Inc.-- Eden Prairie, MN
42. Nol-Tec Systems, Inc.-- Forest Lake, MN
43. General Resource Corp.-- Hopkins, MN
44. Contamination Control Corp.-- Maple Plain, MN
45. Gerber Industries Inc.-- Minneapolis, MN
46. Torit/Day Div., Donaldson Co. Inc.-- Minneapolis, MN (800-365-1331 Ext. 204)
47. Monotech of Mississippi-- Iuka, MS
48. BHA Group, Inc.-- Kansas City, MO
49. Mac Equipment Inc.-- Kansas City, MO
50. Standard Havens Div.-- Kansas City, MO
51. Filtration Systems Products, Inc-- St. Louis, MO (314-721-2888)
52. Willow Springs Mfg., Ltd.-- Willow Springs, MO (417-469-2792)
53. Universal Filters, Inc.-- Asbury Park, NJ
54. Sternvent Co., Inc.-- Bogota, NJ
55. Joule Engineering Corp.-- Edison, NJ
56. Kleisser, G.A.-- Edison, NJ
57. Environmental Dynamics Corp.-- Kresson, NJ (609-768-1100)
58. Miller, Franklin, Delumper-Mixer Div.-- Livingston, NJ (800-932-0599)
59. Sterling Net Co., Inc.-- Montclair, NJ (800-342-0316)
60. National Filter Media Corp. Air Pollution Control Div.--Moorestown, NJ

61. Mikropul Environmental Systems-- Morris Plains, NJ (201-606-5900)
62. Air Kinetics, Inc.-- Morristown, NJ
63. Belco Technologies Corp.-- Parisippany, NJ
64. Sonic Environmental Systems-- Parisippany, NJ (201-882-9288)
65. Rescarch-Cottrell Companies-- Somerville, NJ (908-685-4000)
66. United Process Control, Inc.-- Somerville, NJ
67. CAP Technologies Inc.-- Stirling, NJ
68. Airpol, Inc.-- Teterboro, NJ (201-288-7070)
69. Deiden Industries Ltd.-- Brooklyn, NJ
70. Ducon Environmental Systems--Farmingdale, NY (516-420-4900)
71. Emtrol Corp.--Hauppauge, NY (516-582-9700)
72. Zelcron Industries Inc. C/O Ducon Environmental Systems--Melville, NY (800-394-4990)
73. Cros-Ible, Inc.-- Moravia, NY
74. Regenair Industries Inc.-- Rouses Point, NY (518-297-6966)
75. P & S Filtration Inc.-- Skaneateles Falls, NY
76. Griffin Environmental Co., Inc.-- Syracuse, NY (315-451-5300)
77. Dustex Corp.-- Charlotte, NC (704-588-2030)
78. Pneumafil Corp., Environmental Air Sytems Div.-- Charlotte, NC (704-399-7441)
79. Eakes Building Group Inc.-- Greensboro, NC
80. Eakes Metal Fabricators, Inc.-- Greensboro, NC (800-348-0884)
81. Filtajet Dust Control Dept. T-- Salisbury, NC
82. Staclean Diffuser Co. Dept. T-- Salisbury, NC (800-438-3850)
83. Classic Systems Inc. Dept. T-- Statesville, NC
84. Nordfab Products, Inc.-- Thomasville, NC
85. Northfab Systems, Inc.-- Thomasville, NC (919-889-5599)
86. Famco/Forsyth Inc.-- Winston Salem, NC (919-721-1500)
87. Diversified Specialty Enterprises, Inc.-- Canal Fulton, OH
88. Advanced Standard Products, Div. of Noral, Inc.-- Cleveland, OH (800-348-2345)
89. Sly W.W., Mfg. Co.-- Cleveland, OH (216-238-2000)
90. Barnebey & Sutcliffe Corp.-- Columbus, OH (614-258-9501)
91. Metals Trades, Inc.-- Columbus, OH
92. United McGill Corp.-- Columbus, OH (614-443-0192)
93. Volk Environmental Technology-- Mansfield, OH
94. E-Tech, Inc.-- Tulsa, OK (918-665-1930)
95. Aeropulse, Inc.-- Bensalem, PA (800-544-7393)
96. Fuller Company-- Bethlehem, PA (215-264-6222)
97. Johnson March System, Inc.-- Iryland, PA
98. GE Company, GE Environmental Services, Inc.-- Lebanon, PA
99. Joy Environmental Equipment Co., A Joy Technologies Co.--Malvern, PA (800-TALK-JOY)
100. Pennsylvania Engineering Corp., Engineering Construction Div.-Pittsburgh, PA
101. Vulcan Engineering Co.-- Pittsburgh, PA
102. Wheelabrator Air Pollution Control-- Pittsburgh, PA (800-394-0992)
103. Global Environmental Corp.-- Plumsteadville, PA (800-220-1533)
104. Palladino Metal Fabrication, Inc.-- Pottstown, PA (800-788- 8284)
105. Fabrication Specialists Co., Inc.-- Reading, PA
106. Free Flow, Inc.-- Blaine, TN
107. Esstee Mfg. Co., Inc.-- Cleveland, TN (615-472-6529)
108. Todd Mfg. Co., Inc.-- Cleveland, TN (615-476-5559)
109. ABB Environmental Systems-- Knoxville, TN
110. GMW, Inc.-- Memphis, TN (901-276-4593)
111. Hagan, Vince, Co., The-- Dallas, TX
112. Consolidated Fluidflo Inc.-- Houston, TX

113. PPC Industries-- Longview, TX
114. Monotech Corp.-- San Antonio, TX
115. Noell, Inc.-- Herndon, VA (703-793-6500)
116. Des Champs Laboratories, Inc.-- Natural Bridge, VA (703-291-1111)
117. Eastern Control Systems, Inc.-- Richmaond, VA
118. Midwesco Filter Resources Inc.-- Winchester, VA
119. Dan-Dee Equipment, Inc.-- Honey Creek, WI
120. Ruemelin Mfg. Co., Inc.-- Milwaukee, WI (414-962-6500)
121. Kreamer Tool & Mfg. Co. Ltd.-- ON, Brampton, Canada
122. Cantech Environmental Systems, Inc.-- ON, Mississauga, Canada

CYCLONES

1. Brown International Corp.-- Covina, CA
2. Lakos, Laval Corp.-- Fresno, CA (209-255-1601)
3. South Valley Mfg., Inc.-- Gilroy, CA
4. Krebs Engineers-- Menlo Park, CA (415-325-0751)
5. ITW Irathane Systems-- Colorado Springs, CO (800-397-5434)
6. Dorr-Oliver Incorporated-- Milford, CT (800-547-7809)
7. Linatex Corp. of America-- Stafford Springs, CT
8. Alanx Products L.P.-- Newark, DE (302-454-6900 Ext. 501)
9. Carpco, Inc.-- Jacksonville, FL (904-353-3681)
10. Advanced Metal & Welding Corp.-- Atlanta, GA
11. Roberts & Schaefer Co.-- Chicago, IL (312-236-7292)
12. Meyer, Wm. W., & Sons, Inc.-- Skokie, IL (708-673-0312)
13. Cerline Ceramic Corp.-- Anderson, IN (317-649-7222)
14. California Pellet Mill Co.-- Crawfordsville, IN (317-362-2600)
15. Thombert Inc.-- Newton, IA
16. Champion Div. of California Pellet Mill Co.-- Waterloo, IA
17. Premier Pneumatics, Inc.-- Salina, KA
18. Fisher-Klosterman, Inc.-- Louisville, KY (502-776-1505)
19. Dynadyne, Inc.-- Phoenix, MD
20. Trema North America, Inc.--Registerstown, MD (800-833-2925)
21. P.X. Engineering, Inc.-- Boston, MA (617-269-6200)
22. Polytech Filtration Systems, Inc.-- Sudbury, MA (508-443-4901)
23. Aget Mfg. Company-- Adrian, MI (800-832-2438 Ext. 99)
24. Forrest Brothers Inc.-- Gaylord, MI (517-732-8220)
25. Monlan Corp.-- Kalamazoo, MI (616-382-6348)
26. Beckert & Hiester Inc.-- Saginaw, MI (800-332-4031 Ext. 12)
27. ITW Irathane Systems Inc.-- Hibbing, MN (800-397-5434)
28. Gerber Industries Inc.-- Minneapolis, MN
29. Mac Equipment Inc.-- Kansas City, MO
30. Hydroflow Inc.-- Salem, NH (603-898-3388)
31. Rhone-Poulenc Tech-Sep-- Princeton, NJ (609-987-5046)
32. CAP Technologies Inc.-- Stirling, NJ
33. Clean Gas Systems Inc.--Farmingdale, NY (516-756-2474 Ext. 91)
34. Ducon Environmental Systems--Farmingdale, NY (516-420-4900)
35. Emtrol Corp.--Hauppauge, NY (516-582-9700)
36. Zelcron Industries Inc. C/O Ducon Environmental Systems--Melville, NY (800-394-4990)
37. Marstech-- New City, NY
38. Eakes Building Group Inc.-- Greensboro, NC
39. Eakes Metal Fabricators, Inc.-- Greensboro, NC (800-348-0884)
40. Wilbanks International, A Division of Coors Ceramics Co.--Hillsboro, OR

41. Unicast Inc.-- Easton, PA
42. Andritz Sprout-Bauer T-- Muncy, PA (717-546-8211)
43. Pleiger Plastics Company-- Washington, PA (800-394-5608)
44. Puhl, G.F., Co., Inc.-- Goodlettsville, TN
45. Bailey-Parks Urethane, Inc.-- Memphis, TN (800-238-7638)
46. Allied Industries-- Houston, TX (713-676-6000)
47. Flexibox Inc.-- Houston, TX
48. Quality Solids Separation Co.-- Houston, TX (800-962-0370)
49. PPC Industries-- Longview, TX
50. National Metals Industries-- Salt Lake City, UT
51. Spokane Metal Products-- Spokane, WA (800-541-3601)
52. Blower Application Co., Inc.-- Germantown, WI (414-255-5580)
53. Warman International, Inc.-- Madison, WI (608-221-2261)
54. Maritime Welding Ltd.-- NB, Bathurst, Canada

ELECTROSTATIC PRECIPITATORS

1. Beco Corporation-- Benton, AR
2. STI-- Hayward, CA
3. STI/Envirocees, Inc.-- Hayward, CA
4. Scientific Technologies Inc.-- Hayward, CA (510-471-9717)
5. Joy Technologies, Inc., Western Precipitation Div.-- Monrovia, CA
6. GE Company-- Fairfield, CT (800-626-2004)
7. Aercoogy, Inc.-- Old Saybrook, CT (203-399-7941)
8. Miles Pharmaccuticals-- West Haven, CT
9. McMillan Optical Company-- Murdock, FL (813-627-0100)
10. Car-Mon Products, Inc.-- Elgin, IL (708-695-9000)
11. AAF/Snydergeneral Corp.-- Louisville, KY (502-637-0011)
12. Baltimore Lead Burning-- Baltimore, MD (410-327-3900)
13. Dovco Industrial Fabrication, Inc.-- Baltimore, MD
14. Environmental Elements Corp.-- Baltimore, MD
15. Powrmatic Eltron Inc.-- Finksburg, MD
16. U.S. Automation Co.-- Detroit, MI
17. Specified Design Corp.-- Grand Blanc, MI
18. Shape Corp.-- Grand Haven, MI
19. D-Mark, Inc.-- Mount Clemens, MI (800-343-3610)
20. R.S.E. Inc.-- New Baltimore, MI (313-725-0192)
21. Air Quality Engineering, Inc.-- Minneapolis, MN (612-544-4426)
22. Sonatron Corp.-- Bellmawr, NJ
23. Air Clean Co.-- Elizabeth, NJ
24. North American Pollution Control Systems Inc.--Linden, NJ (800-752-0237)
25. Ambient Engineering, Inc.--Matawan, NJ
26. Bioclimatic, Inc.-- Moorestown, NJ (800-962-5594)
27. Mikropul Environmental Systems-- Morris Plains, NJ (201-606-5900)
28. Belco Technologies Corp.--Parispany, NJ
29. Sonic Environmental Systems-- Parsippany, NJ (201-882-9288)
30. Research-Cottrell Companies--Somerville, NJ (908-685-4000)
31. Airpol, Inc.-- Teterboro, NJ (201-288-7070)
32. Magnetic Specialties, Inc.-- Trenton, NJ
33. Croll-Reynolds Co. Inc.--Westfield, NJ (908-232-4200)
34. Beltran Associates, Inc.--Brooklyn, NY (718-338-3311)
35. Metal Cladding, Inc.-- Buffalo, NY
36. Zelcron Industries Inc. C/O Ducon Environmental Systems--Melville, NY (800-394-4990)

37. Babcock & Wilcox, Power Generation Group, Customer Parts & Service Dept.-- Barberton, OH (800-354-4400)
38. Ceilcote, Air Pollution Control Div. Master Builders Inc.--Berea, OH (216-243-0700)
39. Air Plastics, Inc.-- Cincinnati, OH
40. Effox, Inc.-- Cincinnati, OH
41. United Air Specialists, Inc.-- Cincinnati, OH (513-891-0400)
42. Superior Roll Forming Co., Inc.-- Cleveland, OH (216-524-5040)
43. United McGill Corp.-- Columbus, OH (614-443-0192)
44. ACDC Inc.-- Milford, OH (513-248-1820)
45. CMC Environmental-- Valley View, OH
46. Neundorfer Inc.-- Willoughby, OH
47. Spirex Corp.-- Youngstown, OH
48. Laubeck Corp.-- Carbondale, PA (717-282-4344)
49. Joy Environmental Equipment Co., A Joy Technologies Co.--Malvern, PA (800-TALK-JOY)
50. Universal Air Precipitator Corp.-- Monroeville, PA (800-326-8406)
51. Wheelabrator Air Pollution Control-- Pittsburgh, PA (800-394-0992)
52. Plymoth-- Willow Grove, PA
53. ABB Environmental Systems-- Knoxville, TN
54. Dresser Industries, Inc.-- Dallas, TX
55. CRS Enterprises, Inc.-- Fairfax Station, VA
56. Joy Mfg. Co., Canada, Ltd.-- ON, Kitchener, Canada

SRUBBERS: DUST

1. Beco Corporation-- Benton, AR
2. Advance Fiberglass, Inc.-- Little Rock, AR (800-342-7367)
3. Jaeger Aerospace Engineering-- Costa Mesa, CA
4. ACME Fiberglass, Inc.-- Hayward, CA (510-538-3440)
5. Air Chem Systems Inc.-- Huntington Beach, CA
6. Joy Environmental Equipment Co.-- Monrovia, CA
7. Joy Technologies, Inc., Western Precipitation Div.-- Monrovia, CA
8. Calvert Environmental-- San Diego, CA (619-272-0050)
9. Interel Corp.-- Englewood, CO (303-773-0753 Ext.300)
10. M & S Engineering & Mfg. Co., Inc.-- Broad Brook, CT
11. Entoleter, Inc.-- New Haven, CT (203-787-3575)
12. ABB/ASEA Brown Boveri, Inc.-- Stamford, CT (800-626-4999)
13. Air Purification System-- Tucker, GA (404-292-7195)
14. Savage Industries-- Tucker, GA
15. Hako Minutemen-- Addison, IL (708-627-6900)
16. Advanced Air Technology, Inc.-- Arlington Heights, IL (708-394-9553 Ext.23)
17. Flex-Kleen Corporation-- Chicago, IL (312-648-5300)
18. Nikro Industries Inc.-- Villa Park, IL (708-530-0558 Ext.255)
19. Snodgrass, Brad, Inc.-- Indianapolis, IN
20. AAF/Snydergeneral Corp.-- Louisville, KY (502-637-0011)
21. Fisher-Klosterman, Inc.-- Louisville, KY (502-776-1505)
22. Danzer Metal Works Co., The-- Hagerstown, MD
23. Trema North America, Inc.-- Reisterstown, MD (800-833-2925)
24. Bay Shore Steel Co.-- Bay Shore, MI (616-347-1160)
25. Haden Schweitzer Corp.-- Madison Heights, MI
26. Monroe Environmental Corp.-- Monroe, MI (800-922-7707)
27. Duall Div. Met-Pro Corporation-- Owosso, MI
28. Tri-Mer Corp.-- Owosso, MI (517-723-7838 Ext.77)

29. Beckert & Hiester Inc.-- Saginaw, MI (800-332-4031 Ext.12)
30. CIL Incineration Systems, Inc.-- Blaine, MN
31. Multi-Clean-- St. Paul, MN
32. Anel Industries, Inc.-- Winona, MS (601-283-1540)
33. Monsanto Enviro-Chem Systems Inc.-- St. Louis, MO (314-275-5700)
34. Environmental Dynamics Corp.-- Kresson, NJ (609-768-1100)]
35. North American Pollution Control Systems, Inc.-- Linden, NJ (800-752-0237)
36. Advanced Industrial Technology Corp.-- Lodi, NJ
37. Champion Trading Corp.-- Marlboro, NJ
38. S & S Industrial Corp.-- Marltonm, NJ
39. Ambient Engineering, Inc.-- Matawan, NJ
40. Atlantic Plastics & Fiberglass Co.-- Middletown, NJ
41. Hydronics Engineering Corp.-- Midland Park, NJ
42. Bioclimatic, Inc.-- Moorestown, NJ (800-962-5594)
43. Mikropul Environmental Systems-- Morris Plains, NJ (201-606-5900)
44. Belco Technologies Corp.-- Parsippany, NJ
45. York, Otto H., Co., Inc. (World Headquarters)-- Parsippany, NJ
46. Aer-X-Dust Corp.-- Tennent, NJ
47. Airpol, Inc.-- Teterboro, NJ (201-288-7070)
48. Advanced Oxidation Systems, Inc.-- Wayne, NJ (201-628-0309)
49. Croll-Reynolds Co., Inc.-- Westfield, NJ (908-232-4200)
50. Clean Gas Systems Inc.-- Farmingdale, NY (516-756-2474 Ext.91)
51. Ducon Environmental Sytems-- Farmingdale, NY (516-420-4900)
52. Emtrol Corp.-- Hauppauge, NY (516-582-9700)
53. Zelcron Industries Inc. c/o Ducon Environmental Systems Div.-- Melville, NY (800-394-4990)
54. Swemco, Inc.-- New York, NY (212-645-0440)
55. KCH Services, Inc. Dept. N-- Forest City, NC
56. Filtajet Dust Control Dept. T-- Salisbury, NC
57. Kar-Del Plastics, Inc.-- Ashland, OH
58. Magnum Plastics, Inc.-- Aurora, OH (216-562-9200)
59. Air Plastics, Inc.-- Cincinnati, OH
60. Effox, Inc.-- Cincinnati, OH
61. Kleinfeldt, R.F., Co., Inc.-- Cincinnati, OH
62. Sly W.W., Mfg. Co.-- Cleveland, OH (216-238-2000)
63. Volk Environmental Technology-- Mansfield, OH
64. ACDC Inc.-- Milford, OH (513-248-1820)
65. Ecotreat Process Equipment Corp.-- Toledo, OH (419-729-5443)
66. Aeropulse, Inc.-- Bensalem, PA (800-544-7393)
67. Ketema Inc., Schutte & Koerting Div.-- Bensalem, PA
68. Jones & Hunt, Inc.-- Orwigsburg, PA
69. Pennsylvania Engineering Corp., Engineering Construction Div.-- Pittsburgh, PA
70. E S T Corp.-- Quakertown, PA (215-538-7000)
71. Luftrol, Inc.-- Warminster, PA
72. Dyna-Therm Corp.-- Houston, TX (713-444-9759)
73. Winston Mfg. Corp.-- Longview, TX
74. Tri Dim Filter Corp.-- Louisa, VA (703-967-2600)

SCRUBBERS: VENTURI

1. Joy Technologies, Inc., Western Precipitation Div.--Monrovia, CA
2. Calvert Environmental-- San Diego, CA (619-272-0050)
3. Interel Corp.-- Englewood, CO (303-773-0753 Ext.300)
4. M & S Engineering & Mfg. Co., Inc.-- Broad Brook, CT

5. Andersen 2000, Inc.-- Peachtree City, GA (800-241-5424)
6. Amerex, Inc.-- Woodstock, GA (404-928-0970)
7. Advanced Air Technology, Inc.-- Arlington Heights, IL (708-394-9553 Ext.23)
8. Koch Engineering Co., Inc.-- Wichita, KS
9. Precision Industries Inc.-- Baton Rouge, LA
10. Danzer Metal Works Co., The-- Hagerstown, MD
11. Trema North America, Inc.-- Reisterstown, MD (800-833-2925)
12. Koch Process Systems, Inc.-- Westborough, MA
13. Monroe Environmental Corp.-- Monroe, MI (800-922-7707)
14. Anel Industries, Inc.-- Winona, MS
15. Fox Valve Development Corp.-- Dover, NJ (201-328-1011)
16. DR Technology, Inc.-- Freehold, NJ
17. North American Pollution Control Systems, Inc.-- Linden, NJ (800-752-0237)
18. Advanced Industrial Technology Corp.-- Lodi, NJ
19. Ambient Engineering Inc.-- Matawan, NJ (908-566-6866)
20. Hydronics Engineering Corp.-- Midland Park, NJ
21. Belco Technologies Corp.-- Parsippany, NJ
22. Airpol, Inc.-- Teterboro, NJ (201-288-7070)
23. Advanced Oxidation Systems, Inc.-- Wayne, NJ (201-628-0309)
24. Croll-Reynolds Co., Inc.-- Westfield, NJ (908-232-4200)
25. Ward Automation Inc.-- Buffalo, NY (716-856-6966)
26. Clean Gas Systems Inc.-- Farmingdale, NY (516-756-2474 Ext.91)
27. Ducon Environmental Sytems-- Farmingdale, NY (516-420-4900)
28. Heat Systems Inc.-- Farmingdale, NY (800-645-9846)
29. Emtrol Corp.-- Hauppauge, NY (516-582-9700)
30. Zelcron Industries Inc. c/o Ducon Environmental Systems Div.-- Melville, NY (800-394-4990)
31. Swemco, Inc.-- New York, NY (212-645-0440)
32. Air Plastics, Inc.-- Cincinnati, OH
33. Effox, Inc.-- Cincinnati, OH
34. ACDC Inc.-- Milford, OH (513-248-1820)
35. Ketema Inc., Schutte & Koerting Div.-- Bensalem, PA
36. Jones & Hunt, Inc.-- Orwigsburg, PA
37. Global Environmental Corp.-- Plumsteadville, PA (800-220-1533)
38. E S T Corp.-- Quakertown, PA (215-538-7000)
39. Luftrol, Inc.-- Warminster, PA
40. Hansen Engineering, Inc.-- West Alexander, PA (412-484-7551)
41. Augusta Fiberglass, Inc.-- Blackville, SC (803-284-2246)
42. Chemco Engineering, Inc.-- Belton, TX (817-771-1966)
43. Dyna-Therm Corp.-- Houston, TX (713-444-9759)
44. GPI Corp.-- Schofield, WI (715-359-6123 Ext.25)

SCRUBBERS: WET

1. Zurn Industries Inc., Air Systems Div. Air Quality Control Products-Clarage Fans-- Birmingham, AL (205-853-4112)
2. Saracco Mfg. Corp.-- Larkspur, CA
3. Joy Environmental Equipment Co.-- Monrovia, CA
4. Joy Technologies, Inc., Western Precipitation Div.-- Monrovia, CA
5. Entolater, Inc.-- New Haven, CT (203-787-3575)
6. Flex-Kleen Corporation-- Chicago, IL (312-648-5300)
7. ARI Technologies, Inc.-- Palatine, IL (708-359-7810)
8. Fisher-Klosterman, Inc.-- Louisville, KY (502-776-1505)
9. Trema North America, Inc.-- Reisterstown, MD (800-833-2925)

10. Beckert & Hiester Inc.-- Saginaw, MI (800-332-4031 Ext.12)
11. Atlas Incinerators, Inc.-- Minneapolis, MN
12. Ceilcote, Air Pollution Control Div. Master Builders Inc.--Berea, OH (216-243-0700)
13. Ketema Inc., Schutte & Koerting Div.-- Bensalem, PA
14. DuPont De Nemours, E. L., & Co., Detachad Operations--Kennett Square, PA

Task 5

**ELASTIC WAVE LITHOTRIPSY FOR REMOVAL OF CERAMIC
FROM INVESTMENT CASTINGS**

A.E. Carden, C.R. Evces and C.W. Warren

ELECTROHYDRAULIC REMOVAL OF CERAMIC SHELL AND CORES FROM INVESTMENT CASTINGS

1.0 Introduction

The removal of silicate-bonded cores and shells used in investment casting is often difficult, because the properties of shells and cores which make them attractive as casting cores (strength and resistance to reaction with casting alloys) also make them resistant to removal from the casting. Today shells are removed mechanically, often by subjecting the casting cluster to severe mechanical vibration, and cores are removed chemically, in caustic baths which dissolve the silicate bond. It would be desirable to have a method of core removal which uses less energy, and which does not require the use of potentially hazardous chemicals.

One promising process is the use of electrohydraulic shock waves to remove shells and cores. These waves, which are generated in a fluid such as water by the instantaneous discharge of an electric current (similar to the action of a large spark plug), have sufficient energy to fracture ceramic materials. They have a further advantage in that they act on the entire casting at once, reaching parts of the core which may be difficult to remove by conventional means.

Although electrohydraulic energy has been known to be capable of breaking up ceramics for some time, there has been little work done to determine the feasibility of using it commercially to remove ceramic material from investment castings. The purpose of this investigation, therefore, was to determine the commercial feasibility of using electrohydraulic energy for this purpose. The work was carried out by a team of investigators from The University of Alabama and Texas Tech University.

2.0 Technical Background

2.1 Literature Review

The use of electrohydraulic force to break up refractories has been known for some time. The forces generated by the discharge of an electric spark can be as high as 500,000 psi at the electrodes; this energy dissipates as the pressure wave spreads out when it travels away from the spark. Electrohydraulic shock waves have been used for metal forming,¹ waterwell stimulation,² rock crushing,³ and in a continuously operating mine.⁴ The best known present use of electrohydraulic lithotripsy ("stone breaking") is the shattering of kidney stones in the human body as an alternative to surgery.^{5,6,7,8}

In 1974, the British Cast Iron Research Association reported loosening CO₂ core sand in the internal passages of heavily cored castings⁹ using shock waves. In the same report, BCIRA revealed that electrohydraulic spark cleaning units capable of cleaning castings as large as 15 tons were in use in the USSR.

In 1983 a Hungarian steel foundry reported its experience with electrohydraulic sand removal.¹⁰ The Institute of the Ukrainian Academy of Sciences developed the process which led to the first Soviet installation of an electrohydraulic sand removal facility in 1963. By 1983 there were reported to be over 400 installations in the Soviet Union alone. These facilities used a spark-gap electrode discharging in water to create a pressure wave which impacted the casting and the core. The core was removed by both the direct impact

of the pressure wave on the core prints, and by the pressure transmitted through the casting walls, which made use of the natural vibration characteristics of the casting to transmit tensile and shear forces to the core.

Once the core was broken up, water jets were used to clear the passages of core material. Since the entire core removal process was carried out under water, there was no air pollution, and no dust in the work environment. Specific application of the technology depended on the mechanical properties of the core material and the geometry of the casting. Although the Hungarian foundry was primarily casting steel, they had also carried out experiments on aluminum and iron castings which showed success. Another installation was at Metalguss und Formenbau in Wernigerode, Germany.¹¹ This plant, located in the former East Germany, produced low pressure aluminum die castings.

A process called "Cerabite" is currently being marketed by Alb. Klein GmbH & Co. KG.¹² This process uses focused waves in a recirculating water cycle for cleaning investment and other castings. Shell and core material have been successfully removed from superalloy, steel and aluminum investment castings, and resin-bonded cores from aluminum automotive engine castings. One unit has been installed in a commercial foundry in Germany. The Cerabite development laboratory was inspected as a part of our investigation (see below).

In 1987, Dornier, a manufacturer of medical lithotripters, was successful in removing ceramic shell material from investment castings, and was able to fracture the core, using a clinical lithotripter with focused waves and increased power.¹³ Dornier, however, abandoned the development of this technology as it was not a part of its long-range business plan.

There have been other attempts to use mechanical energy to remove cores involving ultrasonic vibration. In the Soviet Union, initial attempts were made to use ultrasonic vibration alone to remove cores from turbine blades.¹⁴ This evolved into a system where the ultrasonic waves were generated and propagated through the hot caustic in which the castings were immersed, to combine mechanical and chemical core removal techniques. This was similar to a method developed earlier in the United States to remove cores from nickel-base eutectic turbine blades, which also combined ultrasonic vibration with chemical removal methods.¹⁵ Although the development on that project was considered to be successful, the process never reached production because eutectic alloys were rejected as turbine blade materials.

2.2 Pressure Wave Generation Methods

There are a variety of methods which can be used to produce the pressure wave for ceramic removal. The selection of which to use depends on the energy level required and the degree to which the pressure wave must be focused.

Piezoelectric Crystals

A piezoelectric crystal has the property that it will expand or contract when a voltage is placed across the crystal. When a spherical dish is lined with piezoelectric crystals and all of the crystals are simultaneously triggered, an elastic wave is generated which converges toward the center of the sphere with increasing pressure, as shown in Figure 1. The maximum velocity of the movement of one face of the crystal relative to its opposite face is the speed of sound in the crystal. Piezoelectric crystals are usually employed when pulses are relatively small, but their timing must be carefully controlled.

Figure 1. Piezoelectric Shock Wave Generator

Electromagnetic Wave Generator

An alternative to the use of piezoelectric crystals on a spherical dish is the electromagnetic shock wave generator, which uses a strong current passed through an electric coil to cause a metal plate to be rapidly displaced. This motion results in a planar pressure wave when the current is large enough. The planar wave can be passed through an acoustic lens that converts the planar wave into a spherically converging wave, as shown in Figure 2.

Figure 2. Electromagnetic shock wave generator with acoustic lens.

Electrohydraulic Pressure Generators

One of the more common techniques for high pressure wave generation is the electrohydraulic, or spark gap, method. In this technique, electrical energy is stored in a large capacitor bank, and discharged between two electrodes submerged in a fluid, usually water. When the spark is created in the water, the high current causes the water to heat, expand, and vaporize. This explosive vaporization results in the formation of a shock wave that moves away from the source at speeds higher than the speed of sound in the fluid. The resulting pressure wave has a very high rise time at the leading edge of the pulse.

The wave spreads out as it leaves the source. It can also be focused. If an ellipsoidal reflector is used to focus the wave, all paths that touch the boundary of the ellipsoid

during traverse from one focal point to the second have a constant length. Constant-velocity spherically diverging waves generated at the electrode will consequently reflect from the surface of the ellipsoid and simultaneously converge at the target focal point, as shown in Figure 3.

Figure 3. Electrohydraulic shock wave generator.

Other methods have also been used, such as a three Joule capacity Q-switched laser¹⁶ to vaporize water, or the use of a laser to detonate a lead azide pellet submerged in the water.¹⁷

Wave Characteristics of Power Sources

The characteristic parameters of interest in lithotripters are the peak pressures obtained, the focal area of the peak pressure, and the rise-time of the shock front. The first two can be controlled by system design, but the third, the rise time and shape of the pulse, depend on the power generation source used. The wave shape differs for the various types of power source used. The piezoelectric and the electromagnetic types of power sources exhibit a type of vibratory motion resulting from the mechanical oscillation of the generator. The spark gap generator also produces negative pressures when the vapor bubble collapses. The different wave shapes are shown in Figure 4.

Figure 4. Pressure wave forms.

A problem which was discovered during the development of medical lithotripters is the presence of gases in the water bath. Much of the energy of the shock wave is converted to heat (absorbed by the gas), resulting in diminished energy reaching the focal point.

Dissolved gases also appear to play a role in current flashing from the electrode to a ground connection (see below). To remedy this situation, the water bath is degassed prior to the patient's treatment. This is a time-consuming procedure, and the water is easily contaminated with further use. In the application of shock waves to ceramics removal, trapped gasses and suspended solids are expected to be present in the bath, decreasing the efficiency of the process.

The durability of each of the possible methods of producing shock waves is also an important consideration for industrial application. Both the piezoelectric and electromagnetic methods are limited by mechanical breakdown of essential components. Failure due to fatigue and inertial loading may be expected to necessitate frequent repairs to the unit. The use of explosive pellets is not practical because of the high repetition rates required. Laser generation at the industrial power levels is not presently feasible. For this reason, all further work on the project has concentrated on the use of spark gap systems to generate the pressure wave.

3.0 Technical Investigation

The technical investigation was divided into two parts. In the first, the mechanical characteristics of ceramic core materials used in investment casting were evaluated. In the second, experiments were carried out on castings using electrohydraulic methods of generating the pressure wave.

3.1 Mechanical Property Study of Ceramic Core Materials

In using lithotripsy for shell and core removal, it is necessary to know the strength of the materials used in shells and cores. The intensity of the pressure waves transmitted to the part from the shock wave in the water depends on the acoustic impedances of the water, shell, metal, and the core itself. The possibility of fracture occurring in the core depends on the stress state generated by the pulse and the strength of the ceramic. It was therefore necessary to investigate the range of acoustic impedances and strengths for a variety of materials likely to be encountered in investment casting. Experiments were designed to measure the acoustic impedance and wave speed, the dynamic compressive strength, and the dynamic tensile strength of candidate ceramics used in investment casting.

Drop Bar Test

To observe the fracture phenomena of ceramic under impact, the simple drop bar test shown in Figure 5 was used. A steel tube filled with ceramic core material was connected to the incident bar and the transmitter bar at each end; threaded sleeves joined the pieces. The core body was shorter than the tube so that free surfaces existed, and the spaces at both ends were initially equal, as shown in (a). A striker bar was released vertically from a height of 18 feet, and impacted the transmitter bar with an impact velocity of approximately 400 in/sec.

After the first strike, no fracture of the core was observed but after five strikes, both the upper and the lower ends of the core body had shifted, and the distance between the two ends had increased. The increase of the ceramic core length indicated that fracture must have occurred in the interior, as shown in Figure 6 (b). The experiment was designed to produce compression-tension-compression-tension etc. wave reflection in the center of the tube-ceramic core specimen.

Figure 5. Arrangement of the drop bar test. (a) Fracture observation (b) Tube wave signal (c) wave speed measurement

Figure 6. Tube samples before the first strike (a) and after five strikes (b).

To determine the dynamic response of the tube, a drop tower was used to provide an incident elastic wave velocity of approximately 200 in/sec. Semiconductor strain gages were mounted on the incident bar, the transmitter bar and the tube, as shown in Figure 5(b). The signal was recorded by a digital signal oscilloscope and then transferred to a personal computer for digital signal analysis. Comparison of the strain output of the tubes with and without the ceramic core showed little difference. This indicates that the stress field in the tube (at least on the surface) is little changed when a ceramic is cast into a

hollow tube. This was expected since the mass ratio and the elastic modulus ratio of the steel tube to the ceramic core body are approximately 4 and 10, respectively.

Wave Speed and Compressive Strength Measurement

Figure 7 shows a typical digital signal oscilloscope output (voltage vs. time) from a set of strain gages mounted on the transmitter bar, when a ceramic sample was impacted by a strike bar with an impact velocity of 125 in/sec, as shown in Figure 5 (c). Point 1 is the time when the wave reached the gage position, and Point 2 is the time when the reflected wave from the ceramic-steel interface

Figure 7. Digital signal oscilloscope output for wave speed measurement.

reaches the gage and causes an increase in the compressive stress. The stress increase can also be seen in the Time-Space diagram shown in Figure 8, where the right side of the figure represents the theoretical Strain-Time diagram. The time difference between the two Points 1 and 2 provides the time period in which the wave travels through the sample twice (forward and backward). The wave speed is therefore

$$c = (2L)/\Delta T.$$

Based on the wave speed, the modulus of elasticity and the acoustic impedance can be calculated from the relationships

$$E = c^2 \rho$$

and

$$I_m = c \rho$$

respectively.

Figure 8. Space-Time diagram for ceramic impact test.

The compressive strength is the stress at which fracture occurs under compression. From the digital signal oscilloscope output, the time when the strain reaches the peak value (Point 3 in Figure 7) indicates when the sample starts to crack. From the voltage output at this point, the compressive strength is calculated as:

$$s = E_b A_b V_o / S_g A_s V_i$$

Where E_b and A_b are the modulus of elasticity and the cross section area of the steel bar, V_i and V_o are the Wheatstone bridge power supply and digital signal oscilloscope output, respectively, S_g is the gage factor, and A_s is the cross section area of the sample. Once the compressive strength is calculated, the strain energy for the uniaxial stress case (tension or compression) can be calculated as

$$s_f^2 / 2E.$$

The strain energy density is not expected to be independent of the stress state, but the uniaxial strain energy density at fracture does serve as an index for ranking materials. Most of the samples tested failed by shear cracks at the impact end. Fourteen ceramics were tested; results are presented in Table 1.

Dimensional Effect on Wave Speed Measurement

It was observed that the wave speed measured varied with length for samples of the same materials and cross sectional area. Short samples (1" long) have relatively lower wave speed than long samples (6" long). The variance of the wave speed for short samples is larger than for long sample, and the wave speed appears to approach a horizontal asymptote for long rods. This apparent "end effect" on wave speed likely indicates that the wave has not yet fully developed, and there may also be a "side effect" on the wave speed measurement when different diameter samples are tested. The variation in wave

speed with sample length is shown for a typical material supplied by one of the program sponsors in Figure 9.

Table 1. Properties of Cores Tested

Sample Number and Material Source	Density x 10^3 (kg/m ³)	c (m/s)	E (GPa)	Impedance (MPa./s)	Compressive Fracture Strength (MPa)	Calculated Tensile Fracture Strength (MPa)
1 cast	2.23	917	1.87	2.04	15.17	7.58
2 cast	2.27	1415	4.54	3.21	17.24	6.62
3 cast	2.27	1260	3.61	2.86	30.34	15.17
4 cast	1.79	1036	1.93	1.86	13.10	6.55
5 cast	2.57	930	2.22	2.39	15.17	7.58
6 sponsor	1.19	1994	4.72	2.37	8.96	4.48
7 sponsor	1.14	2537	7.37	2.90	23.44	11.72
8 sponsor	1.80	617	0.69	1.11	6.90	3.45
9 sponsor	1.92	2136	8.75	4.10	42.75	21.37
10 sponsor	2.04	1920	7.53	3.92	34.48	17.24
11 sponsor	1.82	1928	6.78	3.52	62.74	31.37
12 sponsor	2.02	2215	9.92	4.48	59.30	29.65
13 sponsor	1.83	1656	5.02	3.03	46.89	23.44
14 sponsor	1.85	2116	8.27	3.91	95.15	47.58

Figure 9. Wave Speed Variation with Sample Length for a Typical Ceramic Core Sample.

Ballistic Test for Tensile Fracture Strength

The measurement of dynamic tensile strength of the core is more complicated. A long steel bar, resting on soft supports, had a ceramic core material cylinder cemented to it on one end. A high intensity short pulse was excited in the bar by firing a small projectile into the opposite end of the bar. The pulse width was about 22 $\mu\text{sec.}$, and the intensity could be as large as 100,000 psi. Strain gages measured the passage of the incident wave. When the wave impinged on the interface of the steel ceramic, some of the energy was transmitted and some was reflected. The difference between the incident and the transmitted wave was the amount of energy imparted to the ceramic. The wave in the ceramic reflected from the free end and produced a tensile stress in the ceramic. If the wave was sufficiently strong, the ceramic fractured and the fractured piece was given a velocity in the direction of the wave propagation. Sometimes multiple fractures occurred. If it is assumed that the total energy consumed by the ceramic is associated with a linear stress-strain function, the energy in producing the fracture can be calculated from linear theory. The leftover energy (that above what is required for fracture) gives the spalled piece kinetic energy. With high speed photography, the velocity of the spalled piece (or pieces) was measured and the dynamic tensile fracture strength was obtained. These fractures were essentially uniaxial tensile stress states. The fracture of core material in a casting is almost never by simple uniaxial tension. Furthermore, the cores have almost no free surfaces. Consequently, it would be almost impossible to produce multiple fractures of a core by one shock wave. However, core material was noticed to degrade when exposed to repeated shocks.

Figure 10 shows the plane wave mathematical model used to calculate power requirements needed to fracture the ceramic cores. This model was also used to size the

Figure 10. Mathematical Model of Stress Wave Propagation in Plane Wave Theory

power requirements for the experimental core removal unit designed and used in the project. A pressure pulse of width T and period t travels through a medium with acoustic impedance of Z_1 , creating an incident stress wave of intensity σ_i on the specimen. A stress wave of intensity of σ_T is transmitted to the fracture specimen, (which has an acoustic impedance Z_2) and a wave intensity of σ_R is reflected back through the transmitting medium. When the transmitted wave reaches the right hand surface of the specimen, the

incident, transmitted and reflected phenomena repeat. Assuming the incident stress is equal to the shock pressure, the equations in the figure can be used to estimate the pressure and acoustic intensity required to create a desired stress in the specimen. The calculated mechanical properties are given in Table 2 for the specimens reported on in Table 1.

The significance of these calculations is that all of the strength values are well below the tensile and compressive strengths of the metal being cast, which means that electrohydraulic core removal should neither fracture nor distort the castings. However, the stresses calculated may be high enough to cause recrystallization in single crystal superalloy castings.

Table 2. Pressure Required to Fracture Core Materials

Sample	Pressures Required to Fail the Ceramic at Each Interface and the Failure Mode, MPa									
	Either		Water-Ceramic-Metal			Water-Ceramic-Water				
	@ 1-2 Initial		@ 2-3		@ 1-2 Rebound	@ 2-3		@ 1-2 Rebound		
1	13.07	c	14.54	c	45.32	t	40.75	t	508.12	c
2	12.59	c	14.88	c	20.13	t	17.03	t	92.20	c
3.	23.00	c	26.69	c	41.83	t	36.04	t	225.88	c
4	11.76	c	12.95	c	56.92	t	51.68	t	908.40	c
5	12.28	c	13.90	c	29.54	t	26.09	t	221.72	c
6	7.28	c	8.24	c	17.84	t	15.77	t	136.63	c
7	17.69	c	20.57	c	31.60	t	27.17	t	166.94	c
8	8.02	c	8.5	c	60.47	c	57.07	c	405.91	c
9	29.08	c	36.01	c	38.32	t	30.95	t	131.74	c
10	23.73	c	29.12	c	32.15	t	26.20	t	115.75	c
11	44.56	c	53.52	c	65.55	t	54.57	t	267.38	c
12	39.43	c	49.82	c	49.44	t	39.14	t	155.38	c
13	34.86	c	40.83	c	59.19	t	50.54	t	293.11	c
14	65.56	c	80.38	c	89.06	t	72.64	t	321.92	c

Power requirements to remove cores were calculated and gave the results shown in Table 3. These results were used to select power supplies for the experimental portion of the program.

Table 3. Power Requirements to Remove Cores

Sample	Maximum Power Required (kW/cm ²)	Minimum Power Required (kW/cm ²)
1	5,822.64	3.85
2	191.70	3.57
3	1,150.62	11.93
4	18,609.97	3.12
5	1,108.66	3.40
6	421.03	1.20
7	628.52	7.05
8	3,715.81	1.45
9	391.41	19.08
10	302.16	12.70
11	1,612.26	44.77
12	544.49	34.55
13	1,937.54	27.41
14	2,337.21	96.94

3.2 Visit to Alb. Klein Co. GmbH KG

Prior to beginning experimental work, a visit was made to Alb. Klein Co. & Co. GmbH KG, located in Niederfischbach, Germany, to see a demonstration of their "Cerabite" process.¹² This process was developed to remove sand and ceramic cores, using electrohydraulic energy.

The installation at the Klein development facility in Halver, Germany consisted of a vertical water tank into which the casting cluster was immersed. The pressure wave was produced by discharging a 12 kJ spark between two electrodes in an auxiliary chamber attached to the main chamber. A reflector behind the spark gap focused the pressure wave on the casting cluster, which could be manipulated during the core removal cycle to present castings at a better angle to the pressure wave. The spark could be programmed to repeat up to 100 times at an interval of just over 1.5 seconds between shocks.

During the demonstration two aluminum cylinder heads with sand cores were de-cored in less than 30 shocks. An investment cast steel pump impeller was cleaned after exposure to 30 shocks. An alloy steel investment casting cluster was also treated to remove the ceramic shell. Although most of the shell was removed after 40 shocks, some still remained in interior areas of the castings on the cluster. Four single crystal test castings containing a serpentine core were provided for test by one of the sponsoring foundries and were exposed to a series of shocks, up to 500. A sketch of the casting is shown in Figure 11.

Figure 11. Superalloy single crystal test casting used in tests at Alb. Klein Co.

It was not possible to remove this core, even after 500 shocks, although at that number of shocks, 70% of the core had been removed. Subsequent analysis by the foundry revealed that the casting recrystallized during the core removal experiments, indicating that this technology is not suitable for use with single crystal castings.

The inability to remove cores with long thin geometries such as that used in the experiment described above, indicated that the process is limited in its application, and is not expected to be suitable for use with the long, thin cores typical of airfoil castings. It is clearly more useful when applied to heavier cores, with aspect ratios closer to one, and to the removal of ceramic shell material. Indeed, the demonstration of the Cerabite process clearly indicates that process feasibility is well established for those types of applications.

3.3 Construction and Operation of the Core Removal Chamber

An experimental program was carried out in the Pulsed Power Laboratory at Texas Tech University to define design considerations to be solved before attempting to commercialize the process. In this program a small electrohydraulic tank was built and castings were treated to remove ceramic shell material and sand cores (no castings containing ceramic cores were tested, as the results from Cerabite confirmed that it was feasible to remove cores from them, provided that the core geometry was suitable).

The basic experimental arrangement is shown in Figure 12.

Figure 12. Experimental Arrangement for Electrohydraulic Ceramic Shell Removal Tests.

A tank was built for the experiments. Because a reflector makes the process more efficient by directing all of the energy released at the spark to the casting, (and, because the energy wave travels a longer distance from the gap to the casting when it is reflected than when it travels direct, one discharge yields two pressure waves at the casting), two co-linear electrodes were designed to be at the focal length of an elliptical reflector. The reflector had a major semi-axis of 6.25 inches, and a minor semi-axis of 5 inches and was 8 inches long. It was placed at the bottom of the tank so that the direct and reflected waves traveled upwards to the pressure transducer (which was also the position of castings used in the experiment). The focal line of the electrodes was 2.5 inches from the back side of the reflector.

The reflector was mounted on a 1 inch thick bottom plate which was welded to a 3 foot diameter by 40 inch high tank. It was backed by a large "I" beam to react against the downward force of the impulse of the pressure wave on the reflector. Forces generated in the tank by the discharge can be very large. In fact, during experiments the tank often jumped off the floor in reaction to these forces. The strength of the force from the spark gap is a major concern in the design of a commercial unit. The experimental tank was built of 1" thick steel; the Cerabite tank used 2" thick steel.

Problems were encountered early in the experimental program when it was discovered that isolating the pressure instrumentation was a problem. A second problem was that the initial firing time was initially too long to produce shock waves. True shock waves were not obtained until nearly a year into the program, when the capacitors were changed to give a faster rise time. However, it was also discovered that true shock waves are not necessary to remove the cores — any pressure wave which exceeds the fracture stress of the core is satisfactory.

The pressure developed depends on the charging voltage, and on the electrode gap length, as well as the rise time of the discharge. Measurements were carried out using a strain gage on a 3/4 inch diameter bar one meter from the gap, and obtained the relationships shown in Figures 13 -15.

Pressure probe calibration is 250 psi / mV.

Figure 13. Acoustic wave pressure vs. charging voltage.

The electrohydraulic pressure generated is a measure of the hydraulic energy, and should be as high as possible. In these experiments the pressure did not reach the 435 ksi level at

Figure 14. Discharge delay time vs. charging voltage, 1/4" gap.

the electrodes which is needed to produce a shock wave in water (though this was later achieved with different capacitors). Note that the pressure increases as the charging voltage increases, and also (over a small operating range of charging voltage) as the

electrode gap width increases. Subsequent experiments indicated that pressure was a maximum when the electrode gap was 1.375 inch. This was determined by testing at eight gap distances from 0.25 to 2.00 inches.

The electrical pulse delay time (the time between the closure of the switch and the high current discharge) shown in Figure 14 is a measure of the electrical/hydraulic efficiency, and should be as small as possible. It decreases with increasing charge voltage, and could be influenced by the conductivity of the water, or the pulse risetime.

Figure 15. Acoustic wave travel time vs. charging voltage, 1/4" gap.

The travel time of the acoustic wave, when combined with the peak pressure readings, is used to determine whether the discharge has produced a shock wave or a simple pressure wave. Note that the production of a pressure wave instead of a shock wave is not necessarily bad, as the only requirement is that the force of the wave be sufficiently strong to fracture the core. For a shock wave to be produced, the travel time should be as short as possible. It decreases with increasing charge voltage.

A particular problem was encountered with the design of the electrodes during the tests. Electrode durability was much more of a problem than first supposed. The electrodes must not only remain insulated from the tank and reflector walls, but they must also withstand the very high impulse generated by the spark without breaking down either electrically or mechanically. Few materials are capable of serving as the electrical insulation, as the electrical insulation must also have good mechanical shock properties. Present electrode design uses copper for the conducting member, and a high density polymer for insulation. Initially, electrodes were able to withstand only ten discharges before the insulation broke down or fractured. By the end of the program they could withstand 75, a great improvement, but still far short of the number needed for a commercial application.

The occurrence of "flashover" was also a problem. Flashover occurs when, 40 to 100 μ sec. after the trigger pulse fires, there is a large electrical disturbance, and an arc from the high voltage electrode to ground is established *over the insulation*. This is believed to be the result of dissolved gases coming out of solution in the water and being deposited as bubbles on the insulator, forming a network over which the electrode can flash to

ground. Although this arc is self-extinguishing, its presence lowers the efficiency of the process by lengthening the discharge delay time. To minimize the flashover problem the electrodes were grooved in a thread pattern, to increase the distance which the arc must travel. It also appears that one of the reasons the medical lithotripsy literature emphasizes the use of deaerated water is to minimize flashover problems.

As an alternative to spark gap discharge, attempts were also made to use exploding wires. However, the pulsed power supply used had a slow risetime, which fused the wires, rather than exploding them. It was concluded that exploding wires were not suitable for this application.

A number of additives were made to the water to determine whether they might affect the conductivity and rise time of the system. No effect was noted for additions of salt, vinegar or bleach solutions.

Pulse attenuation with distance from the spark was measured by placing the pressure probe at varying distances from the spark gap, firing, and recording the pressure. The charging voltage used for these tests was 36 kV, which produced a charge energy of about 32 kJ. As expected, the pressure decreased with increasing radial distance from the spark gap, according to the relationship

$$\frac{P_0}{P} = \left(\frac{R}{R_0} \right)^{1.26}$$

where P_0 is 424 psi when R_0 is 0.1 inch. It is expected that a different charging voltage would produce different values, though not a significantly different relationship. Because of this drop in pressure with distance, actual pressures on castings will be different in different locations. For this reason, it is considered to be advisable to be able to manipulate the casting or cluster in the tank to expose all areas of the casting to the maximum pressure. Note, of course, that the wave bouncing off the sides of the tank also strikes the casting, though with reduced force because of the extra distance traveled.

Two investment cast solid turbine wheel quadrants were exposed to ten discharges at the 32 kV charging level to remove shell ceramic. Prior to exposure the wheels had the appearance shown in Figure 16.

Following exposure to ten shocks (applied to only one side of the wheel), the wheel had the appearance shown in Figure 17. The rounded edges on the ends of the airfoils are the result of misrun during pouring, not damage from the shock waves. However, the eroded trailing edges of two airfoils in the center were caused when the casting quadrant fell from its hanger in the bath into the electrodes.

Figure 16. Turbine wheel quadrant prior to exposure to electrohydraulic shock for ceramic removal.

Figure 17. Turbine wheel quadrant after exposure to ten shocks. (The rounded edges on the casting are the result of misrun during pouring, not damage from core removal, although two blades were burned from a short circuit on the trailing edge when they fell from their hanger).

Large quantities of ceramic have been removed. In fact, the back of the blades (but not the back of the hub portion) was also free of ceramic. It is noteworthy that this cleaning took place in less than the 100 shocks required by the Cerabite machine. It should also be noted that the ceramic shell tested was one of the hardest and strongest in the investment casting industry. Other shells are expected to respond at least as well to electrohydraulic cleaning.

The fact that the casting was dislodged from its hanger above the electrodes indicates that supporting the castings during treatment is not a simple problem. The castings must be held tightly and rigidly, but if the holding fixture is too massive, it will interfere with the passage of the pressure wave. In addition, the casting must be oriented so that the surface containing the ceramic to be removed, or the wall in front of the core, is presented to the full action of the wave for most efficient operation. It was noted at the Cerabite installation that the standard fixture used to hold investment cast clusters interfered with the wave action on the cluster, which increased the number of shots required. This implies that manipulation of the casting or cluster during exposure to the shock waves is necessary for efficient operation of the system. The use of multiple electrode sets, to provide pressure pulses from more than one side of the casting, may also be effective, especially if they are programmed to interact with casting manipulation. It was noted that the entire assembly, tank, electrodes, and holding/hanger assembly must be very rugged to withstand the repeated loading (which may be expected to cause fatigue failure) in a commercial unit.

Because electrohydraulic shell removal takes place under water, there is no dust, no air pollution, and no chemical disposal problem. The only environmental concern is the sound of the discharge, which requires ear protection for those in its immediate vicinity.

No direct information on the economics of electrohydraulic shell removal was gained from these experiments. Although the power levels involved (30 to 50 kJ) in the spark discharge are high, their duration is quite short (20 to 50 μ sec.). Thus the energies are low. Projections indicate that castings and clusters can be cleaned for operating costs of less than 10 cents each. However, the preliminary projected capital costs of installation, including power supply source, switching equipment, tank and casting manipulator, are estimated to be between \$750,000 and \$1,000,000, and annual electrode and capacitor replacement costs between \$100,000 and \$150,000. The process is therefore most probably not economical for small investment foundries. It should be noted that the process has been in production in an investment casting in Canada for over a decade.¹⁸ However, the foundry which uses the process, Vestshell, built the equipment itself, and does not sell the equipment or allow visitors to see it.

3.4 Experiments with Sand Cores

Although the purpose of the program was to evaluate electrohydraulic methods of removing investment casting ceramics, a series of experiments was carried out on aluminum castings containing sand cores. A water crossover pipe was cleaned in ten shots (see Figure 18).

Also cleaned was an intake manifold. Again, only ten shots were required. In this case, the small size of the tank limited the area of the manifold which could be exposed to the action of the pressure wave, so that the entire manifold could not be cleaned in one position. It was clear, however, that repositioning the casting and repeating the treatment would produce a clean manifold. The appearance of the cleaned manifold is shown in Figure 19.

Figure 18. Appearance of water crossover pipe before (left) and after (right) electrohydraulic cleaning.

Figure 19. Cleaned manifold casting.

The use of electrohydraulic shock waves to clean sand cores from castings is also clearly feasible, and, indeed, may represent an excellent choice for high production foundries. The process is easily automated, environmentally benign, and takes up little space. There is the possibility that shock waves may also physically remove binder from the sand grains, an important consideration for inorganic binders such as sodium silicate (such an effect has been noted previously¹⁰). The increasing restrictions on the use of organic binders may someday lead to the increased use of silicate binders in sand foundries; until now, a major drawback to their use has been the difficulty in removing cores made from them and reclaiming the sand.

In addition, electrohydraulic shock waves work on all parts of the casting to which they are exposed. Casting design can benefit from this, as it is no longer necessary to design cored passages with the concern that the cores may not be removable — as long as a shock wave can be transmitted through the wall of the casting, the core can be broken up and removed. The addition of extra material to casting risers so that they can be used as a hammering point for core removal can also be discontinued with electrohydraulic core removal methods.

4.0 Conclusions

1. The feasibility of using electrohydraulic pressure waves to remove shell ceramic from investment castings has been established.
2. Electrohydraulic pressure waves may also be used to remove ceramic cores from investment castings provided their geometry is suitable. Their use for the removal of cores having large aspect ratios (i.e., long, thin cores) is not recommended.
3. The use of electrohydraulic pressure to remove cores from single crystal superalloy castings is not recommended as the pressures involved causes recrystallization in the castings.
4. Electrohydraulic core removal methods also have promise in the removal of sand cores from sand and permanent mold castings, and should be investigated for these applications.
4. Commercial application of this process for removal of ceramic shells and cores appears to be feasible; a commercial unit is marketed in Europe.

Acknowledgments

This report was prepared with the support of the U.S. Department of Energy (DOE Cooperative Agreement No. DE-FC07-92ID13163). However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the view of DOE. Matching funds were received from the Center for Materials Production, and a consortium of foundries and core suppliers organized by the American Foundrymen's Society. Members of the consortium were: Howmet Corp., Precision Castparts Corp., Oremet Corp., CMI Quaker Investment Casting, and Duriron, Inc.

References

-
- ¹M.C. Noland *et alia*, "High Velocity Metal Working: A Survey," Office of Technology Utilization, NASA Report SP-5062, 1967.

- ²M.S. Nissley, "Electrohydraulic Stimulation of Waterwells," *IEEE Transactions on Industrial Applications*, vol. IA-11, no. 6(1975), p. 728.
- ³H.K. Kutter, "Electrohydraulic Effect - Potential Application in Rock Fragmentation," U.S. Bureau of Mines - Report of Investigations, no. 7317 (1969), p. 35.
- ⁴M. Hamelin *et alia*, "Hard Rock Fragmentation with Pulsed Power," Proceedings of the 9th International IEEE Conference, Albuquerque, 1993.
- ⁵W.C. Chapman, W.H. Hoyt and L.F. Williams, "Principles of Bilary Extracorporeal Lithotripsy," *American Journal of Surgery*, vol. 158 (1989), p. 179.
- ⁶S.B. Stroom, "Kidney Stones — How New Technology Has Improved Management," *Postgraduate Medicine*, vol. 84, no. 9 (1988), p. 77.
- ⁷M.J. Coptcoat, R.A. Miller and J.E.A. Wickman, *Lithotripsy II*, BDI Publishing, 16 Woodland Gardens, London N10 3UA, Great Britain, 1987.
- ⁸C.J. Chuong, "Different Stone Damage Modes during Lithotripsy Shock Wave Delivery," in *Biomechanics Symposium — 1989*, presented at the Third Joint ASCE/ASME Mechanics Conference, San Diego, CA, July 9-12, 1989, p. 5.
- ⁹F.M. Shaw and F.K. Garman, "A Review of Specialist Cleaning and Metal Removal Techniques," *Fettling and Cleaning of Castings*, University of Nottingham, Sept. 22 - 24, 1974, BCIRA report 12- 5.
- ¹⁰N. Gobl and L. Monath, "Electrohydraulisches Entsandern — Teil 1 & 2," *Giessereitechnik*, vol. 29, nos. 7 & 8 (1983), p. 205 (7); p. 239 (8).
- ¹¹10 minute video produced by Metalguss und Formenbau, Wernigerode, Germany, 1991.
- ¹²R. Thewes, "Shock Wave Process for the Removal of Mold Residues and Cores for the Production of Castings," *CP & T — Casting Plant and Technology*, Giesserei-Verlag, GmbH, Düsseldorf, vol. 1 (1993), p. 2.
- ¹³Personal communication from D.L. Twarog, American Foundrymen's Society, 1991.
- ¹⁴L.F. Sorokin and V.M. Efimov, "Ultrasonic Removal of Ceramic Bars from Castings," *Energomashinostroenie*, no. 7 (1988), p. 23.
- ¹⁵T. Derkacs, P.N. Atanmo, L. Johnson and T.S. Piwonka, "Rapid Core Removal for Hollow DS Eutectic Turbine Blades: Final Technical Report," AFML TR-77-207, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, 1977.
- ¹⁶D.A. Russell, "Shock Dynamics of Non-Invasive Fracturing of Kidney Stones," *Shock Waves and Shock Tubes, Proceedings of the Fifteenth International Symposium*, Berkeley, CA, July 28 - Aug. 2, 1986, p.641.
- ¹⁷K. Cambia *et alia*, "Underwater Shock Wave Focusing — An Application to Extracorporeal Lithotripsy," *ibid.*, p. 647.
- ¹⁸J. Valenta, "Putzen von Feinguss Durch Elektro-hydraulischer Blasen," Proceedings of the 18th European Investment Casting Federation Conference on Investment Castings, Stockholm, June 18, 21, 1978, paper no. 21.

Task 6

METAL PENETRATION IN SAND MOLDS

D.M. Stefanescu, S.R. Giese, and T.S. Piwonka

AN INVESTIGATION OF THE ROLE OF THE MINOR ALLOYING ELEMENTS, SAND ADDITIVES, ATMOSPHERE, AND MOLDING AGGREGATE ON THE CONTACT ANGLE OF CAST IRON

1.0 Introduction

Metal penetration as defined by Draper et al is the condition in which liquid metal has intruded beyond the midpoint of the first layer of sand grains of the mold interface'. Two commonly accepted mechanisms for metal penetration defects are mechanical and chemical penetration. In mechanical penetration, the liquid metal enters the interstices of the sand grains as a result of excessive hydrostatic pressures and/or capillary forces applied at the mold/metal interface, overcoming the external forces which prevent penetration. Chemical penetration is the result of the oxidation of liquid metal at the casting interface which in turn reacts with the molding medium to form complex silicate compounds that strongly adheres the molding aggregate to the casting surface. Variables affecting the initiation and extent of penetration defects are temperature, mold atmosphere, metallostatic pressure, cooling rate, physical properties of both the sand and metal, thermodynamic properties between the metal and sand, and the sand grain size distribution. Although many practical solutions to prevent metal penetration defects have been proposed and implemented on the foundry floor, these methods do not always successfully eliminate the occurrence of penetration defects.

In 1989, the American Foundrymen's Society (AFS) recognized that the causes of penetration defects were not fully understood based on the costs associated with labor, cleaning, and scrapping in repairing this type of defect. For this reason, AFS, in conjunction with the U.S. Department of Energy, sponsored a research program to gain a better fundamental understanding on the mechanisms of penetration defects for ferrous alloys. During the first year of the program, a literature review of penetration defects was undertaken and an in-situ study of the surface energy relationship between iron, its oxide, and various molding materials under an inert atmosphere was performed and reported^{2,3}. The following year, the in-situ investigation was extended to assess the role of temperature, grain size distribution, alloying elements, sand additives, and molding materials on the surface energy of iron base alloys⁴. Based on the results obtained and reported during the second year, this year's program was divided into three sections. The sections are:

1. an in-situ study of the role of minor alloy elements in cast iron on the surface energy relationship with a molding medium in an inert atmosphere.
2. an in-situ investigation of the role of different molding materials and additives on the surface energy relationship between two iron alloys and a low carbon steel in an inert atmosphere.
3. an in-situ study of the effect of atmosphere composition on the surface energy relationship between an iron alloy and a molding material.

From the data collected in section one, a mathematical model can be developed from a regression analysis to predict the contact angle based on the chemical composition of the alloy and the superheat temperature. Section two and three will answer the question to how the molding material and simulated mold atmosphere will affect the surface tension relationship between a medium carbon steel, a cast iron containing carbon only, and a cast iron containing silicon. These results can then used with the penetration mathematical model to predict if and how far penetration will occur⁵.

2.0 Surface Tension of Iron-Base Alloys

Two principal parameters influencing the surface energy relationships of liquid iron are the chemical composition and temperature⁶. Knowledge of these two parameters is vital to understand the mechanical aspect of metal penetration defects absent the effects of chemical interactions between the metal, molding aggregate, and mold atmosphere.

In order to understand the surface energy relationships of the liquid metal, it is important to understand the physical aspects of surface chemistry. Within the bulk of a pure liquid metal, individual atoms are attracted to each other as a consequence of an equal intermolecular force balance between the atoms. A surface is defined as a region where there is an asymmetrical force field separating the effect of the metallic atoms in its liquid and vapor state. The net resultant force of the surface atoms is from the balance between the liquid atoms leaving the monolayer of the surface and the intermolecular forces of the bulk which attracts the vapor atoms back to the monolayer surface. For a static liquid droplet, the equilibrium configuration resting on a flat surface is an elliptical shape. The final shape of the static drop, familiarly referred to as a sessile drop, can be determined by the force balance that produces a sphere by minimizing the surface free energy of the liquid and the gravitational force of the droplet on the surface of a substrate which tends to flatten the droplet.

The equilibrium configuration of a non-wetting liquid droplet resting on a flat, chemically inert solid surface is determined by the surface tension relationship between the solid and vapor, liquid and solid, and liquid and vapor, assuming that the system is saturated with the liquid vapor as schematically shown in Figure 1^{3,7}. The equilibrium balance, in terms of surface tension and contact angle, can be expressed by Young's equation:

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad \text{Eq. 1}$$

where γ_{lv} is the liquid/vapor surface tension, γ_{sv} is the solid/vapor surface tension, γ_{sl} is the liquid/solid surface tension, and θ is the contact angle. Though θ can be measured directly and γ_{lv} determined from the shape of the droplet, the values of γ_{sv} and γ_{sl} can not be easily determined.

Figure 1. Surface energy balance for the liquid metal - solid silica system.

As the temperature of the system is increased, the atoms in the bulk liquid begin to vibrate more and escape the monolayer more frequently. The intermolecular forces holding the bulk atoms decrease allowing the bulk and the monolayer surface to expand. In order for the sessile drop to maintain its equilibrium shape, the liquid/solid interface expands and the aspect ratio of the elliptical shape of the droplet decreases. Theoretically, the contact angle and the surface tension of the droplet decreases as the temperature increases. This has been demonstrated by several investigators for pure iron, numerous binary alloys, and cast iron alloys^{6,8}. Figure 2 shows the effect of temperature on the contact angle for a cast iron alloy.

Figure 2. Contact angle of synthetic Fe-C-Si alloy on silica sand (AFS GFN 71) in argon atmosphere as a function of temperature⁴.

When a solute is added to the bulk liquid, the surface tension (analogous to the contact angle) changes as result of the intermolecular forces between the solute atoms and solvent atoms. For the case where $\gamma_{lv(Bulk)} > \gamma_{lv(solute)}$ and depending on the total free energy of the system, small additions of elements generally decrease the surface energy of the metal. If the change in surface energy is significant, the solute additive is said to be surface active. For binary iron alloys, this is true for metallic and non-metallic additions as shown in Figure 3⁹.

For ternary and higher order systems, it is expected the alloying elements will further decrease the surface tension of iron. Washchenko and Ruddy have studied the surface chemistry of cast irons and the effect of major alloying elements in cast iron⁸. In their study on the dependence of surface tension on carbon content in a Fe-C-Si alloy system at two temperatures, it was shown that as the carbon content is increased, the surface tension decreases in the hypoeutectic region to a minimum, coinciding with the eutectic composition of cast iron and then increases in the hypereutectic cast irons. Additions of silicon to the Fe-C alloy system shifted the minimum surface tension value at the eutectic point to the left, just as the equilibrium phase diagram shifts to the left when silicon is increased. They also found that phosphorus additions had no effect on the surface tension and that manganese has some effect at concentrations greater than 1.5%Mn. Sulfur was noted to be a strong surface active element in-cast iron. However, from the results of their study, Interaction effects between the alloying additions were unclear.

3.0 Effect of Mold Atmosphere

Gases produced during pouring and solidification of a casting in a mold play an important role in the formation and prevention of penetration defects. Work by previous investigators^{1,10-19} have concluded that the main cause of penetration defects is the presence of an oxidizing atmosphere in the mold. The oxidation of liquid iron can proceed by the following reactions:

Figure 3. Effect of various elements on the surface energy of liquid iron at 1550-1570°C⁹

If the mold atmosphere is thermodynamically favorable for the oxidation of liquid iron, iron oxide forms which in turn wets the silica sand grains of the mold and reacts with the sand grains to form fayalite (Fe_2SiO_4). The extent of the oxidation of iron and fayalite reaction is dependent on the temperature at the mold/metal interface, the gas composition near the interface, and the cooling rate of the casting.

Chechulin has identified two regions in the mold where knowledge of the gas composition and pressure can influence the chemical reaction with the casting interface²¹. The first layer is comprised of the contact area between the molding material and casting and sinter cake zone where allotropic transformations of the molding material occurs²². It is in this first layer where the mold gases are in contact with the casting interface and can react with the liquid iron metal. The second layer, deep behind the first layer, is the region where the gases do not react with the casting interface but is a significant region where gas pressure and condensation of water control the gas composition in the first layer. Several investigators^{1,10-12,16-19,21} have concluded that a good molding aggregate must allow for good ventilation in both regions and control the gas composition during the first few minutes after

pouring through a judicious selection of a sand additive, such as seacoal, to produce a reducing atmosphere near the mold/metal interface.

4.0 Penetration Model

A penetration model is introduced that is a further development of a simple penetration model proposed in reference 3. Figure 4 shows a graphical illustration of the problem. There are competing forces that act at the mold-metal interface. The liquid metal exerts a static pressure (P_{st}) and dynamic pressure (P_{dyn}) 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 grain voids from the pressure drop resulting from the friction between the liquid metal and sand grains (P_f), and the pressure resulting from the expansion of the mold gases (P_{gas}). The liquid metal can also flow between the sand grains because of capillary pressure (P_γ) which is dependent on the surface tension and contact angle of the liquid metal. For capillary pressure, this can be beneficial or detrimental in preventing mechanical penetration. If the metal does not wet the sand grains, capillary pressure will oppose penetration. However, if the metal does wet the molding aggregate, penetration will occur. The governing equation that describes the pressure balance at the mold-metal interface can be written as:

$$P_{st} + P_{dyn} + P_\gamma = P_f + P_{gas} \quad \text{Eq. 2}$$

When the left hand side of Equation 2 is larger than right hand side, liquid metal can penetrate into the interstices of the molding aggregate. Assuming the gas pressure is negligible, each term of Eq. 2 can found as follows:

$$P_{st} = \rho_L gh \quad \text{Eq. 3}$$

$$P_{dyn} = R_p \rho_L \{2g(H-h)\}^{1/2} \quad \text{Eq. 4}$$

$$P_\gamma = \frac{4}{d_e} \gamma_L \cos \theta \quad \text{Eq. 5}$$

$$P_f = \frac{\mu}{K} L_p V \quad \text{Eq. 6}$$

where ρ_L is the density of the liquid metal, g is the gravitational acceleration, h is the metallostatic head, R_p is the pouring rate (m/sec), H is the height of the molten metal, d_e is the equivalent capillary diameter, γ_{LV} is the liquid-vapor surface energy, θ is the contact angle, μ is the dynamic viscosity of the liquid metal, K is permeability of the molding medium, and V is the velocity of the metal.

The permeability of a porous medium can be determined by the Blake-Kozeny equation:

$$K = \frac{(1-f_d)^3 d^2}{180 f_d^2} \quad \text{Eq. 7}$$

where f_d is the fractional density of the molding aggregate, and d is the average grain diameter. The penetration velocity can be calculated as :

Figure 4. Pressure balance during metal penetration in the molding aggregate.

where t_p is the solidification time of the penetrating layer (penetration time). Substituting Eqs (3) through (8) into Eq. (2), the penetration depth can be calculated as:

$$L_p = \left[\frac{d^2 t_p (1 - f_d)^3}{180 \mu f_d^2} \left(\rho g h + 1.41 \rho R_P \sqrt{g(H - h)} + \frac{4}{d_e} \gamma_{LV} \cos \theta \right) \right]^{1/2} \quad \text{Eq. 9}$$

It can be seen that the penetration depth increases as the fractional density of the molding aggregate and viscosity of the metal decreases, and as the average grain diameter, the density of the liquid metal, and the penetration time increases. Whether or not penetration occurs at all is dependent on the ratio between the static and dynamic pressures and the capillary pressure. A theoretical analysis of Eq. 9 is as follows:

if	$h=0$, and $H=0$		
for	$\theta=90^\circ$	$L_p=0$	no penetration
	$\theta>90^\circ$	$P_\gamma<0$	no penetration
	$\theta<90^\circ$	$L_p>0$	chemical penetration
if	$h>0$ and $H>0$		
for	$\theta=90^\circ$	$L_p>0$	mechanical penetration
	$\theta>90^\circ$		penetration may occur depending on P_γ , P_{st} , and P_{dyn}
	$\theta<90^\circ$		mechanical and chemical penetration

From the above analysis, it is interesting to note that the surface energy γ_{LV} plays an important role in penetration. When $\theta>90^\circ$, an increase in γ_{LV} will decrease the penetration depth L_p . However, when $\theta<90^\circ$, penetration will occur.

5.0 Evaluation of Parameters in the Penetration Model

Average grain diameter. The average grain size can be determined by the standard AFS sieve analysis by using a series of screens. The average grain diameter (mm) can be calculated from the GFN with the logarithmic relationship shown in Figure 5. The average grain diameter has a direct influence on the contact angle. Figure 6 shows the relationship between the contact angle and the average grain diameter. As shown by the figure, the contact angle decreases with increasing grain diameter.

Figure 5. Correlation between the average grain diameter and the GFN⁵.

Figure 6. Influence of grain size on contact angle⁴.

Fractional density. 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 ($f_d \times 100$). The fractional density can be directly obtained from experimental measurements since the bulk density and true density of the molding aggregate can be measured.

Penetration time. The penetration time can be approximately calculated by considering the time required for the liquid metal to lose all its superheat. Once the liquidus temperature is reached, solidification begins at the casting interface and moves inward into the casting. At this point, penetration can not proceed since the liquid

at the interface is now solid. Thus it is assumed that any penetration of the liquid metal into the molding medium will occur only when the metal is completely liquid. Under this scenario the penetration time can be calculated as (see Appendix I for details):

$$t_p = \frac{\rho_L c_L \Delta T_{sup} M}{h(T_L - T_0 + 0.5 \Delta T_{sup})} \quad \text{Eq. 10}$$

where c_L is the specific heat of the liquid metal, T_L is the liquidus temperature of the alloy, T_0 is the ambient temperature, ΔT_{sup} is the superheat, h is the metal/mold heat transfer coefficient, and M is the casting modulus.

Equivalent capillary diameter. The equivalent capillary diameter, d_e , can be calculated or measured experimentally for different molding aggregates.

Some simple examples of two-dimensional calculation of the equivalent capillary diameter are given in Figure. 7 for cubic and closed packed configurations. For the closed packed three-dimensional case it can be shown that (see Appendix II for details):

$$d_e = 1.1d(1 - f_d)^{1/3} \quad \text{Eq. 11}$$

Thus the capillary diameter is simply a function of average grain density, d , and of fractional density. It is also directly related to the permeability of the sand as measured by the AFS test.

Figure 7. Examples of calculation of equivalent capillary diameter.

Experimental evaluation of the equivalent capillary diameter can be done with a mercury porosimeter. Samples of the molding aggregate 5 mm in size were evacuated to 50 mm vacuum in the porosimeter's filling apparatus. The sample was then immersed in mercury and the pressure was gradually raised to atmospheric pressure while measuring the volume of mercury intruded into the pores of the sample.

A direct calculation was used to evaluate the pore number distribution at each pore radius. From this curve the average pore size was estimated. Some typical experimental data showing the correlation between the

capillary diameter of dry sand samples, their hardness (before drying), and their permeability is shown in Table 1. It is apparent that as the hardness of the sand increases, the permeability and the capillary diameter decrease.

Table 1. Experimental correlation between the green hardness, dry permeability, and dry capillary diameter.

Hardness	67	74	76.3	80
Permeability	425	424	350	333
Capillary dia., mm	0.11	0.10	0.11	0.094

Liquid-vapor surface energy of alloys. As shown in Figure 3, increased contents of both nonmetals and metals decrease the surface energy of iron. Oxygen, sulfur and nitrogen have a particularly strong influence. As pointed out earlier, when the metal is not wetting the mold ($\theta > 90^\circ$) a decrease in γ_{LV} will result in increased penetration. Thus, an increase in the content of any elements will be conducive to higher penetration tendency, unless the contact angle is increased. As will be shown later, the contact angle decreases with the increase in the content of the vast majority of elements in iron.

6.0 FACTORIAL DESIGNED EXPERIMENTS

In many scientific and engineering disciplines, it is necessary to obtain knowledge about the influence and interactions of several variables affecting the outcome of a process or experiment. One method is to study the individual variables on the outcome of the experiment. Unfortunately, in the case of multiple variables, the number of experiments required to investigate all possible outcomes can be exceedingly large, if not experimentally inefficient. Also, in this method, the interactions between variables are often overlooked.

However, through the use of statistics, it is possible and feasible to study multiple factors at varying levels with the least number of experiments. This can be accomplished by simultaneously studying multiple variables for the price of studying one variable. Though the factorial design method does not directly give insight to the scientific explanation of an outcome, researchers have an available tool in determining strong influential factors and interactions which affect the behavior of a multicomponent system. From the results, researchers can then direct their investigation towards the factors which strongly control the outcome of the event and develop a fundamental understanding of the problem. This method of statistically designed experiments is called the factorial or orthogonal design.

Figure 8 shows an illustrative example of a factorial array where the factors or variables to be studied are designated as A, B, C, D, and E along with interaction factors between A and C and B and C. Methods of assigning the factors to the proper columns can be found in most statistical books on experimental design²³. The trials represent the minimum number of experiments required to study all the factors at their different levels. Numbers 1 and 2 under the factor column signify the level that the corresponding factor is to be studied at. Replication of the trial, particularly when the number of factors are small (usually less than 5 factors), requires at least two duplicate experiments to minimize the estimate of errors. The results are then tabulated according to each trial as shown in Figure 8.

Trial	A	C	A x C	B	D	B x C	E	Results
1	1	1	1	1	1	1	1	y ₁
2	1	1	1	2	2	2	2	y ₂
3	1	2	2	1	1	2	2	y ₃
4	1	2	2	2	2	1	1	y ₄
5	2	1	2	1	2	1	2	y ₅
6	2	1	2	2	1	2	1	y ₆
7	2	2	1	1	2	2	1	y ₇
8	2	2	1	2	1	1	2	y ₈

Figure 8. An illustrative example of a 2³ factorial array showing the factors, the levels, and the results of the trials.

The main effect of a factor is calculated by finding the difference between the mean response of each level to determine the significance of the factor on the outcome of the system, assuming all other variables are fixed at a level. For example, to find the influence of factor A on the outcome of the responses in Fig. 8, the results for A1 (factor A at level 1) are summed and averaged and the results for A2 (factor A at level 2) are summed, averaged, and subtracted from the mean response of A1. This can be mathematically expressed as:

$$\text{Effect of A} = \text{mean response of A1} - \text{mean response of A2}$$

$$\text{Effect of a} = \left(\frac{y_1 + y_2 + y_3 + y_4}{4} \right) - \left(\frac{y_5 + y_6 + y_7 + y_8}{4} \right)$$

In general, the mean response of a factor at a high level is subtracted from the mean response of the factor at the low level. However, the converse calculation can also be performed provided the sign convention used is maintained for all effects calculation (i.e. if level 1 is assigned as positive and level 2 is assigned as negative as was done for the calculation of factor A, then the mean response at level 2 is subtracted from the mean response at level 1; however, if the signs are reversed for both levels, the numerical answer for the effect is the same except with the opposite sign.) The effects of the remaining variables and interactions can be found similarly as shown in Table 2.

Table 2. Mathematical expressions for determining the effect of the factors in Figure 8

<u>Factor</u>	<u>Effect</u>
A	Effect of A = $\left(\frac{y_1 + y_2 + y_3 + y_4}{4} \right) - \left(\frac{y_5 + y_6 + y_7 + y_8}{4} \right)$
B	Effect of B = $\left(\frac{y_1 + y_3 + y_5 + y_7}{4} \right) - \left(\frac{y_2 + y_4 + y_6 + y_8}{4} \right)$
C	Effect of C = $\left(\frac{y_1 + y_2 + y_5 + y_6}{4} \right) - \left(\frac{y_3 + y_4 + y_7 + y_8}{4} \right)$

D	Effect of D = $\left(\frac{y_1 + y_3 + y_6 + y_8}{4}\right) - \left(\frac{y_2 + y_4 + y_5 + y_7}{4}\right)$
E	Effect of E = $\left(\frac{y_1 + y_4 + y_6 + y_7}{4}\right) - \left(\frac{y_2 + y_3 + y_5 + y_8}{4}\right)$
A x C	Effect of A x C = $\left(\frac{y_1 + y_2 + y_7 + y_8}{4}\right) - \left(\frac{y_3 + y_4 + y_5 + y_6}{4}\right)$
B x C	Effect of B x C = $\left(\frac{y_1 + y_4 + y_5 + y_8}{4}\right) - \left(\frac{y_2 + y_3 + y_6 + y_7}{4}\right)$

Another method of determining the effect of a factor or interaction factor is to plot the mean response at the high level and low level. Three types of effects are graphically illustrated Figure 9 to show the different interpretations of the main factor that can be observed. If the slope of the line is steep, then that factor strongly influences the outcome of the results. A factor that is considered to be weak will exhibit a shallow slope. Determination of the effects as shown in Table 2 can be used in conjunction with the plotted mean response values to interpret and assess the degree of influence of the factor.

Figure 9. Graphical illustration of the possible relationships between the main variables.

Interactions effects can also be found in a similar manner as main effects. Mean responses are calculated for all conditions in which an interaction occurs at a particular level. For example, there are four mean response values that can be calculated for the interaction between A and C from Table 2. The four possible combinations of factors are: A1C1, A1C2, A2C1, and A2C2. The mean response values are then plotted, as shown in Figure 10, to see the effect of one factor level on the results when the level of the other factor is held constant. Figure 11 shows the possible plotted outcomes for interaction effect between two factors. An interaction does not exist if the lines of the constant factor are parallel. Non-parallel lines indicate that an interaction may exist between the two variables. Lines that intersect and are not parallel show a large magnitude of the interaction. Again, as was the case in assessing the influence of the independent variables, the difference in the mean responses determined from Table 2 can be used along with the plotted interactions combinations to evaluate the degree of interaction between the two variables.

Figure 10. Graphical illustration of plotting a factor when the level of the other factor is held constant.

Figure 11. Schematic illustration of the possible slopes of plotting interaction effects.

When two or more variables are inherently related to each other, it is necessary to investigate the relationship between each variable. An equation modeling the response of an outcome based on the experimental window of the variables of interest can be developed by using a statistical technique called regression analysis. From this mathematical model, it is then possible to predict future outcomes. The reader is referred to reference 23 for a detailed mathematical description on the development of the regression variables. There are two types of regression models; linear regression and multiple regression. Linear regression models are developed by evaluating only the single independent variables or the main effects. Multiple regression model account for higher ordered regressor variables to develop a mathematical model.

Once the regressor variables have been evaluated, it is necessary to measure the adequacy of the regression model. One method of testing the adequacy of the model is the use of residual analysis. This analysis is particularly useful for checking the assumption that the errors are normally distributed about the regression model and to evaluate if additional regressors terms are needed to improve the predictiveness of the model. The residuals for any regression model can be calculated by:

$$e_i = y_i - \hat{y}_i$$

Eq. 12

where y_i is the experimental observation and $\hat{y}_i$ is the estimated outcome from the regression model. The residuals are then plotted against $\hat{y}_i$ to assess the behavior of the model. The plot also evaluates abnormalities in the data. Residuals that show a nonlinear behavior indicate that higher order terms are needed to improve the model.

A problem generally encountered in multiple regression models is the selection of regressor variables to be used in the model. Some regressor variables can be eliminated from the model based on the significance of the variable without altering the predicted outcome of the model. One method of eliminating insignificant regressors variables from the model is stepwise regression. The procedure consists of constructing regression models by adding or removing variables at each step. The analysis begins by forming a one-variable model starting with the variable that has the highest correlation. A variable is then added to the one-variable model and a new regression model is constructed and tested statistically to evaluate the significance of the new variable on the regression model. This procedure is then continued until no other variables are added or removed from the model. Generally, a new model with less variables is developed that accurately predicts the dependent variable just as well as the full regression model.

7.0 Sessile Drop Sample Preparation

For the statistical array of experiments as shown in Table 7 (located in the Results and Discussion section), four base alloys, were prepared with high purity pig iron in a 50 lb. 100 kW high frequency induction furnace, and poured into a cylindrical copper mold. The carbon and silicon contents were adjusted according to column one and two of the experimental array prior to tapping the furnace. 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. After the sample was melted and alloying elements added to the melt, a 5 mm diameter quartz tube with a suction bulb attached to one end was inserted into the melt and a cylindrical rod, approximately 2-3 inches 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 using a Spectro spectrometer. Chemical compositions for all experiments are given in Table 7. Discs, 5 mm high, were sectioned from these rods for the sessile drop experiment. Before each experiment, the metal sample was polished using fine emery grinding paper with 97% isopropyl alcohol to remove any oxides on the surface. The sample was then dried in acetone and immediately placed on the substrate.

For experiments using loose granular sand, sand was placed in a 35 mm by 6 mm circular alumina crucible. For substrates containing no clay binder additives, the crucible was filled with the dry sand, leveled, and then sonically vibrated for 5 minutes. Additional sand was added to the surface, leveled, and vibrated for an additional 5 minutes. This step was repeated two more times. The sieve analysis for all sands tested are given in Table 3. The chemical composition for chromite and silica sand is reported in Table 4. The chemical composition of alloys used for the molding aggregate experiments and sand additive experiments are given in Table 5.

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

Table 3. Characteristics of Ceramic Materials

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

Table 4. Chemical composition (wt.%) or specification of materials 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

Table 5. Chemical analysis (wt.%) of ferrous alloys

Alloy	C	Si	Mn	P	S	Mg
Alloys prepared from high purity pig iron (commercial grade)						
Fe-C	3.67	0.0225	0.0086	0.013	0.0086	0
Fe-C-Si	3.68	1.25	0.0202	0.015	0.0104	0
Alloys prepared from pure elements (synthetic grade)						
Fe-C	0.50	0.084	0.0032	0.016	0.015	0

7.1 Vacuum Furnace Method

Figure 12 shows a schematic diagram of the Centorr furnace chamber assembly used for sessile drop experiments. The Centorr Model 15 is a doubled-walled, water cooled stainless steel jacketed furnace chamber assembly. Inside the assembly is a cylindrical, meshed heating element made of tungsten metal. The

heating element is resistance heated. Surrounding the heating element are radiation heat shields consisting of concentric layers of molybdenum metal sheets. The furnace chamber assembly is evacuated using a mechanical pump and diffusion pump capable of maintaining pressure down to 10^{-5} to 10^{-6} Torr (10^{-7} to 10^{-8} atm.). The furnace can operate under vacuum or in an argon atmosphere.

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

As soon as the experimental temperature was controlled, a series of pictures were taken in two minute intervals. The temperature was recorded for each photograph.

Figure 12. Schematic drawing of the experimental apparatus for the measurement of the wetting angle and of the surface energy.

7.2 Tube Furnace Method

The experimental method used for the oxidizing/reducing atmosphere experiments is similar to the sessile drop experiments conducted in the vacuum furnace. The ferrous samples and ceramic substrates were prepared in the same manner as those prepared for the vacuum furnace. Figure 13 shows the experimental setup used for the tube furnace experiments.

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 for 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 for 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.

7.3 Contact Angle Measurements

Contact angle measurements between the sessile drop and sand substrate consisted of projecting the photograph image onto to a screen and transferring that image to an Olympus C-222 Image Analyzer via 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.

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 made at two minute time intervals. The average contact angles over the time interval for the six experiments are given in table 6. The mean contact angle was calculated to be 122.7° with a standard deviation of 1.1°.

Table 6. Average contact angles for individual experiments

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

8.0 INFLUENCE OF ALLOYING ELEMENTS ON THE CONTACT ANGLE OF IRON ALLOYS

An L32 factorial experimental array was used to assess the role of alloying elements on the contact angle in cast iron on monolithic quartz substrates. Previous results⁴ showed that alloying elements significantly affect the contact angle. It was shown that silicon addition to a base Fe-3.6C alloy increased the contact angle, though it was unclear if this was the result of the silicon addition, the effect of superheat temperature (Fe-C has a lower superheat temperature than Fe-C-Si), or the deoxidization of the base alloy by

Fig. 13 Schematic drawing of the vacuum tube furnace.

1. Gas Cylinders	9. Gas Analyzer Probe
2. Flow meters	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

silicon. Also from this study, it was determined that magnesium has the highest influence on decreasing the contact angle followed by sulfur, manganese, and phosphorus, respectively. However, it could not be determined from the study the role of varying alloying additions and the influence of interactions between the other alloying additions in the melt. For this reason, a statistically designed experimental array was developed to determine the role and interactions of alloying additions on the contact angle.

Table 7. 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

Table 7 shows the L32 experimental array used for this study. The chemical composition and superheat temperature are given for each corresponding trial. Using the statistical method previously described, it was observed that silicon has a very strong positive effect on the contact angle of iron alloys.

Manganese and sulfur have a strong negative effect on the response of the contact angle, followed by carbon and temperature which has a moderate negative effect. Phosphorus, like silicon, has a positive effect but weak. Carbon, manganese, sulfur, and temperature produced expected results by decreasing the mean response of the contact angle. Silicon showed a positive response possibly indicating that silicon controls the dissolved oxygen concentration. This is supported by the interaction effect between carbon, silicon, and superheat temperature. Phosphorus also exhibited a positive effect. It is unknown why phosphorus has this effect since it is generally believed that solutal additions reduce the surface tension of iron, based on data presented by Keene⁶. It could possibly be associated with a common foundry practice of adding phosphorus to increase the fluidity of cast iron²⁴. A linear and a multiple regression was developed from the experimental results to predict the contact angle based on the chemical composition and superheat temperature.

8.1 Evaluation of the Role of Atmosphere Composition (Oxygen Potential)

The effect of the mold atmosphere on the contact angle is more difficult to assess by sessile drop experiments since chemical reactions occurring with the sessile drop and the atmosphere can influence both the surface tension of the droplet and the furnace chamber atmosphere. Nevertheless, the contact angle and atmosphere can be monitored to determine the role of the oxygen potential. This was demonstrated in a previous report⁴ and shown in Figures 14 and 15. In both experiments, the oxygen potential, which can also be expressed as the CO₂/CO ratio, decreases the contact angle over time.

In one experiment an Fe-3.7C-1.25Si sample was melted at 1205°C on a silica sand 71 + 3% Western bentonite substrate in the tube furnace. At the beginning of the experiment the atmosphere was 100% argon. During the experiment CO₂ was added to the argon stream, resulting in an increase in the CO₂ content in the furnace atmosphere. An attempt to stabilize the atmosphere composition at two different levels of CO₂, 7% and 14% was made. The data are plotted in Figure 16, and they clearly indicate that the contact angle continuously decreases with increasing CO₂ content in the atmosphere. Thus, it is demonstrated that an oxidizing atmosphere decreases the contact angle. By decreasing the contact angle, mechanical penetration is favored even if chemical reactions with the metal and molding material are absent.

Figure 14. Fe-C-Si Alloy on Silica Sand AFS GFN 108+ 9% Western Bentonite in Carbon Dioxide/Carbon Monoxide Atmosphere.

Figure 15. Fe-C-Si Alloy on Silica Sand AFS GFN 108+ 9% Western Bentonite in 95% Argon/5% Oxygen Atmosphere.

Figure 16. Influence of increasing CO₂ concentration in the furnace atmosphere on the contact angle.

8.2 The Role of Sand Additives

The results of the influence of the bentonite content in silica sand on contact angle are given in Table 8. The results obtained for Table 10 is plotted in Fig. 35 to show the influence of temperature and western bentonite addition to silica sand. Although the temperatures at which the measurements were performed were different, the superheating temperature was 150 °C for all samples. In general, as the bentonite addition is increased for all ferrous samples tested, the contact angle increases. Though it is not clear if bentonite has a direct influence on the surface energy of ferrous alloys, it can be surmised that increasing bentonite content decreases the surface roughness of the molding aggregate based on previously published results on the influence of sand grain size distribution⁴.

Table 8. Contact angles measured for various contents of bentonite in silica sand GFN 71

Temperature	1600 °C	1300 °C	1300 °C
Bentonite, %	Fe-0.5C	Fe-3.7C	Fe-3.7C-1.3Si
0			
3	95.5°	130.8°	127.8°
6	96.5°	131.2°	137.9°
9	107.2°	131.2°	136°

Figure 17. Influence of temperature and bentonite content of the silica sand on the contact angle of three types of Fe-C alloys.

8.3 The Role of Different Molding Aggregates

A number of experiments were conducted to assess the role of the type of molding aggregate on contact angle. The experimental results for measurements held at 1600 °C for 36 minutes are tabulated in Table 9 as a function of carbon equivalent. Figure 18 shows that as the carbon equivalent increases, the contact angle increases for all molding aggregates investigated. With respect to the type of sand, chromite sand consistently gives higher contact angle than silica sand and carbon sand. In the interpretation of the results presented in Table 9, grain fineness is also a competing factor on the contact angle. As mentioned previously, the average grain fineness has an influence on the contact angle. Though chromite sand gave a lower contact angle than the zircon sand for the Fe-0.5C alloy, this could be the result of the grain fineness. However, it can be definitely concluded that for the same alloy, zircon sand has a higher contact angle than silica sand since both have comparable grain fineness.

For silica sand, it can be indirectly shown that chemical composition of the liquid metal again affects the contact angle. As the carbon concentration is increased, the contact angle increases. This is also observed for carbon sand and chromite sand. When silicon is added to the higher carbon alloy, there is a dramatic

increase in the contact angle. Evidently, silicon has an important role on the surface energy relationship between iron-carbon alloys and silica sand.

Table 9. Contact angle measurements for various molding aggregates

Alloy	Carbon equiv.	Chromite sand GFN 55	Silica sand GFN 108	Zircon sand GFN 106	Carbon sand
Fe-0.5C	0.5	106.1°	93.4°	125.8°	91.8°
Fe-3.7C	3.7	124.2°	95.8°		108.0°
Fe-3.7C-1.25Si	4.08	**	115°		**

** contact angle measurements were not made because sessile drop vibrated

Figure 18. Influence of the carbon equivalent of Fe-C alloys on their contact angles on various molding aggregates.

9.0 Conclusions

The surface tension of cast iron is dependent on the metal composition, sand composition, and atmosphere. The results obtained from the statistically designed experiment on the influence of metal composition have shown that alloying additions directly change the surface tension of cast iron. There is indirect evidence based on the main effect and interaction effects of carbon, silicon, and superheat temperature that dissolved oxygen plays an important role on the surface energy behavior of cast iron on monolithic silica. A simple linear and a multiple regression model was developed to predict the contact angle of cast iron alloys based on the chemical composition and superheat temperature from the experimental conditions used in this study.

An experiment was conducted to demonstrate that a oxidizing atmosphere strongly influence the surface energy of cast iron. As the oxidizing atmosphere is increased, the contact angle decreases. It is

unclear, however, if the dissolved oxygen concentration of cast iron or the surface formation of iron oxide is the underlying cause for the decrease in the contact angle.

A full factorial array was used to demonstrate experimentally that the sand composition affects the contact angle for three different carbon equivalent alloys. As the carbon equivalent is increased, the contact angle increases for all sands tested at 1600°C. For a medium carbon steel, zircon sand produced the highest contact angle, followed by chromite sand, silica sand, and carbon sand, respectively. All sands exhibited a linear increase in the contact angle when the carbon content was increased.

Western bentonite additions to silica sand increase the contact angle between the sand and a medium steel and two cast irons. A possible reason for this is that bentonite additions decrease the surface roughness of the sand.

A new model describing metal penetration into the molding aggregate has been introduced. The model was derived based on the pressure balance at the metal/mold interface, and takes into account the following variables: average sand grain size (GFN), solidification time of the casting, fractional density of the mold (mold hardness), liquid metal viscosity and density, metallostatic pressure, pouring rate, and contact angle between the metal and the molding aggregate. A description of the methods that can be used to evaluate these variables for different metal-mold couples was given.

Acknowledgments: This work has been supported by AFS (grant no.11-90-91) and by the U.S. Department of Energy (DOE Cooperative agreement No. DE-FC07-92ID13163). However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the view of DOE.. The authors are pleased to acknowledge the active support of the monitoring committee and in particular the direct involvement of L. Stahl, W. Marchisin, D. Jablonski and P. Cary. Mr. Dan Twarog has also gracefully contributed his knowledge and time to both the technical and financial aspects of this project. The authors are also indebted to Spectro Analytical Instruments for the generous donation of a Spectrolab on which the chemical analyses of the alloys were run.

References

- 1 Draper, A.L. and Gaiendar, J.L. "The Role of Mold Atmosphere in the Penetration of Steel in Sand Molds." *AFS Transactions* 83 (1975): 593-615.
- 2 Delannoy, P., et al. "A Critical Review of Theories for the Formation of Casting Metal Penetration Defects." AFS Research Report: April 1990.
- 3 Stefanescu, D.M. et al. "An Investigation on the Role of Sand-Metal Contact in the Formation of Casting Penetration Defects: Part 1." *AFS Transactions* 99 (1991): .
- 4 Giese, S. et al. "An Investigation on the Role of Sand-Metal Contact in the Formation of Casting Penetration Defects: Phase 2." *AFS Transactions* 100 (1992): 792-98.
- 5 Stefanescu, D.M. et al. "Metal Penetration in Sand Molds - A Fundamental Approach to Solving the Problem" to be published in *AFS Transactions*.
- 6 Keene, B.J. "Review of Data for the Surface Tension of Iron and Its Binary Alloys", *International Materials Reviews* 33:1 (1988):2-37.
- 7 Adamson, A.W. *Physical Chemistry of Surfaces*, 4th Ed. New York: Interscience Publishers, Inc., 1988.
- 8 Washchenko K.I. and Rudoy, A.P. "Surface Tension of Cast Irons", *AFS Transactions* 70 (1962):855-64.
- 9 Allen, B.C. "The Surface Tension of Liquid Metals", *Liquid Metals: Chemistry and Physics*, edited by Beer, S.Z., New York, Marcel Dekker Inc., 1972.
- 10 Goodale, P.L. "Notes on Behavior of Sand Molds in Steel Foundries." *AFS Transactions* 38 (1930): 471-480.
- 11 Thorpe, J.P. "Avoidance of Metal Penetration and Sand Burn-on in Iron Castings." *The British Foundryman*, 10 (1950): 380-482.
- 12 Savage, R.E. and Taylor, H.F. "Fayalite Reaction in Sand Molds Used for Making Steel Castings." *AFS Transactions* 58 (1950): 564-577.
- 13 Colligan, G.A. "The effect of Temperature and Atmosphere on Iron-Silica Interface Reaction", *AFS Transactions* 66 (1958), 457.
- 14 Svoboda, J.M. "Effect of Oxygen Content on Metal Penetration in Steel Castings", *Journal of Metals* 20:3 (1968): 85-87.
- 15 Fawley, J.J. et al. "Simulating Mold-Metal reactions in a Small Laboratory Test." *AFS Transactions* 82 (1974): 561-570.
- 16 Svoboda, J.M. and Geiger, G.H. "Mechanism of Metal Penetration in Foundry Molds", *AFS Transactions* 86 (1978):281.
- 17 Scott, W.D et al. "Gas Generation at the Mold-Metal Interface", *AFS Transactions* 86 (1978): 599-610.
- 18 Wagner, C.G. "Observations on the Penetration of Steel into High Density Clay Bonded Molds With Controlled Atmospheres." *AFS Transactions* 87 (1979): 573-592.
- 19 Flinn, R.A. et al. "Mold-Metal Reactions in Ferrous and Nonferrous Alloys", *AFS Transactions* 94 (1986):29-46.
- 21 Chechulin, V.A. "Chemical Reactions of Gases Evolved from the Mold with Steel and Cast Iron" *Gases in Cast Metals*. e dited by Gulyaev B.B., Soveshchanie Po Teorii Liteinykh Protssosov, 9th Ed. Moscow, 1963: 214-17.
- 22 Owusu, Y.A. and Draper, A.B. "Metamorphic Zones in Green Sand Molds Poured with Steel", *AFS Transactions* 86 (1978):589-98.
- 23 Hines, W.H. and Montgomery, D.C. *Probability and Statistics in Engineering And Management Science*. 3rd Ed., New York, John Wiley & Sons, 1990.
- 24 J. Campbell. *Castings*. Boston: Butterworth-Heinemann Ltd, 1991.

 

Task 7

MOLD-METAL INTERFACE GAS COMPOSITION

A.M. Lane and R. Pattabhi

GAS COMPOSITION AT THE MOLD/METAL INTERFACE IN SAND MOLDS

1.0 Introduction

Metal penetration has been a major problem in the metal casting industry, causing an estimated loss of \$60 million annually. Metal Penetration is defined as the condition where metal enters the sand in the mold beyond the midpoint of the sand grains at the mold/metal interface. The severity of penetration depends on the distance to which the metal penetrated, and on the extent to which it has reacted with the sand. Penetration-type defects have been classified¹ as burn-on, burn-in, and metal penetration, representing the least severe to the most severe cases. The exact mechanisms that cause penetration are still under investigation; however, it seems clear that they can be broadly divided into two classes:

1. Physical penetration of metal into the mold.
2. Chemical reaction between the metal and the mold.

Physical penetration depends on the metal forcing its way in between the sand grains, and is the subject of Task 7 of the program carried out under this Cooperative Agreement. Chemical reactions, however, may occur directly between the metal and the mold material, or, the metal may react with the atmosphere in the mold, forming a compound which then reacts with the sand. Indeed this is postulated to happen in iron (which does not directly react with silica sand), as it oxidizes to form iron oxide, which, in turn is capable of reacting with (or dissolving) silica.

Evidence that such reactions may occur is found in the work of Draper and Gaindhar,¹ who showed the effect of deliberately producing oxidizing, neutral and reducing atmospheres on the existence of penetration-type defects in steel castings poured in sand molds. Oxidizing atmospheres yielded penetration defects; neutral and reducing atmospheres did not. Obviously, the remaining question is what the composition of the atmosphere at the mold/metal is during pouring and solidification. If it is naturally oxidizing, then chemical penetration is likely to occur. If, however, it is neutral or reducing, then no chemical penetration should be found. Because most of the previous work on chemical penetration has been performed on steel castings poured into resin bonded molds, the purpose of this project was to measure the composition of the gas generated at the mold/metal interface when *cast iron* is poured into *green sand* molds as a function of time, and determine whether it could cause penetration.

2.0 Technical Approach

The first step hypothesized for chemical penetration to occur is the oxidation of liquid iron to iron oxide, FeO. FeO is liquid at the temperature of solid steel, and can react with and dissolve silica sand, SiO₂, to form fayalite, FeO•SiO₂.^{2,3,4} When this happens, fayalite penetrates the mold, followed by liquid iron, which then solidifies. Iron oxide is formed when iron is oxidized by oxygen in the air initially in the mold, or by reaction with water vapor released when the moisture in the mold turns to steam on contact with the liquid iron. One method used to maintain a reducing atmosphere at the mold interface is to add carbonaceous materials, such as cellulose or seacoal (finely ground coal) to the sand mix. As a result, it is not intuitively clear whether the atmosphere at the mold/metal

interface will be oxidizing or reducing when metal is poured into the mold. The only way to ascertain the gas composition at the interface is to measure it directly.

2.1 Pouring Experiments

The composition of the atmosphere liberated when metal is poured into a resin bonded sand mold has been measured previously.⁵ In this work the gases were collected during pouring and then analyzed. This method did not allow the continuous change in gas composition as a function of time to be determined. Therefore, it was essential in this program to find a way to continuously measure gas composition after the metal was poured into the mold. This was accomplished by measuring the composition of gas evolved at the mold/metal interface when cast iron was poured into a sand mold. The apparatus sketched in Figure 1 was used for this purpose.

The casting used was 6 inches in diameter and 12 inches high, and bottom gated. The casting was formed in the mold cope, with the probes inserted in the drag. Probes were positioned 1/8 inch from the drag surface, which was as close as they could be placed without being plugged by metal. The distance from the interface to the probe tips was controlled by setting them up with a spacer plate that was removed before molding.

The temperature of the metal and the mold interface was determined using 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 affixed to a 1/4 inch diameter stainless steel tube which served as a pressure probe, and read out on a strip chart recorder. The transducer was calibrated to read in the 0 - 15 psig range.

The gas composition was tapped from the mold surface though a 1/8 inch diameter stainless steel tube using a vacuum pump at the rate of 2 cc/min. The small amount of gas thus removed from the surface is not enough to alter gas composition at the surface. The moisture content of the gas trapped from the mold surface was determined using a digital hygrometer from which the amount of water vapor in the gas could be estimated. The gas was filtered through a 2 μ filter and then dried by passing it through a desiccant (CaSO_4). The desiccant does not absorb any of the gases analyzed, and thus did not alter the measured gas composition. Provision was also made to remove dry gas across septa by taking an injection for analysis by gas chromatograph to distinguish between nitrogen and carbon dioxide, which have the same molecular weights, and thus cannot be differentiated by the mass spectrometer.

Sand molds were prepared from washed silica sand with an AFS grain fineness number of 71. The clay binder used in all molds was 6% Western bentonite. Moisture, seacoal and cellulose contents were varied in the experimental program, having high and low values as follows:

	<u>High Level</u>	<u>Low Level</u>
Moisture Content	3.7%	2.3%
Seacoal Content	4.9%	2.1%
Cellulose Content	0.5%	0.2%

Batches of sand were prepared in 100 lb quantities by mulling for ten minutes in a Beardsley & Piper muller. The muller was kept closed during mulling to avoid evaporation of the moisture during mulling. New sand (not reclaimed) was used for each

Figure 1. Experimental setup for measuring mold/metal interface gas composition, pressure and temperature.

experimental run to avoid contamination from previous experiments. The carbonaceous additions (seacoal and cellulose) were added after the clay addition was made. Cellulose was added first, followed by seacoal.

Loss (LOI) tests were used to determine the actual carbonaceous addition content of the sand. An LOI sample was drawn after the cellulose addition, and a second LOI sample drawn 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 220 F for three hours, and re-weighing.

Molds were prepared by hand ramming and use of a pneumatic rammer, with the probes fixed to the flask. The mold parting line was at the bottom of the flask, so that maximum pressure could be exerted during ramming to achieve mold hardnesses in the 80 to 85 range.

Iron was melted in a 100 kW high frequency induction furnace. The iron was covered by charcoal to protect it during melting. Iron composition was 3.5% C, 1.8% Si, 0.7% Mn, 0.12% P, and 0.12 S.

Gas composition data were recorded for approximately 15 minutes after pouring. An injection sample was taken for gas chromatography after the gas composition had reached steady state as measured by the mass spectrometer. Note that in these experiments the mold was open to the atmosphere.

2.2 Instrument Calibration

Calibration of the mass spectrometer was necessary because the gas composition measured by it is non-linear. This means that the calibration procedure requires a large number of data points. On the basis of a review of literature and an analysis of likely products of combustion at the mold/metal interface (which indicated that the atmosphere should be mostly N_2 and O_2 at the beginning of pouring and mostly H_2 and CO , with small amounts of CO_2 and CH_4 at the end of solidification), the mass spectrometer was calibrated using mixtures of pure gases in the following ranges:

Hydrogen	0% $\square$ 80%
Nitrogen	15% $\square$ 79%
Oxygen	0% $\square$ 21%
Methane	0% $\square$ 5%
Carbon Monoxide	0% $\square$ 100%
Carbon Dioxide	0% $\square$ 5%.

These gas mixtures were also used to calibrate the gas chromatograph, which was used to determine nitrogen and carbon monoxide contents of the gas at steady state.

2.3 Experimental Design

An L16 designed experiment was used to determine the effect of four variables on gas evolution. The four variables, each held at two levels, were sand moisture content, sand seacoal content, sand cellulose content, and metal pouring temperature. In addition, one mold was poured that contained no carbonaceous additions, and one that contained only seacoal as an addition. The experimental grid was as shown in Table 1:

Table 1. Variables for Designed Experiment

Experiment #	Moisture %	Seacoal %	Cellulose %	Pour Temp. °C
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 and Discussion

3.1 Mold Properties Obtained

Actual properties measured on the molds used in the experiments are shown below in Table 2. It will be seen that not all the objectives of the designed experiment were realized in the actual experiment. Green sand properties are difficult to control, and the scatter, while disappointing, is not considered to invalidate the experiments. Because of the difficulty in controlling the cellulose content, its effect could not be determined.

Table 2. Properties of the Molds Used in the Experimental Program

Mold Number	Mold Hardness	Compact-ability	Gas Perm-ability	% Moisture	% Seacoal	% Cellulose
1	78	42	112.13	4.24	4.81	1.20
2	79	30	97.01	4.02	4.81	1.62
3	82	30	93.98	3.20	4.99	1.32
4	84	25	103.70	3.25	4.78	1.16
5	83	35	106.07	3.99	1.69	1.26
6	88	35	107.40	4.10	2.13	1.10
7	84	35	89.42	3.92	2.22	1.11
8	84	30	96.91	4.11	2.03	1.17
9	77	15	93.98	2.22	4.89	1.61
10	79	30	89.79	2.77	4.64	1.20
11	83	25	107.36	2.44	4.77	0.94
12	81	25	79.22	3.05	1.74	1.12
13	80	25	127.59	2.78	2.10	1.39
14	-	-	-	2.98	2.19	1.16
15	88	30	129.56	2.81	2.10	0.93
16	83	35	114.26	2.97	2.05	0.99
*1	85	35	105.44	3.30	-	-
*2	85	30	119.00	2.74	0.60	-

*These molds were added to the experiments to evaluate casting quality without carbonaceous additions, or with only seacoal added.

3.2 Temperature and Pressure

The temperature in the mold at a distance 1/8" from the interface reached 1400 C within a minute after pouring, and remained above 1000 C during the period when the mold atmosphere was measured (15 minutes).

Gas pressure in the mold was hardly changed during pouring. Only 0.1 psig was detected at pour. This is consistent with results from earlier investigators.⁶ This gas pressure is not sufficient to resist penetration from molten metal, and thus the presence or absence of penetration cannot be explained on the mechanical action of gas generated at the mold/metal interface. In molds of this hardness and permeability, it also appears that the gas is able to escape the mold at a rate which makes explosion defects (in which moisture in the mold layer next to the interface is heated and explodes, blowing sand into the casting and forming a surface defect) very unlikely. There was no difference between vented and un-vented molds.

3.3 Gas Composition

Mold/metal interfacial gas compositions were collected for all molds prepared, as a function of time with the mass spectrometer. Following establishment of steady state conditions, a sample was drawn for gas chromatography to determine the proportion of nitrogen and carbon dioxide gas present. Results for the mold containing no carbonaceous additions are shown in Figure 2.

The nitrogen and oxygen contents of the gas rapidly fall off as the air in the mold at the beginning of pouring is expelled by the vaporization of the moisture in the mold. Water in the mold atmosphere reacts with the carbon in the alloy to form CO, which, as it has the same molecular weight as nitrogen, now appears as the nitrogen curve. A substantial amount of CO₂ and some methane is also formed.

When carbonaceous additions are made to the mold, the curves have the appearance of Figure 3, representative of all carbon-containing molds.

Figure 2. Gas composition vs. time for mold containing no carbonaceous additions. Note the difference in scales on the right and left abscissas.

The curves are similar, only now there is more methane and much less CO₂ present, showing clearly that the addition of carbonaceous materials decreases the oxidation tendency of the mold atmosphere at the mold/metal interface.

Calculations indicated that the atmospheres produced at the mold/metal interface in *all* mold compositions tested reached a 50/50 mix of CO and H₂ gas within five minutes after pouring. None of the variables studied (pouring temperature, moisture content or seacoal content) showed significant effects on the steady-state gas composition. The

CO₂/CO ratio (which is a good indication of the oxidation potential of the atmosphere) during the first few minutes after pouring did depend on seacoal content, especially when compared to molds that contained no carbon. However, the high carbon content of the metal quickly removes the oxygen, producing a reducing atmosphere in the mold. Hence, it can be concluded that chemical penetration caused by oxidizing atmospheres in the mold does not exist in cast iron poured in sand molds.

Figure 3. Gas composition vs. time curves for molds containing carbonaceous additions.

Because time is required for the gas to migrate through the gas collection system to the mass spectrograph, it is necessary to correct the time from pouring and the time when the gas composition is noted on the mass spectrograph. The curves presented above have been corrected.

No metal penetration defects were found on any of the drag surfaces in any of the castings.

4.0 Conclusions

The conclusions that can be drawn from this project include:

1. The pressure rise at the mold/metal interface is small, of the order of approximately 0.1 atmosphere.
2. At steady state, the atmosphere at the mold/metal interface when cast iron is poured into a green sand mold is approximately 50% hydrogen and 50% carbon monoxide, a reducing atmosphere which cannot cause chemical penetration.
3. The results discussed above hold for the moisture and temperature ranges investigated.

4. Carbonaceous additions decrease the amount of CO₂ present at the mold/metal interface immediately after pouring. This was true of both high levels of carbonaceous additions and low levels of carbonaceous additions.

5. Chemical penetration caused by oxidation of the atmosphere at the mold/metal interface does not exist in cast iron poured in sand molds.

References

¹A.B. Draper and J.L. Gaindhar, "The Role of Mold Atmosphere in the Penetration of Steel in Sand Molds," *AFS Transactions*, vol. 83, (1975), p. 593.

²P.L. Goodale *et alia*, "Notes on the Behavior of Sand Molds in Steel Foundries," *AFS Transactions*, vol. 38 (1930), p. 471.

³G.A. Colligan, L.H. Van Vlack and R.A. Flinn, "The Effect of Temperature and Atmosphere on the Iron-Silica Interface Reaction," *AFS Transactions*, vol. 66 (1958), p. 452.

⁴G.A. Colligan, L.H. Van Vlack and R.A. Flinn, "Factors Affecting Metal Mold Reactions," *AFS Transactions*, vol. 69 (1961), p. 52.

⁵W.D. Scott, P.A. Goodman and R.W. Monroe, "Gas Generation at the Mold/Metal Interface," Southern Research Institute report SORI-EAS-78-118 to the American Foundrymen's Society, March, 1978.

⁶U.A. Owusu and A.B. Draper, "Metamorphic Zones in Green Sand Molds Poured with Steel," *AFS Transactions*, vol. 86 (1978), p. 589.

Task 8

IMPROVED ALLOY 718

R.G. Thompson

MAKING COMPETITIVE ALLOY 718 CASTINGS

1.0 Introduction

Investment castings of superalloys such as alloy 718 have been used for many years in radial turbine wheels^{1,3}. Development of techniques to minimize superheating prior to pouring have resulted in refinement of grain size in the castings^{3,6}. It is now possible to obtain an equiaxed, ASTM grain size of about 5 - 6 (55 μ) in the casting and about 3 - 4 (95 μ) after final heat treatments^{3,4,6,7}.

Based on various grain growth and grain boundary pinning theories, it is reasonable to expect that a certain volume of second phase is desirable for retarding grain growth in this process. In alloy 718 two phases, carbide and Laves, are present in the cast structure^{8,13,24} to facilitate the grain growth control. Both phases however are also expected to compromise mechanical properties^{7,14-16}. They also getter a large amount of Nb from solution which is suspected of reducing strength by limiting the production of gamma double prime strengthening^{10,11,17-23}. Thus a tenuous balance might be expected between the benefits of retarding grain growth and the detriments of reduced mechanical properties.

No study has been found in the literature that attempts to quantitatively establish either the detrimental effects of carbide and/or Laves on mechanical properties or the beneficial effects of these phases on grain size control. This study was undertaken to do these two things.

2.0 Experimental Procedure and Results

Eight alloy heats of alloy 718 were prepared with the compositions given in Table 1. This composition scheme provided a variable range in C, Nb, Al, and Ti. For each of the eight compositions, four test slabs were cast according to the drawing in Figure 3. A section of the 0.25 inch slab from each chemistry was heat treated to Pratt and Whitney standard PWA 1490 specification. This heat treatment is shown in Table 2.

2.1 Microstructure

Typical microstructures of the cast and heat treated material are shown in Figures 1 and 2. It was noted in all cases that the heat treatment fully eliminated the Laves phase from the microstructure as viewed in the light microscope.

2.2 Quantitative Microscopy

2.2.1 Carbides

Samples for quantitative microscopy were taken from the top, middle and bottom of each slab as shown in Figure 3. Quantitative microscopy of carbide particles was taken from the as polished surface of the specimen. The Laves phase is softer than the carbides and

is not seen on the polished surface. The carbides stand out on the polished surface and are easily counted. A Ziess SEM-IPS system was used with the appropriate filters and background adjustment to count particles larger than about 0.5 μ . Spots smaller than this were eliminated. Forty placements per sample were used with the SEM-IPS system.

Table 1. Heat Chemistries

Element	Heat Number								
	Master Heat	1	2	4	8	9	10	11	12
Al	0.47	0.44	0.44	0.45	0.76	0.48	0.76	0.75	0.74
Ti	0.69	0.69	0.66	1.10	1.10	1.03	0.67	0.66	1.11
Nb(+Ta)	4.82**	5.01	5.68	5.60	5.64	4.91	5.00	5.60	4.96
C	0.50	0.05	0.08	0.05	0.08	0.08	0.09	0.05	0.05
Ni	51.75	51.76	51.20	51.30	50.97	51.49	51.23	51.06	51.16
Cr	17.29	17.26	17.17	16.93	16.89	17.20	17.32	17.15	17.17
Fe*	Bal	21.43	21.41	21.22	21.22	21.44	21.54	21.38	21.43
Mo	3.02	3.02	3.02	3.00	3.00	3.01	3.04	3.00	3.03
B	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.004	0.003
Mg	0.0048	>0.001	>0.001	>0.001	>0.001	>0.001	>0.001	0.002	>0.001
Si	0.01	0.02	0.02	0.03	0.02	0.03	0.03	0.03	0.03
Co	0.32	0.28	0.28	0.28	0.28	0.29	0.28	0.28	0.28
Zr	>0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
P	0.002	0.002	0.003	0.003	0.003	0.003	0.003	0.003	0.003

Table 2. Heat Treatment

AC	as-cast
HIP	2050°F @ 15,000 PSI for 4 hours
HIP + S	HIP + 2000°F for 1 hour and cool @ 40°F/minute to below 1000°F
HIP + S + A	HIP + S + 1350°F for 8 hours and cool @ 100°F/hour to 1225°F and hold for 8 hours

The results of carbide measurements in the as-cast condition are shown in Tables 3a and b, and Table 4. The results have been plotted in a number of ways and a correlation was found between carbon concentration and carbide volume fraction (f_v^C). Correlations were also found between f_v^C and carbide size and heat treatment. It was found that a 60% increase in carbon concentration produced about a 60% increase in carbide volume fraction when measured in the Ziess SEM-IPS system. It was also found that the carbide size grew by 20% and f_v^C increased by 36% during heat treatment.

Quantitative microscopy did not show a correlation between the carbides and thickness of the test slab or position in the test slab. However, one of the authors visually noticed a correlation between carbide morphology and cooling rate. In the high carbon alloys, the fastest

A. As-cast 1.25 in. slab

B. As-cast 0.25 in. slab

C. Fully Heat Treated 0.25 in. slab

Figure 1. Heat 8 Microstructures.

A. As-cast 1.25 in. slab

B. As-cast 0.25 in. slab

C. Fully Heat Treated 0.25 in. slab

Figure 2. Heat 11 Microstructures.

cooling rate (smallest thickness and bottom of mold) produced a preponderance of small spotty carbides. As the cooling rate was reduced, the carbides tended toward a

Table 3 a. Volume Fractions (Std. Dev. approx. $\pm 0.35\%$)
Carbide Volume Fractions
(all thicknesses, all heats, all positions)

HEAT #	AS-CAST					HIP + S + A
	slab thickness					0.25
	1.25"	0.75"	0.50"	0.24"	average	average
1	1.01	0.89	0.87	0.87	0.91	1.06
2	1.49	1.53	1.45	1.27	1.43	1.26
4	0.96	0.93	0.94	0.82	0.91	1.35
8	1.57	1.54	1.21	1.19	1.38	2.28
9	1.53	1.50	1.30	1.22	1.39	2.15
10	1.52	1.05	1.15	1.29	1.25	1.12
11	0.77	0.81	0.76	0.71	0.76	1.19
12	0.73	0.94	0.86	0.85	0.85	1.70
Avg. low C	0.87	0.89	0.86	0.81	0.86	1.33
Avg. high C	1.53	1.41	1.28	1.24	1.36	1.70

Average low C is the average for the low Cheats (1, 4, 11, 12).

Average high C is the average for the high C heats (2, 8, 9, 10).

Each bar thickness is the average of the top, middle and bottom positions.

Table 3 b. Laves Volume Fractions
(three thicknesses, all heats, only middle positions)

HEAT #	SLAB THICKNESSES				Average
	1.25"	0.75"	0.50"	0.25"	
1	1.09	NA	0.64	0.32	0.68
2	0.28	NA	1.94	0.73	0.98
4	1.97	NA	2.67	1.56	2.07
8	2.33	NA	2.83	2.07	2.41
9	1.15	NA	1.23	1.98	1.45
10	0.66	NA	1.31	0.29	0.75
11	0.57	NA	1.34	0.32	0.74
12	1.89	NA	1.94	1.85	1.89
Avg. High Ti	1.84	0.00	2.17	1.87	1.96
Avg. Low Ti	0.65	0.00	0.42	0.42	0.79
Average	1.24	0.00	1.14	1.14	1.37

pronounced script morphology. At the slowest cooling rates (largest thickness and top of mold), the carbides appeared to be large and blocky and concentrated on the grain boundaries. The lower carbon alloys showed this transition of carbon morphology to a lesser extent with the tendency not to form a script morphology.

Table 4. Carbide Size (microns)
Std. Dev. approx. +/- 2.0 microns

HEAT #	AS-CAST					HIP + S + A
	slab thickness					0.25
	1.25"	0.75"	0.50"	0.24"	average	average
1	3.51	2.07	3.67	3.37	3.15	3.90
2	4.43	3.62	3.09	2.84	3.50	4.01
4	4.30	4.17	3.95	4.67	4.27	4.28
8	4.37	4.03	3.16	3.02	3.65	4.30
9	3.62	1.24	1.03	1.47	1.84	4.17
10	3.33	3.09	2.80	2.92	3.04	3.74
11	4.64	4.35	3.87	3.61	4.12	4.25
12	3.99	3.95	3.50	3.00	3.61	4.38
Avg. low C	4.11	3.64	3.75	3.66	3.79	4.20
Avg. high C	3.94	3.00	2.52	2.56	3.00	4.06

Average low C is the average for the low C heats (1, 4, 11, 12).

Average high C is the average for the high C heats (2, 8, 9, 12).

Each bar size is the average of the top, middle and bottom sections of the bar.

2.2.2 Laves

Quantitative microscopy of the Laves phase was performed on samples polished and etched electrolytically in saturated oxalic acid. This treatment reveals both the Laves and

carbides. Automated counting cannot be used because of etching artifacts and the similar appearance of the phases. In the present evaluation, manual counting in a light microscope was used with the operator selecting the Laves phase to count. Both f_v^C (carbide volume fraction) and f_v^L (Laves volume fraction) measurements were made with 100 manual placements of a 64 point grid.

A spin-off of this analysis was a comparison between f_v^C obtained using the image analyzer and that obtained manually. This comparison is given in Table 5. It was found that there was a 73% increase for automatic counting over manual counting. It was also found that for manual counting there was almost no difference between counting before etching and counting after etching.

Table 5. Comparison of QM Data from Different Techniques

Heat #	Thickness	Position	Before	Etch	(Carbides)	After Etch	(Manual)
			Manual	Auto A	Auto B	Laves	Carbides
1	0.5	middle	0.50	0.89	0.92	0.64	0.38
2	0.5	middle	1.11	1.47	1.13	1.94	9.95
4	0.5	middle	0.34	1.00	0.76	2.67	0.64
8	0.5	middle	0.69	1.25	1.11	2.83	0.78
9	0.5	middle	0.41	1.36	0.97	1.23	0.38
10	0.5	middle	0.52	1.43	0.97	1.31	0.41
11	0.5	middle	0.33	0.79	0.79	1.34	0.45
12	0.5	middle	0.34	0.69	0.69	1.94	0.44

As with carbides, the distribution of Laves phase was studied as a function of position in the test slab, composition, cooling rate (slab thickness and position) and heat treatment. The results are shown in Table 3b. The results have been plotted in a number of ways and correlations were found between f_v^L and Ti content (Figure 4) and heat treatment. It was found that an increase in Ti content of 60% produced an average 137% increase in Laves content. The effect of heat treatment was to dissolve the Laves phase completely after the homogenization heat treatment. Although no attempt was made to measure the delta phase, it was noted that some delta precipitation occurred around the Laves eutectic. This delta was also dissolved during the homogenization heat treatment.

2.2.3 Grain Size

Grain size was determined using an ASTM grain-size grid eyepiece. This technique requires the operator to visually match a grid to the observed microstructure. Each grid represents a standard ASTM grain size number, graduated in 0.5 of a full number, i.e., 6, 5.5, 5, 4.5, etc.. The measured grain sizes are given in Table 6. No correlation was found between grain size and carbide or Laves volume fractions. Heat treatment was found to increase grain size.

Figure 4. As Cast Laves Fraction

Table 6. ASTM Grain Size

Heat #	AC	HIP	HIP+S	HIP+S+A
1	5	4	4	3
2	5	4	3	3
4	6	4	3	3
8	5	4	4	3
9	6	4	4	3
10	6	4	3	3
11	6	4	3	3
12	5	4	4	3

2.3 Mechanical Properties

2.3.1 Hardness Tests

Hardness tests were performed using a microhardness machine. Polished and etched specimens were viewed in the microscope attached to the indenter column. Microhardness was measured in the center of selected grains. The weight and position of the indentation was carefully selected to avoid hitting a grain boundary or carbide particle. In an attempt to determine how many indentations to average per sample, the coefficient of variation was measured for making 10 indentations versus 25 indentations per sample. It was found that the coefficient improved only from 0.4 to 0.3 with increasing the number of indentations, the average hardness changed only 3.7% and the standard deviation was unaffected. Thus it was decided to take 10 indentations per sample.

The hardness values are given in Table 7. It was found that the alloys with extra Al had 25% higher as-cast hardness than their low Al counterparts. Also of interest was the finding that the alloys with extra Ti, Nb and C exhibited the greatest increase in hardness during aging, about 43%. The heats low in these elements showed only a 34% increase in hardness with aging. This trend was reversed in the high and low Al heats.

Table 7. Vickers Hardness of the Matrix
Typical Standard Deviation ≈ 30

	As Cast	As Cast (Average for all thicknesses)			Full Heat Treatment	
Heat	0.5% Thicknes	Top	Middle	Bottom	0.25" Thkns	
	Middle				Middle	% Increase
1	201				232	15
2	211				277	31
4	204				325	59
8	280				380	36
9	221				376	70
10	251				355	41
11	232				340	47
12	277	307	260	285	320	16
Avg. High Al	260				349	34
Avg. Low Al	209				303	45
Avg. High Ti, High Nb, High C	239				343	43
Avg. Low Ti, Low Nb, Low C	230				309	34

2.3.2 Tensile Tests

Tensile test specimens were cut from the 0.5 inch slab of each composition as shown in the drawing of Figure 3. The tensile tests generated yield strength, tensile strength, elongation and reduction in area data.

The results of tensile testing are given in Table 8. The results are most striking in terms of the poor ductility and elongation relative to the extra C content. Another interesting observation is the poor correlation of the microhardness of the heat treated alloys with the yield strength.

Table 8. Room Temperature Tensile Properties

Heat #	PSI x 10 ³			Per Cent	
	UTS	0.2% YS	0.02% YS	%El	%RA
1	177	152	123	20	25
2	181	159	136	9	16
4	194	175	153	14	21
8	181	157	125	14	20
9	173	149	132	15	20
10	159	130	108	15	17
11	179	152	134	19	23
12	177	147	121	21	24

3.0 Discussion

3.1 Grain Size Control

Two issues arise immediately relative to grain size control in fine grain castings; one is control of the grain size during solidification and the other is control of grain growth during cooling of the casting and subsequent heat treatment. DTA studies of alloy 718^{8,13,20,24} show that the carbides precipitate during the primary solidification of the matrix while the Laves phase precipitates at the end of solidification as a eutectic phase. Furthermore, the carbides and Laves phase both appear to be positioned at the grain boundaries suggesting that the carbide is pushed ahead of the solidifying solid interface, thus having no effect on nucleation. From these observations we conclude that the carbides and Laves phase have no effect on the solidified grain structure. The effects of these precipitates relative to grain size control is on their role as pinning phases during solid state grain growth.

A Zener pinning model for grain size control would use a relationship between precipitate volume fraction (f), precipitate size (r), and maximum average grain size (D) as follows:

$$D = 4r/3f$$

For precipitates like carbides in the size range of 3 - 5 μ , the following volume fractions of precipitates would be required for grain size control in the solid state.

D(μ)	ASTM #	f(%)
45	#6	9 - 15
65	#5	6 - 10
90	#4	4 - 7
127	#3	3 - 5
180	#2	2 - 4

The as-cast microstructures of this study contained 1% - 1.5% carbide and 1% - 2% Laves. Thus their potential pinning would lead to an average grain size of about 125 μ (#3). The actual as-cast grain size of about 90 μ (#4) is smaller than the potential maximum grain size predicted by a Zener model.

During heat treatment, grain growth is observed to increase the average grain size from about 90 μ to 125 μ (#3). The dissolution of the Laves phase causes a general decrease in the volume fraction of potential precipitate pinning phase. After the various heat treatments the volume fraction of carbide was measured at between 1 and 2.5%. It is also possible that submicroscopic phases existed along grain boundaries and were not resolved in the quantitative microscopy technique. The small volume fraction of precipitate also made it difficult to count. All of these things taken together suggests a 150 μ (#2) to 300 μ (#1) grain size from a Zener model. The fact that the grain size was remarkably constant for all samples at about 125 μ (#3) suggest one of several possibilities: the grain size has not reached its maximum value and will continue to increase given the opportunity, the Zener model doesn't work well with the small volume fractions observed in these studies, and/or submicron, intergranular precipitates (found to be prevalent in a TEM study of this alloy^{10,25,23,19}) have a strong effect on grain pinning. Of these three possibilities, the authors believe that all are equally probable.

The data does suggest that a significant increase in carbon content would be necessary to produce a significant reduction in grain size. For example, as much as 10% carbide might be required to maintain an ASTM #5 grain size. The cost of such a procedure would be a dramatic loss of ductility. On the other hand, it is not obvious that a reduction in carbon content would cause an increase in grain size. Such a reduction in carbon content might pay benefits in increased ductility^{7,14,16,27}

3.2 Laves Content

The Laves content of the as-cast microstructure was found to increase with increased Ti content. The f_v^L , which ranged from about 0.5 to 3.0, was found to dissolve completely during heat treatment. The HIP treatment serves to close microporosity and dissolve the Laves phase^{11,28,29}

If the casting could be produced without Laves present, then it might be possible to reduce or eliminate the HIP/homogenization treatment after casting. It has been suggested in the literature^{30,31} that an increased carbon content might reduce the Laves content. Presumably this would happen by the carbide using excess Nb and thus "starving" the Nb-rich eutectic from the microstructure. A calculation can be made on how much carbon would be required to "getter" the excess Nb into MC carbides. Microprobe data from Howmet Corporation on fine grain 718 castings similar to those of this study show that the as-cast matrix solubility for Nb is about 3 w/o. The excess Nb is the difference between the alloy Nb concentration and the 3 w/o Nb assumed to go into solution. The amount of C (0.08 w/o) used in the present study would only getter about 10% of the excess Nb available for Laves formation in the 5.5 w/o Nb heats. It would take about 3.0 w/o C to getter all of the excess Nb from these heats. This indicates that

the amount of carbon used in the present study would have little effect on the amount of Nb being segregated into the eutectic Laves phase. Consequently the amount of Laves present in the as-cast microstructure should not be strongly dependent on the carbon content. This was found to be the case in this study.

3.3 Hardness Tests

In examining the microhardness relationship with Al content, it was found that Al accomplished most of its hardening during the casting process. All four heats with extra Al had the highest as-cast hardness. These heats only had a relatively small 34% increase in hardness after heat treatment. However, heats containing extra Ti without extra Al showed more dramatic increases in hardness (60%-70%) following heat treatment. This suggests that there may be potential for replacing some Nb with Ti while still maintaining the alloy's resistance to strain age cracking.

The most striking observation was the lack of correlation of hardness with yield strength or tensile strength.

3.4 Tensile Tests

Data from tensile tests at room temperature confirms what might have been expected; increasing the volume fraction of carbide phase decreases ductility. No other relationship was found between microstructure and mechanical properties. The relationship between mechanical properties and microstructure is being studied more closely in another report which is still in progress at this time.

3.5 Comparison of Test Slab Data to Production Hardware

Two pieces of Pratt Whitney SSME/AT liquid oxygen preburner flight hardware were cast for comparison to test slab data. The hardware had a variation of cross-sections that spanned the range of thicknesses used in the test slabs. Two chemistries were used in the hardware as given in Table 9. Although these two chemistries are not identical to any of the test slabs, they are reasonably close to experimental chemistries numbers 1 and 8. Data from these two chemistries are also shown in Table 9 for comparison to the hardware. Data that was collected on the hardware included tensile strength (UTS), 0.02 offset yield strength (YS), percent elongation (EL), percent reduction in area (RA), ASTM grain size, carbide volume fraction (f_v^C), Laves volume fraction (f_v^L), and microhardness.

The results suggest that the test slabs give very good information on microstructure and properties of potential production hardware. The data for hardware item #2 and test heat #8 are remarkably similar in most respects. The results for hardware item #1 and heat #1 are not quite so close but are still very similar. It appears from these experiments that the test slabs are reliable simulations of production hardware. Furthermore, the trends that were seen in the test slabs such as increased strength with Ti and Nb were transferred to

the production hardware. Thus the performance trends found in test slab data serve as reliable indicators of hardware performance.

Table 9. Comparison of Test Slab to Hardware
(Full Heat treatment)

Control Element	Chemistry A (see Table 1)		Chemistry B (see Table 1)	
	Test Slab # 1	Hardware # 1	Test Slab # 8	Hardware # 2
Al	0.44	0.55	0.76	0.40
Ti	0.69	0.95	1.10	1.16
Nb	5.01	4.80	5.64	5.22
C	0.05	0.04	0.08	0.07
Mechanical Properties (PSI x 10 ³)				
UTS	176-179	161-164	176-185	
YS	150-153	134-138	160-166	
EL	19-20	21-27	9.2-12.5	
RA	23-26	25-34	16.2-22.6	
Grain Size (ASTM) (Typical Section)				
	3	2	3	4
Carbide Values (Typical)				
Volume	1.06 (± 0.3%)	NA	2.28	1.65
Size	3.9 (± 2.0 μ)	NA	4.3	6.0
Laves				
	None	None	None	None
Hardness (Vickers) (Typical Section)				
	325	NA	329	450

4.0 Conclusions

Fine grain castings of alloy 718 are dependent on their nucleation and growth in the liquid-solid state for their fine grain size. The role of precipitate pinning in controlling grain size in the solid state is relatively independent of the volume fraction of precipitates present in commercial alloy 718. If further advances are to be made in grain refinement, they must be made in the nucleation process.

The dependence of tensile strength on Ni₃Nb(γ'') strengthening in alloy 718 is well known. The ability to maximize Nb concentration in solution so that it is available for strengthening is hampered by segregation during casting. Higher strengths and reduced homogenization treatments will only be obtained through alloy modifications which increase the Nb solubility or substitute other strengthening phases.

An approach to increasing the strength of alloy 718 type compositions while maintaining or improving ductility must reduce Nb segregation and reduce f_v^C . This approach is self consistent since reducing Nb segregation would eliminate the need for homogenization

treatments. Without a significant homogenization treatment, there would be no need for carbides for grain size control.

Quantitative microscopy of alloys like 718 is difficult because of the small volume fraction of phases and the need to correctly identify each precipitate. Operator bias will produce over-counting due to a natural desire to "find" something. This tendency can be reduced in image analysis systems where the results are less dependent on operator bias. Because the Laves phase must be counted on the etched surface, highly trained operators are required. A check of the investigator accuracy for both Laves phase and carbide phase can be made by comparing the f_v^C value obtained on the polished surface to that obtained on the etched surface.

Alloys with chemical compositions similar to alloy #8 offer advantages in strength over conventional 718, and are recommended for high-strength applications.

Since the experimental test slabs behaved very much like the cast hardware, it was concluded that alloys with compositions similar to that of number 4 would give an increase in strength of 20% without loss of ductility.

Acknowledgments

The authors would like to thank Y. Shen and P. Scarber for their work on image analysis. The authors also thank Jan Lane and Roger Dunham of Howmet, and the Rocketdyne Division of Rockwell for their support. This paper was prepared with the support of the Department of Energy on Cooperative Agreement No. DE-FC07-921D13163. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily express the views of the DOE.

References

1. A. H. Jones, "An Overview of Alloy 718 in Large Structural Castings," *Superalloy 718 Metallurgy and Applications*, E. A. Loria, TMS, 1989, pp. 307-318.
2. O. W. Balloy and M. W. Coffey, "History of Cast Inco 718," *Superalloys 1988*, D. N. Duhl et al., TMS, 1988, pp. 469-474.
3. B. A. Ewing and K. A. Green, "Polycrystalline Grain Controlled Castings for Rotating Compressor and Turbine Components," *Superalloys 1984*, Maurice Gell, et al., TMS, 1984, pp. 33-42.
4. L. A. James, "Fatigue Crack Propagation in Alloy 718: A Review," *Superalloy 718 Metallurgy and Applications*, E. A. Loria, TMS, 1989, pp. 499-516.
5. M. Woulds and H. Benson, "Development of a Conventional Fine Grain Casting Process," *Superalloys 1984*, M. Gell et al., TMS, 1984, pp. 3-12.
6. J. R. Brinegar, L. F. Norris, and L. Rozenberg, "Microcast-X Fine Grain Casting-A Progress Report," *Superalloys 1984*, Maurice Gell, et al., TMS, 1984, pp. 23-32.
7. G. K. Bouse and M. R. Behrendt, "Mechanical Properties of Microcast-X Alloy 718 Fine Grain Investment Castings," *Superalloy 718 Metallurgy and Applications*, E. A. Loria, TMS, 1989, pp. 319-328.
8. M. J. Cieslak, G. A. Knorovsky, T. J. Headley, A. D. Romig, Jr., "The Solidification Metallurgy of Alloy 718 and Other Nb-Containing Superalloys," *Superalloy 718 Metallurgy and Applications*, E. A. Loria, TMS, 1989, pp. 59-68.

9. G. K. Bouse, "Application of a Modified Phase Diagram to the Production of Cast Alloy 718 Components," *Superalloy 718 Metallurgy and Applications*, E. A. Loria, TMS, 1989, pp. 69-77.
10. R. G. Carlson and J. F. Radavich, "Microstructural Characterization of Cast 718," *Superalloy 718 Metallurgy and Applications*, E. A. Loria, TMS, 1989, pp. 79-96.
11. J. F. Radavich, "The Physical Metallurgy of Cast and Wrought Alloy 718," *Superalloy 718 Metallurgy and Applications*, E. A. Loria, TMS, 1989, pp. 229-240.
12. D. D. Wegman, "Compositional Control and Oxide Inclusion Level Comparison of Pyromet 718 and A-286 Ingots Electroslag Remelted Under Air vs. Argon Atmosphere," *Superalloys 1988*, D. N. Duhl, TMS, 1988, pp. 427-436.
13. W. D. Cao, R. L. Kennedy, and M. P. Willis, "Differential Thermal Analysis (STA) Study of The Homogenization Process in Alloy 718," *Superalloys 718, 625 and Various Derivatives*, E. A. Loria, TMS, 1991, pp. 147-160.
14. J. M. Moyer, "Extra Low Carbon Alloy 718," *Superalloys 1984*, M. Gell et al., TMS, 1984, pp. 443-454.
15. J. J. Schirra, R. H. Caless, and R. W. Hatala, "The Effects of Laves Phase on the Mechanical Properties of Wrought and Cast + HIP Inconel 718," *Superalloys 718, 625 and Various Derivatives*, Edward A. Loria, TMS, 1991, pp. 375-388.
16. W. J. Mills, "Effect of Microstructural Variations on the Fracture Toughness of Wrought Alloy 718," *Superalloys 718 625 and Various Derivatives*, Edward A. Loria, TMS, 1991, pp. 573-588.
17. G. Chen, Q. Zhu, D. Wang, X. Xie, and J. F. Radavich, "Effects of Magnesium on Niobium Segregation and Impact Toughness in Cast Alloy 718," *Superalloy 718 Metallurgy and Applications*, E. A. Loria, TMS, 1989, pp. 545-552.
18. S. M. Jones, J. F. Radavich, S. Tian, "Effects of Composition on Segregation Microstructures and Mechanical Properties of Cast Alloy 718," *Superalloy 718 Metallurgy and Applications*, E. A. Loria, TMS, 1989, pp. 589-598.
19. G. Sjöberg and N. G. Ingesten, "Grain Boundary δ - Phase Morphologies, Carbides and Notch Rupture Sensitivity of Cast Alloy 718," *Superalloys 718, 625 and Various Derivatives*, Edward A. Loria, TMS, 1991, pp. 603-620.
20. U. Heubner, M. Kohler and B. Prinz, "Determination of the Solidification Behaviour of Some Selected Superalloys," *Superalloys 1988*, D. N. Duhl, TMS, 1988, pp. 437-448.
21. Z. Yaoxiao, Z. Shunnan, X. Leying, B. Jing, H. Zhuangqi and S. Changxu, "Superalloys with Low Segregation," *Superalloys 1988*, D. N. Duhl, TMS, 1988, pp. 703-712.
22. X. Xie, Y. Zhang, Z. Xu, K. Ni, Y. Zhu, T. Zhang, Y. Tong, X. Ning, S. Zhang, and J. F. Radavich, "Effect of Oxygen, Nitrogen, and Magnesium on Segregation, Solidification and Mechanical Properties in Alloys 718," *Superalloys 718, 625 and Various Derivatives*, E. A. Loria, TMS, 1991, pp. 241-250.
23. M. G. Burke and M. K. Miller, "Precipitation in Alloy 718: A Combined AEM and APFIM Investigation," *Superalloys 718, 625 and Various Derivatives*, Edward A. Loria, TMS, 1991, pp. 337-350.
24. C. Chen, R. G. Thompson, and D. W. Davis, "A Study of Effects of Phosphorus, Sulfur, Boron and Carbon on Laves and Carbide Formation in Alloy 718," *Superalloys 718, 625 and Various Derivatives*, Edward A. Loria, TMS, 1991, pp. 81-96.
25. A. Oradei-Basile and J. F. Radavich, "A Current T-T-T Diagram for Wrought Alloy 718," *Superalloys 718, 625 and Various Derivatives*, Edward A. Loria, TMS, 1991, pp. 325-335.
26. G. Muralidharan, R. G. Thompson, and S. D. Walck, "Analysis of Precipitation in Cast Alloy 718," *Ultramicroscopy 29*, North-Holland, Amsterdam, 1989, pp. 277-283.
27. T. Banik, P. W. Keefe, G. E. Maurer, and L. Petzold, "Ultra Fine Grain/Ultra Low Carbon 718," *Superalloys 718, 625 and Various Derivatives*, Edward A. Loria, TMS, 1991, pp. 913-924.
27. J. W. Brooks and P. J. Bridges, "Metallurgical Stability of Inconel Alloy 718," *Superalloys 1988*, D. N. Duhl, TMS, 1988, pp. 33-42.
28. R. E. Painter and J. M. Young, "Liquid Metal Treatments to Reduce Microporosity in Vacuum Cast Nickel Based Superalloys," *Superalloys 1988*, D. N. Duhl, TMS, 1988, pp. 417-426.
29. P. Siereveld, J. F. Radavich, T. Kelly, G. Cole and R. Widmer, "Effect of HIP Parameters on Fine Grain Cast Alloy 718," *Superalloys 1988*, D. N. Duhl, TMS, 1988, pp. 459-468.

30. B. Radhakrishnan and R. G. Thompson, "A Phase Diagram Approach to Study Liquation Cracking in Alloy 718," *Metallurgical Transactions A*, Volume 22A, April, 1991, pp. 887-902.
31. B. Radhakrishnan and R. G. Thompson, "Solidification of the Nickel-Base Superalloy 718: A Phase Diagram Approach," *Metallurgical Transactions A*, Volume 20A, December, 1989, pp. 2866-2868.

Task 9

**SPECIFICATIONS FOR IRON OXIDE ADDITIONS TO NO-BAKE
SANDS**

J.B. Andrews

SPECIFICATIONS FOR IRON OXIDE ADDITIONS TO NO-BAKE SANDS

1.0 Introduction

This study is aimed at understanding the influence of iron oxide additions on the reduction of several common casting defects and at the establishment of specifications for iron oxides utilized by the metals casting industry.

Some of the most common defects found in castings are surface roughness, surface carburization, pinholes and veining.⁽¹⁾ Veining appears on a casting as irregular fins of metal protruding from the surface. This defect occurs when expansion-contraction forces cause cracks to occur in the core or mold wall and the liquid metal subsequently fills the crack. As common practice, many foundries use iron-oxide additions to no-bake sands to prevent casting defects, and in particular to prevent veining. However, the specific mechanisms operative and the benefits of any particular grade of iron oxide are not clear.⁽²⁾ Work carried out at the University of Alabama at Birmingham has resulted in interesting findings concerning thermal expansion characteristics of sand-oxide-binder mixtures.⁽³⁾ It appears that iron oxide additions enhance the formation of cristobalite in sands subjected to a simulated mold environment (1300°C with a 5 to 1, CO/CO₂ ratio). This cristobalite formation alters the expansion/contraction characteristics of the mold over a temperature range and helps prevent veining.

Work on this project was carried out in three distinct phases. The first phase of this project involved testing using simulated mold conditions. In the second phase of the project, actual casting trials were carried out using representative red, and black iron oxides and yellow ochre. The results obtained from these trial castings were compared with results obtained from simulated mold conditions in order to obtain a better understand of the effects of iron oxides on molding sands. The third phase of this project involved the development of specifications for iron oxides and again utilized casting trials.

2.0 Influence of Iron Oxide Additions on Defect Prevention

2.1 Veining

One of the primary uses of iron oxide additions to no-bake sands is to prevent veining.⁽⁴⁾ This defect consists of small projections or metal fins which often occur in inaccessible areas and require grinding for removal. One of the most popular current theories for this defect assumes that veining occurs when sand expansion stresses open up a crack in the sand which is subsequently filled by the molten metal.⁽⁴⁾ One of the mechanisms that has been proposed for the elimination of veining by oxide additions involves a softening of the sand/oxide mixture at elevated temperature which allows deformation without failure.⁽⁵⁾ This softening is generally attributed to interactions between the iron oxides present and the silica sand (or other impurities) to form low-melting phases such as fayalite. Our laboratory results indicate that this hypothesis may not fully describe the events leading to

vein formation.⁽³⁾ Whatever the case, it is an established fact that the addition of iron oxide to a no-bake sand reduces both the amount and severity of veining defects.

2.2 Pinholes

It has also been shown that iron oxide additions reduce the tendency toward pinhole formation in castings.⁽⁶⁾ The pinholing which occurs is primarily attributed to the insolubility of gases in the metal from melting or from mold-metal interactions. A principal source appears to be from binder decomposition.⁽⁵⁾ Iron oxide additions of approximately 2% seem to have a significant effect on the reduction of pinhole formation.⁽⁵⁾ However, the mechanism responsible for this improvement is still unknown at this time.

2.3 Surface Carburization

Another use of iron oxide is for the prevention of surface carburization.⁽⁶⁾ Surface carburization (and in extreme cases carbon deposition) occurs primarily from decomposition of organic binders. Such carburization can adversely affect not only the surface quality of steel castings but also the corrosion resistance of stainless steels.⁽⁶⁾ It is postulated that the mechanism responsible for the improved resistance to surface carburization due to iron oxide additions involves the decomposition of the iron oxides with subsequent combination of the released oxygen with excess carbon from the binder.⁽⁶⁾ Fundamental studies at elevated temperatures using a 5 to 1 CO/CO₂ ratio have shown that extensive breakdown of red iron oxide (Fe₂O₃) occurs at temperature. Black iron oxide (Fe₃O₄) also breaks down but to a lesser extent.⁽³⁾ As a result, partial neutralization of the highly reducing mold atmosphere by iron oxide breakdown appears to be a valid mechanism for the prevention of carburization.

The beneficial effects of iron oxide additions to no-bake sands are well known⁽⁷⁻⁹⁾. Iron oxide additions are standard practice in the foundry industry. However, there is still only a limited understanding of the true mechanisms responsible for the enhanced casting qualities. It is the objective of this project to provide the knowledge necessary to permit an engineer to make a logical decision on the best type of iron oxide for a particular situation.

3.0 Experimental Approach

The experimental approach used in this study involved several steps. First, binder systems and oxide types were selected and analyzed. Next, test castings were poured into molds prepared using representative oxides from each category. After casting, visual analysis was carried out of the mold-metal interface and x-ray analysis was carried out on sand-oxide-binder samples taken directly adjacent to the mold/metal interface of the casting. The third and current phase of the project involves the production of trial castings utilizing various grades of oxides within a particular group in order to establish specifications on purity levels and particle size distribution.

3.1 The Casting

A step-cone test casting was used for the casting trial portion of this study. A schematic of this casting is shown in Figure 1. This casting contains a cylindrical cavity produced using a stepped cylindrical core to achieve core-to-metal volume ratios ranging from 0.125 to 1.0, to 1.35 to 1.0. Each casting weighs approximately 24 pounds. The castings are typically poured four to a mold. This test casting is particularly susceptible to veining and surface finish defects.

3.2 The Binders and Oxides: Phase II

The binders and oxides used to produce the cores for the second phase of this investigation are listed in Tables 1 and 2 respectively. A silica sand with an AFS grain fineness number of 60 was used. Each of the four cores in an individual mold were produced using the same binder. The first was made with no oxide addition and served as the control. The second core contained 2% by weight of red iron oxide, the third core contained 2% black iron oxide and the fourth core contained 2% yellow ochre. The five binder types resulted in five molds for a total of 20 castings. Two sets of casting trials were carried out. One set involved the use of 1035 steel, the other type CF8M stainless steel. Experiments were limited to the 2% level to provide a common comparison between oxide types. No experiments were performed to optimize oxide addition level.

3.3 Phase II Casting Trials

The first set of trial castings were produced using 1035 steel (composition range 0.4-0.6% Si, 0.65-0.85% Mn, 0.32-0.39% C, 0.04-0.08% Al, 0.05% S) and a pouring temperature of 2860°F. A silica sand with an AFS grain fineness of 60 was used. In all cases, the molds were produced using a phenolic urethane binder.

All five molds were aligned side-by-side and poured from one ladle. The pouring time for each mold was approximately eight seconds. The castings were allowed to cool completely before opening the molds.

After cooling, the molds were shaken out and sand samples taken from the mold-metal interface. The sodium silicate core had to be chipped out with an air hammer. However, the other cores had broken down to the point where sand samples could be spooned out.

The five casting trees were next shot blasted, the gates and runners cut off with an oxygen-acetylene torch, and the risers cut off with a horizontal band saw. The castings were then split vertically with a bandsaw followed by an additional shot blasting.

The second set of casting trials were poured using CF8M (19.76% Cr, 9.91% Ni, 1.10% Si, 0.72% Mn, 0.046% C, 0.023% P and 0.019% S) and a pouring temperature of approximately 2810°F. Pouring times ranged from approximately 10 to 13 seconds. A

Figure 1. Schematic drawing of the test casting and core utilized in this study.

silica sand with AFS grain fineness of 60 was again used to produce the cores. Care was taken during the production of these cores to maintain a consistent degree of compaction. This consistency was monitored using the weight of the cores. Within a particular binder type, all cores had weights within 2.5% of each other.

Table 1. Binders Used in Phase II Casting Trials

1. Phenolic Urethane - Three Part System
2. Furan - Two Part System
3. Phenolic Ester - Two Part System
4. Sodium Silicate - Two Part System
5. Shell Sand

Table 2. Oxides Used in Phase II. Casting Trials

1. Red Iron Oxide
2. Black Iron Oxide
3. Yellow Ochre

3.4 Phase III Casting Trials

The third phase of this project was aimed at the determination of specifications for iron oxide materials used by the steel industry. In this portion of the study, various grades of oxides of the same type are being utilized in an attempt to determine the influence of purity level and particle size distribution on the performance. Table 3 shows the code number and a brief description of each of the oxides utilized in this portion of the study.

Table 3. Oxides Used in Phase III Casting Trials

Code Number	Type	Comments
1B	Black	High Fe - 96%
2B	Black	Med Fe - 93%
3B	Black	Low Fe - 86%
4B	Black	Very Low Fe - 75%
1R	Red	Low Fe - 82%
2R	Red	High Fe - 88%
1Y	Yellow	High MnO ₂ - 7%
2Y	Yellow	Low MnO ₂ - 1 %
1S	Black	Granulated
1N	No Oxide	----

As is apparent from Table 3, four grades of black iron oxide were utilized in the casting trials. These oxides ranged from a high purity materials containing approximately 96% Fe₃O₄ (oxide 1B) to a low grade large particle size material containing only 75% Fe₃O₄.

(oxide 4B). For the red iron oxides only two distinctive grades were available in the oxides collected. One of these oxides (1R) contained approximately 82% Fe_2O_3 and the other (2R) approximately 88% Fe_2O_3 .

Two types of yellow ochre were also used. A complete analysis was not available for these materials. However, the two selected grades had a significant difference in MnO_2 content, with oxide 1Y containing approximately 7% MnO_2 and oxide 2Y approximately 1% MnO_2 . A granulated oxide product, 1S, was also tested and several castings were produced with no oxide additions (1N).

4.0 Results and Discussion

4.1 Phase II Trials

The castings produced in the second phase casting trials were visually inspected, primarily for veining and surface roughness, and given a rating. The results are shown in Tables 4 and 5. It should be noted that the ratings are subjective and may vary from one inspector to another. In addition, it must be stressed that these results are preliminary. A quick review of the data shown in Tables 4 and 5 makes it apparent that additional casting trials are necessary before any firm conclusions can be made on the ability of various oxide types to solve particular casting problems. However, these are some trends apparent from these results. These trends are discussed below.

4.1.1 Phenolic Urethane

In both cases (1035 and CF8M trial castings), extensive veining was observed in the phenolic urethane cores when used without oxide additions. The addition of 2% red iron oxide reduced the veining tendency significantly. Mixed results were obtained with black iron oxide which eliminated veining in the case of the 1035 steel castings but did not in the case of the CF8M trial castings. When yellow ochre was added to the phenolic urethane bonded cores, veining was reduced significantly over the no-oxide results.

These results imply that more testing is needed in this area. Again, results must be considered preliminary due to the poor statistics from having only two samples for each combination.

4.1.2 Furan Binder

The results obtained from furan bonded cores were more consistent. For both metals poured, extensive veining was observed when no oxide was added. However, the addition of iron oxides totally eliminated veining in the 1035 castings and dramatically reduced veining for the CF8M castings. No discernible differences were noted between the effectiveness of the various types of oxides.

Table 4. Results from Step-Cone Castings in 1035 Steel

<u>Casting</u>	<u>Core Mix</u>	<u>Veining</u>	<u>Surface</u>
1	Phenolic Urethane	Extensive	Very rough
2	Phenolic Urethane-Red Oxide	Slight	Very rough
3	Phenolic Urethane-Black Oxide	No Veins	Good
4	Phenolic Urethane-Yellow Ochre	Slight	Fair
5	Furan-No Oxide	Extensive	Very Rough
6	Furan-Red Oxide	No Veins	Very Rough
7	Furan-Black Oxide	No Veins	Very Rough
8	Furan-Yellow Ochre	No Veins	Very Rough
9	Phenolic Ester-No Oxide	No Veins	Rough
10	Phenolic Ester-Red Oxide	No Veins	Rough
11	Phenolic Ester-Black Oxide	No Veins	Good
12	Phenolic Ester-Yellow Ochre	No Veins	Rough
13	Sodium Silicate-No Oxide	No Veins	Terrible
14	Sodium Silicate-Red Oxide	Slight	Very Rough
15	Sodium Silicate-Black Oxide	Moderate	Very Rough
16	Sodium Silicate-Yellow Ochre	Moderate	Very Rough
17	Shell Sand-Black Oxide	Slight	Very Rough
18	Shell Sand-No Oxide	Slight	Fairly Rough
19	Shell Sand-Red Oxide	Slight	Very Rough
20	Shell Sand-Yellow Ochre	Slight	Very Rough

4.1.3 Phenolic Ester Binder

One of the advantages claimed for the use of the phenolic ester binder system is the ability of the system to reduce veining defects. In this study, when phenolic ester was used, even without oxide additions, veins were not observed in the casting. The addition of iron oxide had no effect on veining in these castings. These results indicate that, at least from the standpoint of veining defects, iron oxide additions are not necessary when using an phenolic ester binder system. However, it should be pointed out, that if reduced surface carbon pick up and improved surface finish are required, iron oxide additions may still be desirable.

4.1.4 Sodium Silicate Binder

The results obtained from the sodium silicate binder casting trials were somewhat inconclusive. For the 1035 steel casting, no veining was observed when the sodium silicate was used without an oxide addition. However, when iron oxides were added, castings were obtained that exhibited slight to moderate veining. In the case of the CF8M castings, slight veining was observed for the core produced with no oxide addition. Veining was eliminated when any of the oxides were added to the core mix. The inconsistency

observed with these castings points out that additional testing is desirable before any firm conclusions are made concerning oxide additions with this binder system.

Table 5. Results from Step-Cone Casting Using CF8M Steel

<u>Casting</u>	<u>Core Mix</u>	<u>Veining</u>	<u>Surface</u>
1A	Phenolic Urethane-No Oxide	Extensive	Good
2A	Phenolic Urethane-Red Oxide	Moderate/Ext.	Fair
3A	Phenolic Urethane-Black Oxide	Extensive	Good
4A	Phenolic Urethane-Yellow Ochre	No Veins	Rough
5A	Furan-No Oxide	Extensive	Fair
6A	Furan-Red Oxide	Moderate	Good
7A	Furan-Black Oxide	Moderate	Fair
8A	Furan-Yellow Ochre	Moderate	Rough
9A	Phenolic Ester-No Oxide	No Veins	Fair
10A	Phenolic Ester-Red Oxide	No Veins	Fair
11A	Phenolic Ester-Black Oxide	No Veins	Fair
12A	Phenolic Ester-Yellow Ochre	No Veins	Fair
13A	Sodium Silicate-No Oxide	Slight	Fair/Rough
14A	Sodium Silicate-Red Oxide	No Veins	Rough
15A	Sodium Silicate-Black Oxide	No Veins	Fair
16A	Sodium Silicate-Yellow Ochre	No Veins	Rough
17A	Shell Sand-Black Oxide	Slight	Terrible
18A	Shell Sand-No Oxide	Slight	Rough
19A	Shell Sand-Red Oxide	Slight	Terrible
20A	Shell Sand-Yellow Ochre	Slight	Terrible

4.1.5 Shell Sand

Slight veining was observed in all of the shell sand castings produced in this study. Essentially the same results were obtained for castings produced with and without iron oxide additions. The test matrix utilized in this study called for a 2% iron oxide addition by weight for each binder system investigated. A higher oxide content, approaching 6% by weight, is generally utilized in the metal casting industry for shell sand. The results obtained in the current study simply indicate that the iron oxide percentage was too low for this system. Additional testing should be carried out using a 6% by weight iron oxide level.

4.2 Phase III Trials

This portion of the study focused on determining the differences in behavior between different grades of oxides within the same basic type. The main variable between the different grades was purity level. However, in some cases there were also significant variations in the particle sizes of the products.

Table 6 summarizes the results obtained during the casting trials. Two castings were produced from each oxide grade and the results shown are an average of the results. All of the cores were produced using a phenolic urethane binder.

It should be pointed out that the castings reported on this portion of the study were inadvertently produced without a riser. This change in procedure resulted in severe gas defects in the upper portion of the casting which made analysis of this upper region impossible. However, it was still possible to determine surface finish and veining tendencies from the remaining portion of the casting.

From Table 6 it is apparent that the two highest purity black iron oxides reduced veining tendencies significantly over the results obtained with no oxide additions. However, a slight increase in veining tendency over these high purity oxides was observed for the moderate purity (86% Fe_3O_4) black oxide. The lowest purity black oxide (75% Fe_3O_4) produced results similar to those obtained with no oxide additions at all, yielding extensive veining and a rough surface finish. It should be pointed out that, this product had a significantly more coarse particle size than the other black iron oxides

Two red iron oxides were also investigated in this portion of the study. One of the oxides contained 82% Fe_2O_3 , the other 88% Fe_2O_3 . Both of these oxides significantly reduced veining tendencies in the castings. There were no apparent differences between the veining reduction effectiveness of the two oxides. However, the higher purity product produced a better surface than the lower purity material.

A detailed chemical analysis was not available for the two yellow ochres investigated in this study. However, it was known that the two materials differed significantly in their MnO_2 contents. Oxide 1Y contained 7% MnO_2 , while oxide, 2Y contained only 1% MnO_2 . Both of the yellow ochres were successful in completely eliminating veining in the test castings. It is interesting to note that the castings produced with these oxides were the only vein-free castings produced in this study. The surface finish produced with the low MnO_2 content oxide was fair while that obtained with the high MnO_2 content oxide was quite rough.

The last oxide investigated in this study was a granulated black iron oxide product. This material was utilized at concentration of 2 weight percent to permit direct comparison with the other oxides. At this concentration level only a very slight reduction in veining was noticeable over the no-oxide castings. In addition, a rough surface was produced. The performance of this product was quite similar to that of the coarse, low purity black iron oxide, 4B. Improved results may be obtained at higher percentages. This effect will be investigated in future trials.

Table 6. Influence of Oxide Grade on Phenolic Urethane Step-Cone Castings

<u>Casting Number</u>	<u>Oxide Description</u>	<u>Veining</u>	<u>Surface</u>
1B	Black - 96%Fe ₃ O ₄	Slight	Fair
2B	Black - 93%Fe ₃ O ₄	Slight	Fair
3B	Black - 86%Fe ₃ O ₄	Moderate	Fair
4B	Black - 75%Fe ₃ O ₄	Extensive	Rough
1R	Red- 82%Fe ₂ O ₃	Slight	Rough
2R	Red- 88%Fe ₂ O ₃	Slight	Fair
1Y	Yellow - 7% MnO ₂	No Veins	Rough
2Y	Yellow - 1%MnO ₂	No Veins	Fair
1S	Black - Granulated	Extensive	Rough
1N	No Oxide	Extensive	Rough

5.0 Conclusions

5.1 Phase II Trials

The results obtained in this study indicate that iron oxide additions at a level of 2% by weight are quite effective at reducing veining defects for castings produced using phenolic urethane furan and sodium silicate binder systems. The results obtained from the shell sand trial castings were inconclusive and should be re-run utilizing a higher oxide level. Iron oxide additions were not necessary for the elimination of veining defects for castings produced in this study using an phenolic ester binder.

5.2 Phase III Trials

Oxide purity and particle size appear to have a significant influence on the effectiveness of an oxide at reducing veining and improving surface finish. Additional testing is being carried out in this area in an attempt to establish guidelines for the purity levels of oxides to be used by the steel casting industry.

References

1. R. W. Monroe, "The Use of Iron Oxides in No-Bake Bonded Sand Molds," *Steel Founders' Research Journal*, pp. 9-20.
2. K. R. Hancock, "Mineral Pigments," *Industrial Minerals and Rocks*, 5th edition, S. J. Lefonded, AIME, 1983, pp. 349-372.
3. J. B. Andrews, D. Swain, "Report to the Steel Founders' Society of America," 1990.
4. R. L. Naro, J. F. Hart, "Phenolic Urethane No-Bake Binders: Ten Years of Progress," *AFS Transactions*, Vol. 88, pp. 57-66 (1980).
5. S. F. Carter, W. J. Evans, J. C. Harkness, J. F. Wallace, "Factors Influencing the Formation of Pinholes in Gray and Ductile Iron," *AFS Transactions*, Vol., 87, pp. 245-268.
6. R. L. Naro, R. D. Tenaglia, "Formation and Control of Lustrous Carbon Surface Defects," *AFS Transactions*, Vol. 85, pp. 65-74 (1977).

7. W. D. Scott, C. E. Bates, "Decomposition of Resin Binders and the Relationship Between Gases Formed and the Casting Surface Quality," *AFS Transactions*, Vol. 83, pp. 519-524 (1975).
8. C. E. Bates, W. D. Scott, "The Decomposition of Resin Binders and the Relationship Between Gases Formed and the Casting Surface Quality, Part 2 - Gray Iron," *AFS Transactions*, Vol. 84, pp. 793-804 (1976).
9. C. E. Bates, W. D. Scott, "Decomposition of Resin Binders and the Relationship Between the Gases Formed and the Casting Surface Quality - Part 3," *AFS Transactions*, Vol. 85, pp. 209-224 (1977).

Task 10

CRITERIA FUNCTIONS FOR DEFECT PREDICTION

J.T. Berry

CRITERIA FUNCTIONS FOR DEFECT PREDICTION

1.0 Introduction

Porosity refers to both massive shrinkage cavities (macroporosity) and dispersed pores (microporosity). The former is caused by the failure to compensate for bulk solidification shrinkage, and is generally associated with short freezing range alloys. The latter, however, results principally from either the failure of interdendritic feeding, precipitation of dissolved gases, or both, and is especially troublesome in long freezing range alloys. Inclusions and other minor solid phases also play a part in microporosity formation, acting as nuclei for dissolved gas precipitation within the solidifying melt. Additionally, dependent on the range of freezing, the effects of mass feeding, involving the flow of semisolid material and of surface sinking, may also come into play. Porosity may seriously degrade the quality of cast products, for example, their mechanical behavior and pressure tightness. Thus it is desirable that it be excluded from castings as far as is possible.

One of the most effective ways to minimize such porosity defects is to design a feeding system and evaluate its efficiency using solidification modeling. In this process, a feeding system is frequently designed based on previous knowledge and experience. A computer model is then used to determine where porosity is likely to occur in the design. This design is then modified if the occurrence of porosity within the casting is predicted. The process is then repeated until porosity is not likely to appear in the casting itself. Thus, the design of an appropriate feeding system design may be accomplished before the first casting is produced.

Several commercially available computer codes, intended for modeling shaped casting solidification, permit the user to view isotherm patterns, as well as various thermal parameters. In some cases, the codes will provide information on certain combinations of thermal parameters. These combinations are called, "criteria functions". However, they will frequently leave the user to choose a criteria function, as well as its critical level. Thus, to predetermine the presence of porosity defects, various criteria have been advocated and attempts made to apply them to shaped castings. The present task is to evaluate the applicability of such criteria functions for microporosity prediction in long freezing range alloys, as part of an effort to promote application of solidification modeling to feeding systems design.

2.0 Previous Work

Microporosity is a widely recognized problem in cast aluminum alloys, as such alloys shrink on solidification, possess high thermal conductivity and long freezing ranges, and undergo a large hydrogen solubility decrease on freezing. Two of the principal sources of dispersed microporosity are the failure of interdendritic feeding and the precipitation of dissolved gases. Because gas porosity can be significantly reduced using both improved degassing and melt cleaning techniques, this project concentrated upon the remaining and more intractable problem of the breakdown of interdendritic flow.

The feeding of solidification shrinkage normally experiences little resistance before its path becomes restricted and liquid metal is trapped in the dendritic network. A casting of an alloy with a long freezing range and high thermal conductivity usually solidifies with a shallow thermal gradient and thus a large mushy zone. A mushy zone that contains an extensive dendritic network presents a serious resistance to interdendritic feeding. Consequently, microporosity may easily initiate within such a dendritic network due to this resistance. Although subsequent mass

feeding of the semi-solid material may occur, attention must be focused initially on pore nucleation and growth.

During interdendritic feeding, liquid metal flows through the dendritic network much as fluid flows through a porous solid. The resistance to the flow may be expressed in terms of pressure drop. In 1966, Piwonka and Flemings² introduced Darcy's Law, which is valid for fluid flow through a permeable material, into microporosity prediction. They also evaluated the efficiency of interdendritic feeding through the knowledge of local pressure drop. Following this pioneering study, many others³⁻¹³ have taken this approach to investigate the relative importance of interdendritic feeding in microporosity. With the desire to apply the knowledge of solidification modeling to metal casting practice, Hansen and Berry¹ suggested the necessity of developing reliable porosity criteria to predict casting defects. Since then, the concept of criteria functions has commanded considerable attention in the area of solidification modeling. Table 1 lists several criteria functions, which have been advocated for porosity prediction. Some of them^{14, 15} were obtained from direct experimental observation. Others were derived from the assumption of Darcy's Law. The last criterion listed was derived from first principles, considering frictional resistance encountered in interdendritic flow¹⁶.

Table 1. Selected Criteria Functions for Porosity Prediction

<i>Investigators Year</i>	<i>Criteria Function</i>	<i>Comments</i>
Pellini (1953)	G, V_s	steel
Henzel and Keverian (1965)	f_s or f_l	steel
Piwonka and Flemings (1966)	ΔP	aluminum alloys
Davies (1975)	l	steel, cast iron, Al and Cu alloys
Niyama, Uchida, Morikawa and Saito (1982)	$G\sqrt{R}$	steel
Lee, Chang and Chieu (1990)	$\frac{Gt_s^{2/3}}{V_s}$	aluminum alloy
Huang, Suri, El-Kaddah and Berry (1993)	$\frac{216\mu L}{\sigma V_s \beta D_o^2}$	equiaxed grain structure

ΔP = pressure drop

$F_{s, a}$ = solid, liquid fraction

G = thermal gradient

l = capillary length

R = cooling rate

V_s = solidus velocity

μ = viscosity

L = mushy zone length

β = solidification shrinkage

D_o = equiaxed grain diameter

t_s = local solidification time.

Criteria functions are frequently associated with thermal parameters, such as cooling rate, thermal gradient, solidus velocity, and local solidification time, which can be derived from the numerical solutions of solidification heat transfer. More recently, further studies of criteria functions, based on a statistical approach,^{3, 12} or upon casting geometry considerations,¹¹ have come to light. Certain effects of melt treatments and casting geometry may now be accounted for in these newly developed criteria functions. However, some parameters in criteria functions generally may not be easily obtained for an arbitrarily shaped casting. It is clear that much remains to be done in the development and application of such criteria functions. The present task was intended to evaluate their utility in the casting of long freezing range alloys.

3.0 Experimental Results

The current experimental program was both computational and practical in nature. Various test plate castings were poured under controlled conditions and then evaluated for porosity distribution. In all, four aluminum alloys were represented (A356, 319, A206 and 535). The castings concerned, which were fed from one end, frequently contained thermocouples, permitting the validation of the computational models which were subsequently run. The following sections discuss the pouring of the castings concerned, their evaluation, as well as various aspects of the casting rigging arrangements. A concise description of the computer code (ALCAST 3D) used for simulating the solidification of the various plate castings, which comprised the bulk of the investigation, appears in an earlier report along with validation aspects.¹⁷ A full account of its development is also available.¹⁸

The simulation of the freezing of a small commercial casting, chosen to evaluate the practicability of the various criteria functions chosen for examination, was undertaken using commercially available codes.^{19,20} Additionally, a further commercial code was used to check the criteria function distribution in two of the test plate castings.²¹

3.1 Casting Poured in Commercial Foundries

To obtain the best possible reproducibility among sets of castings poured, arrangements were made to pour specially monitored heats in a number of commercial foundries. These foundries have been designated as follows:

<u>Foundry</u>	<u>Alloy Poured</u>
A	A 356
B	319
C	A 206
D	A 356

The castings poured at Foundry A (1/2 inch, 12.5 mm thick plates) and the results of this phase of the investigation have been described earlier.²²

The patterns for the one-half inch (12.5 mm) thick plate castings, together with patterns for a heavier section plate (3/4 inch, 19 mm thick) were also used in the tests undertaken at foundries B, C and D. The sand practice followed in all cases was essentially similar, i.e. an organically-bonded (Pepset_{TM}) medium-fine grained silica sand.

The three-quarter inch (19 mm) thick plate design poured at foundries B, C, and D was associated with a simple gating system similar in design proportions to that used for the one-half inch (12.5 mm) thick castings.²² This thicker plate casting was used in an earlier investigation at Foundry A.²³ In the pours undertaken in connection with the present investigation, no screens were used for either of the plate castings.

Both chilled and non-chilled versions of the plate castings were poured in all foundries concerned. The molten metal treatments used are specified in the results section of this report. Full details are contained in Tables 2 - 4. From the tables it will be seen that for the pours undertaken at foundries C and D, the different melt treatments permitted the overall effects of the variables involved (gas content, grain refiner, modifier) to be gauged. Hydrogen contents of the melts concerned were monitored throughout testing using a Telegas_{TM} probe device. This

equipment was not available for the initial set of tests undertaken in Foundry A. However, reduced pressure tests (RPT) were taken and coupon density values checked after these tests. Non-degassed RPT coupons exhibited a density of 2.09 gm/cc, while the degassed samples showed levels of 2.66 gm/cc. In addition, during the final stage of the investigation, two pours were made at Foundry D of a small commercial casting, referred to as the filter bracket casting. Figure 1 contains details of this configuration together with the rigging arrangements concerned with each pour. (Design of rigging is discussed in subsection 3.3.)

Table 2. Details of Molten Metal Treatment at Foundry A

Alloy: A356; Heat Size: 400 lb. Furnace Type: Heated Ladle

Average Pour Temperature: 730 - 740°C

<u>Treatment Number</u>	<u>Degassing Details</u>	<u>Treatment *</u>	<u>Hydrogen Content**</u>
1, 2, 3	none	Strontium (0.02%)	$\rho = 2.09$ gm/cc
4, 5, 6	Ar/Flux	Strontium (0.01%)	$\rho = 2.66$ gm/cc
7, 8, 9	Ar/Flux	Strontium (0.02%) Grain Refined (Ti $\approx$ 0.20%)	$\rho = 2.65$ gm/cc

*Titanium content as melted, 0.16%.

**Hydrogen determinator not available, figures given are densities for reduced pressure test samples.

Table 3. Details of Molten Metal Treatment at Foundry B

Alloy: 319; Heat Size: 8,000 lb. Furnace Type: Reverberatory

Average Pour Temperature: 700°C

<u>Treatment Number</u>	<u>Degassing Details</u>	<u>Additions</u>	<u>Hydrogen Content</u>
1	Rotary	Ti $\approx$ 0.16% Sr $\approx$ 0.002%	0.127 mls/100 gm
2	Rotary	Ti $\approx$ 0.15% Sr $\approx$ 0.09%	0.139 mls/100g

Table 4. Details of Molten Metal Treatment at Foundry D

Alloy: 356.1; Heat Size: 400 lb.; Furnace Type: Resistance

Average Pour Temperature: 732°C

<u>Treatment Number</u>	<u>Degassing Details</u>	<u>Additions *</u>	<u>Hydrogen Content</u>
R	As melted	none	0.105 mls/100 gm
S	Moist Ar	none	0.325
G	Ar	none	0.187
BL	Ar/Flux	none	0.312
BR	Ar/Flux/Ar**	Sr = 0.010%	0.266
W	Ar/Flux/Ar**	Ti/B add. (Ti = 0.20%)	0.217

* Sr = 0.005% and Ti = 0.070 as melted. ** After addition was made, Ar used to stir bath

(a)

(b)

Figure 1. Filter bracket casting with rigging
 (a) top poured, uphill
 (b) bottom gated (3rd riser, not shown, is located over first ingate)

Finally, as a result of outside interest shown in the above tests, an independent supplementary series of experiments has been undertaken in a fifth foundry. The purpose of the supplementary tests was to elucidate further the controversial effect of strontium modifier addition on porosity distribution in A356. A different configuration (long horizontal one and two inch, 25 and 50 mm square-section bars) was chosen for these tests. Preliminary runs confirmed the adverse effect of strontium on feeding, but also revealed a hitherto unreported aspect of the types of porosity associated with this treatment; a metal-mold reaction which occurred only with the two inch (50 mm) square bars. Hence, a second pour has been undertaken, wherein an addition of beryllium has been made in an attempt to preclude this reaction. This supplementary work was reported at the 1994 AFS Castings Congress.²⁴

3.2 Castings Poured at The University of Alabama

Throughout the program, a number of test castings were poured in alloys A356, A206 and 535 in the foundry at The University of Alabama (UA). Two sand practices were adopted, green sand and chemically, bonded (Pepset_{TM}) sand. The results of the experiments with A356 poured in green sand have been reported previously^{9, 13} and were concerned with both one-half and two inch (12.5 and 50 mm) section thickness plates. The majority of the tests with A356 utilized one particular metal source, a foundry pig which contained both strontium and titanium¹⁷. No further melt additions were made. Degassing was undertaken for all heats poured using dry argon (15 minute treatment). Reduced pressure tests indicated a satisfactory degassing treatment.

3.3 Rigging Design

The term "rigging" is often used to describe the gating and feeding system used in pouring a casting. For the test plate castings involved in the current investigation the rigging designs were either those provided on the pattern by Foundry A, or were designed by the UA team. Where such design was undertaken, the recommendation for feeding of Jacob et al.²⁵ and/or the data provided by Pan et al. (26) was taken into account. This information, which is of considerable interest to practicing foundries, and which is not widely known in the aluminum casting industry, is presented in Figure 2. It is presented in the form of required volume ratio ($VR = \text{volume riser} / \text{volume casting}$) plotted against modulus ratio ($MR = \{V/A\}_{\text{riser}} / \{V/A\}_{\text{casting}}$). The solid line is that given by Pan et al. for an alloy equivalent to A356. This type of relationship follows the type of recommendation made by Caine for low carbon steel castings²⁷. Reference should be made to Table 5 for details of the risers used in the current program. The modulus ratio (MR) selected ensures that the riser freezes after the casting (or adjacent portion of the casting, if the design is complex), while the volume ratio (VR) provides for a sufficiently large volume of feed metal in the riser. Jacob and co-workers suggest:

$$1.2 < MR < 1.3$$

and

$$V_{\text{riser}} \sim 0.5 V_{\text{casting}}$$

that is

$$VR \sim 0.5$$

The approximate co-ordinates of this recommendation are considerably to the left of the line drawn by Pan et al.

Regarding range of action of the riser (i.e. feeding distance), no particular axiom was used in the design. Indeed, the hope was that the experiments conducted might shed light on this aspect.

(Note: Davies has suggested that feeding range for Al - 7Si type alloys is approximately five multiples of the average thickness of the casting, see reference 4). Rigging details are given in Table 5.

Gating of all plate casting was arranged to be on the parting plane. All plate castings were molded in the cope portion of the mold. Illustrations of the various gating systems are provided in references 17 and 22.

Table 5. Details of Rigging for Various Castings Poured

Table 5a. Plate Castings

Casting	Dimension s (in)	Riser Height (in)	Riser Cross Section		MR	VR
			Top	Bottom		
Plate (UA)	12 x 4 x 0.5	4	2.5 x 12	0.7 x 2.0	1.3	0.4
Plate (C)	12 x 4 x 0.5	3	4.0 x 1.5	4.0 x 1.0	1.7	0.6
Plate (C)	13.5 x 5.9 x 0.75	4	6.7 x 1.8	1.8	0.9	0.9
Plate (UA)	12 x 4 x 2.0	4	4.76 x 4.0	4.0 x 3.0	1.2	0.6

All plates gated on pouring plane and molded in cope. For typical gating, see references 17 and 22.

UA plate also cast with alternate riser, 3 inch diameter x 3.75 in high; MR = 2.5, VR = 0.9.

Table 5b. Shaped Castings
(Filter Bracket, 7 x 3.2 x 2 inches)

(Pillar Bracket, 1' X 5.2' X 2' inches)									
Riser	Height	Riser Diam.				MR ₁	MR ₂	VR ₁	VR ₂
Riser 1	Riser 2	Riser 1		Riser 2					
		Top	Bottom	Top	Bottom				
3.75	4.75	2	1	1.5	1	1.6	1.4	0.9	0.8

First pour: Riser 1 fed heavy boss and Riser 2 fed lighter boss (see Figure 1).

Second pour: incorporated three risers (see Figure 1)

MR₁ = 1.4, MR₂ = 2.0, MR₃ = 1.6, VR₁ = 0.5, VR₂ = 1.2, VR₃ = 1.3.

Finally it should be noted that for the second pour of the filter bracket casting a rigging design was drawn up using a knowledge base expert system developed at the University of Alabama²⁸. This rigging system provides for a more quiescent entry of liquid metal into the mold cavity than that associated with the first pour, which involved pouring uphill, but through one of the risers (above boss 2).

3.4 Evaluation of Castings

All castings poured during the present program were divided and systematically assessed for porosity distribution. The method for porosity determination chosen was gravimetric. In this method, samples from the divided castings were weighed in air and in water and their densities, as cast, determined using the method of Archimedes. The differences between this density (ρ) and the maximum theoretical density ($\rho_{\max}$) attainable in the alloy concerned were then compared according to

$$\text{Porosity (\%)} = (\rho_{\max} - \rho) 100/\rho.$$

Figure 2. Volume Ratio (V_R/V_c) plotted against freezing of modulus ratio (M_R/M_c) for Al-7Si-Mg alloy castings produced by various investigators. Acceptability criteria based on density distribution, except for Pan *et al.*

Although this technique works well for A356 and 535 alloys, great difficulty was encountered in the copper containing alloys A206 and 319 because of the confounding action of the macrosegregation of copper. Although this effect had been reported in the French literature,²⁵ it has apparently not been taken into account by some previous investigations and may well have contributed to the wide scatter of experimental values of porosity reported for A206 and similar alloys.^{7,29}

Thus, to obtain a more accurate assessment of local porosity, it was necessary to determine the *local* maximum density, that is, eliminate the effect of the copper segregation, as otherwise this effect was frequently sufficient to lead to negative porosity values where copper enrichment occurred. The local values required were estimated using hot pressing or upsetting samples bidirectionally to close up porosity, and subsequently calculating local maximum density.

4.0 Results

Although tests have been conducted using four aluminum base alloys, correlational work has been concentrated on alloy A356. Consequently, results presented here and the following discussion reflect this distribution of activity.

4.1 Results with A356 Test Castings

Test castings in plate form of various thicknesses were poured in both green sand and chemically bonded sand. The widest range of criteria function values was encompassed in tests conducted at UA using green sand practice. Figure 3 shows the results of the tests performed. The measured porosity values are plotted against the criteria function (in this case the Niyama or NUMS function). It will be seen that the criteria function (CF) values with the largest magnitude are associated with the chilled two-inch (50 mm) thick section, while the smaller values are associated with the one-half inch (12.5 mm) section. This data was then used to predict porosity distribution in individual green sand cast plates. Figure 4 presents a comparison between measured and predicted data for a two-inch (50 mm) thick chill. Comparisons were also made between the various criteria for the green sand castings.

Figure 3. The relationship between $G/\sqrt{R}$ (NUMS) and porosity for A356 alloy and green silica sand (melt degassed with pure Ar for 15 minutes).

Figure 4. Predicted porosity profile for a 2 inch (50 mm) slab gated and risered at one end (opposite to free end) as predicted from data in Figure 3

Figures 5 and 6 show correlations existing respectively between the NUMS criterion and the newly developed Feeding Resistance Number Criterion (FRN)¹³ and porosity. It will be seen that while the NUMS criterion only warrants an R^2 value of 0.54, the FRN possesses an R^2 value of 0.84, which indicates that a reasonably high degree of confidence may be placed in this approach. Figure 7 compares the prediction of porosity distribution in a two-inch (50 mm) plate casting in green sand with a pure aluminum chill, using the NUMS, LCC and FRN criteria. Again the excellent agreement with the FRN is apparent.

Figure 5. Correlation of measured porosity and computed values of NUMS criteria function for 2 inch bars with and without an end chill.

Figure 6. Correlation of measured porosity and computed values of the Feeding Resistance Number, Co, for 2 inch bars with and without an end chill.

Figure 7. Measured porosity and porosity predicted by various criteria functions along a 2" A356 cast bar with and end chill.

Results of the tests conducted in commercial Foundry A were confined to one-half inch (12.5 mm) section castings poured in chemically bonded sand. Consequently they cover only a narrow range of CF values. Nonetheless, because all castings were poured from a single heat of metal, the effects of flux-degassing and of subsequent grain refinement additions are very clearly seen (Figures 8-10). Although, like the results of the green sand castings, considerable scatter is still present, the general features of the relationships or maps concerned again indicate that there exists a range of small CF values where there appears to be a strong effect of thermal parameters upon porosity. There is also a region of each map where the level of porosity is relatively independent of the CF value and more dependent upon the metal treatment, in particular the degassing treatment. It is also seen, however, that for this combination of melt treatments, the addition of the titanium boron slightly lowers the level of porosity, as the chilled locations (high CF values). This effect may not be present at very low CF's, however.

4.2 Results with 319 Castings

Using Foundry A's tooling and chemically bonded molds produced by that organization, castings were poured in alloy 319 in Foundry B. The alloy again came from one heat, melted on this occasion in a large reverberatory furnace fitted with rotary degassing equipment. The hydrogen content of the melt ranged between 0.12 and .014 ml/100 gm. One-half and three-quarters inch thick plate (12.5 and 19 mm) castings, with and without end chills were poured.

The castings were evaluated gravimetrically for porosity distribution and solidification simulations undertaken, which were then validated with thermocouple data. The simulation results were interrogated to produce CF data (undertaken at 520°C) and a porosity - CF map produced (Figure 10). At this point in the investigation, the team was made aware of the

Figure 8. Porosity-criteria function map for A356 (no degassing, no Ti/B, but Sr modified) poured in chemically bonded silica sand

Figure 9. As Figure 8, but using flux degassing

Figure 10. As Figure 9, but Ti/B grain refiner stirred in with Ar.

potential effects of copper segregation upon porosity calculations, as discussed previously. Examination of the results for porosity coupons excised from the casting which were at the top

of the scatter band in Figure 11 indicated that they contained a low copper content. Those in the lower portion of the scatter band exhibited high copper contents. After the application of the hot upsetting (pressing) treatment to a representative number of samples to determine local maximum densities, a corrected map was produced. (Figure 12).

Figure 11. Porosity-criteria function map for alloy 319, rotary degassed, uncorrected data.

Figure 12. Porosity-criteria function map for alloy 319 rotary degassed, corrected data.

4.3 Results with A206 Castings

Again using Foundry A's tooling but the mold making capacity of Foundry C, a large number of molds were produced, again for one-half and three-quarter inch (12.5 and 19 mm) thick plates. Both chilled and non-chilled versions were again prepared. Foundry pig melted in 400 lb.

capacity gas fired crucible furnaces was prepared for pouring and a number of different degassing practices followed. These treatments were performed in such a way that minimum interaction occurred. For example, metal was regassed prior to any second further degassing treatment. Fluxing degassing treatments, if practiced were performed only *after* non-fluxing type treatments.

The results of these tests, again showed that those porosity coupons yielding results in the upper part of the scatter band were those containing low copper contents, while those at the bottom of the band possessed high copper levels.

4.4 Results with 535 Castings

A limited number of tests were performed with alloy 535, a magnesium aluminum alloy, known to be prone to layer porosity, and sensitive to mass feeding. This alloy appeared to be an ideal choice therefore to study the effects of riser size. Two one-half inch (12.5 mm) thick plates were poured from one heat of this material. However, each plate was associated with a riser of different configuration (see Table 5).

The striking difference in the porosity distribution obtained will be seen from Figures 13 and 14. It will also be noted that the distributions are not symmetrical with respect to transverse cross-section. The resulting porosity maps (Figures 15 and 16) would seem to suggest that the mass-feeding effect encouraged by the large cylindrical riser pushes down the upper boundary of the porosity- CF map. However, further castings should be poured to separate this effect from that of riser modulus upon CF values.

Figure 13. Porosity surface for the 0.5 inch alloy 535 plate, degassed 15 mins with Ar, cylindrical riser.

Figure 14. As Figure 11, but plate fed by rectangular riser

Figure 15. Portion of porosity-CF map for alloy 535. Refer to Figure 12.

Figure 16. Portion of porosity-CF map for 535. Refer to Figure 13.

4.5 Results with A356 Commercial Castings

A series of castings of a small but relatively complex shape (the filter bracket casting) was poured in Foundry D from a resistance-heated 400 lb. capacity furnace. A number of different melt treatments were conducted. They were again arranged so that minimal interaction occurred.

The castings were sectioned and sampled for porosity distribution. Using commercial software codes, freezing and filling simulations were performed and various maps produced. The maps obtained displayed such data as temperature distribution in filling, temperature distribution after filling at different elapsed times, as well as CF data. Figures 17-20 show representative information from a typical simulation of the first series of tests which employed the top poured rigging arranged with uphill pouring (see Figure 1). Porosity distributions are shown in Figures 21 and 22 for castings subjected to two different melt treatments.

5.0 Discussion

In order to properly interpret the data presented in the various porosity maps, this information must be viewed collectively, especially since the *range* of the criteria function concerned (NUMS function) varies unavoidably from one set of experiments to another. The CF range concerned is dependent on three principal factors:

- (a) the controlling geometric feature of part (e.g. thickness, in the case of plates)
- (b) the location of the region under consideration within that geometry (e.g. distance from 'free' end, in the case of plates)
- (c) the presence, or absence, of a chill

Thus, for a particular plate thickness, a range of CF values will be occupied.

The place of the CF within that range will be governed by its position with respect to the 'free' end, that is the end of the casting away from the riser. Finally, the CF range for any given casting will be extended towards higher values of CF, if a chill is located at the free end. Typical CF ranges observed are given below (NUMS Values):

Plate Thickness (in) (mm)	Chilled (C) or Nonchilled (N)	Range (SI units)
1/2 (12.7)	N	200-500
	C	500-2000
3/4 (19)	N	500-1400
	C	1500-2600
2 (50)	N	200-2500
	C	1500-7500

Beyond this, the volume of the riser chosen, together with the thermophysical properties of the alloy poured, and the point during solidification at which the output of the simulation is interrogated to obtain the appropriate thermal parameters (G, R, V, etc.), will also have important but secondary effects upon the CF.

If it is assumed that these secondary effects can be set aside for the purposes of discussion, it will be seen that for the results which cover the widest range of CF's, i.e. those involving the experiments in A 356 poured in green sand molds at the University, two regions exist on the CF-porosity map, represented by Figure 3:

- (i) A region associated with lower CF values (NUMS <2000 in SI units) where there appears to be a strong dependence of maximum porosity observed upon CF
- (ii) A region associated with higher CF values (NUMS >2000 in SI units where there is considerably less dependence of porosity on CF)

Although embracing a much narrower range of CF values, the results obtained in foundry A for one-half inch (12.5 mm) thick castings poured in a chemically bonded sand (Pepset_{TM}) also follow this general trend. Reference to the various data presented on the porosity maps (Figs. 8-10) suggests the following *maxima* for porosity at high CF's, that is at more highly chilled locations, as each is associated with an asymptote (P_{max})_{chill}:

- Green sand / Argon degassing combination
(P_{max})_{chill} ~ 0.5% porosity maximum
- Pepset / Flux-degassing combination
 - (i) without TiB grain refiner ~ 0.35%
 - (ii) with TiB grain refiner ~ 0.25%
- Pepset / no degassing treatment ~ 1.0%

However, it should be noted that the first porosity level listed may be more a reflection of the limited scale of success in degassing small induction melted 30 lb. batches, as compared to that of degassing a 400 lb. resistance furnace melted heat. This possibility of inadequate degassing associated with small batches of molten metal may well have had an effect on the limited data provided for alloy 535, Figures 15 and 16, which were concerned with castings poured into the chemically bonded sand using

Figure 17. Isotherms after 10% of alloy has solidified, A356 filter bracket

Information

Time 00:00:14.74
 Date 10/20/14
 User 10/20/14

Product: 210101
 Version: 011
 Number of CVs: 1053040
 File Size: 1111111111

0.300	0.286	0.271	0.257	0.243	0.229	0.214	0.200	0.186	0.171	0.157	0.143	0.129	0.114	0.100

Figure 18. NUMS
distribution for
filter bracket
(Simulation
interrogated at
solidus)

Information

Project: 2000
Version: 2000
Number of CV's: 100000
Min-Max: 1.000000

21
273

Figure 19. Flow
potential CF
distribution for filter
bracket

100.0
97.1
95.7
94.3
92.9
91.4
90.0
88.6
87.1
85.7
84.3
82.9
81.4
80.0

Feeding
[%]

100.0
97.1
95.7
94.3
92.9
91.4
90.0
88.6
87.1
85.7
84.3
82.9
81.4
80.0

Project: 20010
Version: 0.01
Number of CVs: 100000
File: May 25 11:12 10 1991

Information

— Figure 20. Porosity distribution for A356 alloy filter bracket which was treated with moist argon and had hydrogen content of 0.325 mls/100g

induction melted metal (~ 30 lb. batch). More experiments should be undertaken to determine the reason for the wide range of porosity change for a small change in CF value with this alloy. Such experiments might also confirm or deny the effects of possible mass-feeding.

It is next appropriate to examine the results of all the experiments performed in the various commercial foundries. If the corrected porosity maps for 319 and A206 are compared with A356 which was both strontium treated and grain refined, some interesting conclusions arise. All the data are encompassed by a line drawn from about 0.75% near the porosity axis to a point about 2500 NUMS along the CF axis. This suggests that with moderately well degassed melts (hydrogen content no greater than 0.20 cc/100 grams), less than 1% porosity is probably readily achievable with NUMS CF values above 100 SI units.

All of the above discussion has revolved around use of the NUMS CF. From what has been observed thus far, similar behavior would be expected using the LCC criterion and also the Feeding Resistance Number, FRN criterion. It will be recalled that the high correlation coefficient with data for A 356 in green sand favored the FRN criterion over that of either the NUMS and LCC criteria.¹⁶ Consequently, the various thermophysical constants needed to compute the FRN values should be determined, and

Figure 21. Porosity distribution for A356 filter bracket to which TiB_2 was added, argon degassed, and which had hydrogen content of 0.217 mls/100g.

porosity data plotted as a function of FRN for each of the other aluminum alloys concerned. These values could then be used to evaluate the predictive power of the new criteria function more fully.

Finally, turning to the data generated in connection with the filter bracket casting, the predictions of the commercial simulation programs indicate that porosity criteria function maps are clearly capable of locating possible porosity. Sectioned castings did indeed show significant porosity levels in two of the areas predicted. The NUMS criterion also incorrectly predicted porosity in the inner rim of the heavier section of the casting. The reasons for this are not clear. However, it should be noted that, at present, the commercial software concerned interrogates the simulation at the end of solidification, whereas the present investigation has recommended interrogation just prior to the eutectic arrest for A356. However, it is gratifying to note that this NUMS prediction erred on the conservative side. Consequently, more work will be required to specify exact levels of porosity with accuracy. Nonetheless, the overall predictive capacity of such codes represents a highly viable new tool for the foundry methods engineer and tooling builder.

6.0 Conclusions

The following general conclusions can be drawn from the current investigation:

1. The level of criteria function exhibited at a particular point in a shaped casting depends on casting geometry, the location of that point within the casting, and the presence or absence of a chill. In particular, chills widen the range of CF values encountered.
2. A number of other factors appear to affect CF distribution. They are the relative volume of the riser with respect to the portion of the casting it feeds, the thermophysical properties of the alloy and the point during solidification at which the simulation is interrogated to obtain the thermal parameters used in computing the CF value.
3. From the data assembled with alloy A 356, there appears to be two regions of importance on the porosity-CF map. The first, which is found at low CF's (<2000 SI units with the NUMS CF), where there may be a strong dependence of porosity on the criteria function. The second, at higher CF value (>2000 SI units with the NUMS CF), where the porosity level is strongly dependent on hydrogen content and much less dependent upon the CF value.
4. For moderately-well degassed aluminum alloys of the type investigated (hydrogen contents below 0.20 ml/100 gm), it would appear that porosity levels below 1% are achievable above CF's of 100 for the NUMS scale in SI units and levels below 0.5% with CF's greater than 1000. However, from the results of the filter bracket casting tests, it is suggested that the availability of feed metal (i.e. sufficiently large riser volume) must be assumed. This emphasizes the point made by others that the freezing pattern within the riser itself assumes special importance²⁹ and should form part of the criteria used in designing rigging.
5. Given the assumption of the availability of liquid feed metal, it is believed that CF's calculated from the interrogation of a solidification simulation should provide conservative predictions of the location of porosity prone areas.
6. From the limited data presently available, the FRN criterion appears to be superior to both the NUMS and LCC based approaches. The two latter criteria yield closely similar predictions.

Regarding future work, additional experiments evaluating the utility of the feeding resistance number (FRN) CF should be undertaken. This activity should be focused on alloys other than A 356, such as 319, 206, B 201 and A 357 which are also of growing commercial importance. A more in-depth examination of the problem of determining porosity with good accuracy at low levels should also be carried out. In particular, image analysis methods should be compared with those based on gravimetric measurements. This will be needed to distinguish more clearly between the effects of different degassing methods, different inclusion levels and the possible effects of mass feeding related phenomena. At present, these effects are probably masked by uncertainty of porosity level measurement.

6.0 Technology Transfer Activities

From its inception, this task has received the expert guidance of the AFS Heat Transfer Committee (now renamed the Process Design and Modeling Committee). Representatives of foundries, research organizations and software houses hold membership of the committee. As well as providing guidance, the committee members have already incorporated a number of the findings of the project into their modeling activities.

Additionally, the presentation of papers at the AFS Castings Congress (1992 and 1993) has made many other members of the cast metals industry aware of this work. Furthermore, Professor Berry, through his membership of the AFS Aluminum Division's Research Committee has been able to brief that group of the progress of the investigation.

Finally, through contact with the investigation, at least three casting related organizations have intensified their own research in this area. In collaboration with the UA Team, papers on these spin-off activities, as well as from the current investigation, have been presented at AFS Casting Congress sessions.

Acknowledgments

In the course of this task, many organizations contributed materials, instrumentation, and services. They are listed below.

Beck Aluminum
Reynolds Aluminum
Morris Bean and Company
Reliable Castings, Inc.
ECK Industries, Inc.
Southern Aluminum Castings, Inc.
Foundry Information Systems
Wedron Fluxes
Ford Motor Company
CMI, Inc.
Magma Foundry Technologies, Inc.
UES, Inc.
A. Kearney and Company
CTC, Inc.

References

1. P.N. Hansen, J.T. Berry, "The Simulation of Heat Transfer in Castings and Weldments - Some Thoughts on Needed Research," *Modeling of Casting and Welding Processes, I*, (H. Brody and D. Apelian, Eds.) 1981, pp. 497-501.
2. T.S. Piwonka, M.C. Flemings, "Pore Formation in Solidification," *TMS-AIME Transactions*, Vol. 236, 1966, pp. 1157-1165.
3. W.D. Walther, C.M. Adams, H.F. Taylor, "Mechanism for Pore Formation in Solidifying Metals," *AFS Transactions*, Vol. 64, 1956, pp. 658-664.
4. V. de L. Davies, "Feeding Range Determination by Numerically Computed Heat Distribution," *AFS Cast Metals Research Journal*, Vol. 11, 1975, pp. 33-44.
5. E. Niyama, T. Uchida, M. Morikawa, S. Saito, "A Method of Shrinkage Prediction and its Application to Steel Casting Practice," *AFS Cast Metals Research Journal*, Vol. 7, No. 3, 1982, pp. 52-63.
6. Y.W. Lee, E. Chang, C.F. Chieu, "Modeling of Feeding Behavior of Solidifying Al-7Si-0.3Mg Alloy Plate Casting," *Metallurgical Transactions*, Vol. 21 B, 1990, pp. 715-722.
7. Y.W. Lee, E. Chang, Y.S. Kuo, Y.L. Lin, C.H. Yeh, "Effects of Casting Geometry on the Feeding Behavior on an A 206 Aluminum Alloy Plate Casting," *Cast Metals*, Vol. 3, 1990, pp. 106-111.
8. S. Shivkumar, L. Wang, D. Apelian, "Molten Metal Processing of Advanced Cast Aluminum Alloys," *Journal of Minerals, Metals, and Materials Society*, Vol. 43, 1991, pp. 26-32.
9. V.K. Suri, H. Huang, J. T. Berry, J.L. Hill, "Applicability of Thermal Parameter Based Porosity Criteria to Long Freezing Range Aluminum Alloys," *AFS Transactions*, Vol. 100, 1992, Paper 92-166.
10. V. Laurent, C. Rigaut, "An Experimental and Numerical Study of Criteria Functions for Predicting Microporosity in Cast Aluminum Alloys," *AFS Transactions*, Vol. 100, 1992, Paper 92-163.
11. G.K. Sigworth, C. Wang, "Evolution of Porosity During Solidification," *AFS Transactions*, Vol. 100, 1992, Paper 92-191.
12. K. Tynelius, J.F. Major, D. Apelian, "A Parametric Study of Microporosity in the A 356 Casting Alloy System," *AFS Transactions*, 1993, paper 93-166.

13. H. Huang, V.K. Suri, N. El-Kaddah, J.T. Berry, "The Effect of Interdendritic Feeding on Microporosity Formation," *Modeling of Castings, Weldments and Advanced Solidification Processes, VI*, (T. Piwonka, V. Voller, and L. Katgerman, Eds.) TMS, 1993.
14. W. S. Pellini, "Factors Which Determine Riser Adequacy and Feeding Range," *AFS Transactions*, Vol. 61, 1953, pp. 61-80.
15. J.G. Henzel, J. Keverian, "The Theory and Application of a Digital Computer in Predicting Solidification Patterns," *Journal of Metals*, Vol. 17, 1965, pp. 561-568.
16. V.K. Suri, "Theoretical and Experimental Studies on Pore Formation During Casting Solidification," Ph.D. Dissertation, The University of Alabama, 1993.
17. J.T. Berry (Ed.), Final Report, Phase 1, "Determination of Correlation Factors for the Prediction of Shrinkage in Castings," AFS, 1993.
18. H. Huang, "An Investigation of Thermal Contact, Phase Change, and Computational Efficiency in Modeling Shaped Casting Solidification," Ph.D. Dissertation, The University of Alabama, 1992.
19. RAPIDCAST Program, CTC Corporation, Johnstown, PA, 1992.
20. MAGMA Program, Magma Foundry Technology, Inc., Arlington Heights, Illinois.
21. CAP Program, EKK Computer Modeling and Analysis, Rochester, MI.
22. H. Huang, J.T. Berry, "Evaluation of Criteria Functions to Minimize Porosity Formation in Long Freezing Range Alloys," Presented at 1993 AFS 97th Casting Congress, Chicago, IL.
23. L.E. Marsh, G. Reinemann, "Premium Quality Aluminum Castings Theory, Practice and Assurances," *AFS Transactions*, Vol. 87, 1979, pp. 413-422.
24. G. Sigworth, J.T. Berry, et al, unpublished data, 1993.
25. S. Jacob, M. Drouzy, "Contribution a L'etude du Masselottage des Alliages D'Aluminium Coules en Sable," *Foundrie*, No. 296, 1970, pp. 395-406.
26. E.N. Pan, C.S. Lin, C.R. Loper, "Effects of Solidification Parameters on the Feeding Efficiency of A 356 Aluminum Alloy," *AFS Transactions*, Vol. 56, 1948, pp. 492-501.
27. J.B. Caine, "A Theoretical Approach to the Problem of Dimensioning Risers," *AFS Transactions*, Vol. 99, 1991, pp. 91-96.
28. J.L. Hill, J.T. Berry, S. Guleypoglu, "Knowledge Based Design of Rigging Systems for Light Alloy Casting," *AFS Transactions*, Vol. 99, 1991, pp. 91-96.
29. H.D. Brody, S. Viswanathan, R.A. Stoehr, "Predicting Shrinkage Microporosity in Aluminum Copper Alloys," *Modeling of Castings, Weldments, and Advanced Solidification Processes*, Vol. V, (M. Rappaz, M. Ozgu and K. Mahin), 1991, pp. 455-460.
30. L. Backerud, G. Chai, J. Tamminen, "Solidification Characteristics of Aluminum Alloys, Vol. 2, Foundry Alloys," AFS/Skanaluminium, 1990.

Task 11

COMPUTER AIDED COOLING CURVE ANALYSIS

D.M. Stefanescu and S. Viswanathan

COMPUTER-AIDED COOLING CURVE ANALYSIS FOR DUCTILE IRON

1.0 Introduction

Statistical methods are being widely used for engineering purposes. In this work a statistical design based upon the Taguchi method was developed to attempt to predict the microstructure of ductile iron from the data obtained through cooling curve analysis. The correlation of three microstructural parameters, the nodule count, nodule shape factor and the nodularity of the structure, to the liquid processing of the iron and selected cooling curve parameters was attempted. Processing parameters studied were the amount of pig iron used in the charge, the superheat temperature, the holding time at superheat temperature, and the pouring temperature. Second order interactive terms were also considered, to develop a regression equation between the variables and final microstructural parameters (nodule count, shape factor and nodularity).

2.0 Background

Cast iron is basically a ternary alloy system of Fe, C, and Si. Cast irons are classified by the form that the carbon takes on solidification as flake graphite (FG), compacted graphite (CG), spheroidal graphite (SG — also known as "ductile" or "nodular" iron) and white iron, where the carbon is present as iron carbide.

Graphite can be stabilized during solidification by the addition of graphitizers to the alloy. Examples of graphitizers are Si, Ni, Cu, Co, Al, P and As. In the same manner, iron carbide can be stabilized by the addition of carbide formers such as Cr, B, Mn, Mo, and W. Graphitizers increase the interval between the stable and the metastable eutectic temperatures, thus providing a wide range for gray iron solidification. Carbide promoters, however, decrease this interval. Because of this effect, it appears that thermal analysis can be used to judge the suitability of the melt to produce a particular type of casting.

Thermal analysis is the process of determining the temperature at which changes occur in atomic arrangement, such as phase transformation, by observing the changes which the evolved heat imposes on the rate of temperature change in the metal.¹ Cooling curve analysis is by far the most widely used method for chemical composition evaluation of cast iron because of the established relationships between some features of the cooling curve and the composition.

Other thermoanalytical methods² include differential thermal analysis (DTA), dilatometry, calorimetry, and thermal conductivity tests. The main disadvantage of DTA is that a neutral reference is required which has the same thermal characteristics as the sample but does not undergo any transformations. Though this technique is very sensitive to the phase transformations occurring, it requires experienced persons and good laboratory equipment. Calorimetry measures the heat evolved during each phase transformation. Though this can be found by simply integrating the area under the DTA curve, a greater degree of precision is required than is normally available from a DTA test. Dilatometry measures the volume change of the specimen at each phase transformation. Larger sizes of samples are used for this to increase the volume affected. However, this technique takes more time than is appropriate for use as a production process control test.

Cooling curve analysis (CCA) is a temperature-time that contains the solidification history of the molten metal. This means that it can be an important tool in the control of molten

metal. Indeed, the information obtained from CCA can be used for the control of molten metal processing and to obtain a quantitative understanding of solidification phenomena.

As shown in Figure 1, the experimental set up for CCA consists essentially of a small sand cup with a thermocouple embedded in its center. The thermocouple is usually sheathed in a refractory tube, and its leads are connected to a microprocessor or data acquisition system.

Figure 1. Cooling Curve Analysis Experimental Set-Up.

A typical cooling curve and its first derivative are given in Figure 2. The shape of the cooling curve is affected by phase transformations occurring in the casting and heat extraction from the mold. The zero curve is an exponential or polynomial curve connecting points in the first derivative curve in which no phase transformation occurs. The area between the zero curve and first derivative curve is proportional to the amount of austenite and eutectic formed.³ Hence the cooling curve gives microstructural information that cannot be obtained by quantitative metallography. For example, the amount of primary austenite formed cannot be obtained from quantitative metallography because of solid state transformations which occur on cooling to room temperature, but it can be estimated from the cooling curve.

There is a definite correlation between the cooling curve and the as-cast microstructure.^{4,5,6} Significant differences also exist between the shape of the cooling curves in the case of each of the types of cast iron which can be produced. These differences may be attributed to the different nucleation and growth conditions prevailing during solidification. Figure 3 illustrates cooling curves of FG, SG, CG, and white irons of similar composition (having a carbon equivalent of 4.03).

Flake graphite irons show a shallow dome-shaped eutectic arrest. The amount of undercooling, however, depends on the graphite type and inoculation. Spheroidal graphite irons exhibit a flatter dome-shaped arrest. This is because of the addition of magnesium, which introduces nuclei in the melt. This results in a higher nucleation potential of the SG iron melt compared to an FG iron melt. The cooling curve of CG iron exhibits a pronounced dome shaped eutectic with a prominent recalescence. This is because of the

Figure 2. Cooling Curve, First Derivative, and Zero Curve.

Figure 3. Cooling Curves, showing differences for various hypo-eutectic cast irons.

lower number of nuclei present. White irons exhibit a flat eutectic arrest, because the entire solidification process in white iron takes place under the metastable eutectic temperature.

The addition of magnesium does not change the austenite arrest temperatures significantly. The addition of magnesium suppresses the bulk eutectic arrests significantly. This is different for hypo- and hyper-eutectic compositions. The hypo-eutectic compositions show a dome-shaped eutectic arrest with a considerable recalescence, while the hyper-eutectic compositions show a flat arrest with hardly any recalescence. An increase in the carbon equivalent raises the eutectic plateau and brings down the austenitic arrest temperature.

Therefore, at a particular value of carbon equivalent near the eutectic, it can be very difficult to distinguish between the austenitic arrest and the eutectic start temperatures. For hypo-

and mildly hyper-eutectic compositions the primary graphitic arrest is not visible because the latent heat evolved from the solidification of small amounts of graphite is very small. For strongly hyper-eutectic compositions an arrest corresponding to the precipitation of pro-eutectic graphite becomes prominent. These arrests are shorter than austenite arrests and have a prominent recalescence. The tail of the cooling curve corresponding to the end of solidification includes the growth of some intercellular carbides, depending on its slope. Post inoculation with FeSi brings the eutectic arrest temperatures closer to the equilibrium and raises the rate of recalescence. A good nodular iron has an absence of primary austenite liquidus arrest, a higher eutectic plateau, negligible recalescence and a slow cooling rate near the end of solidification.

3.0 Statistical Design

Mathematics

A regression equation is an equation for determining a dependent variable, say X_1 , from independent variables, say $X_2, X_3, \dots$ and is called a regression equation of X_1 on $X_2, X_3, \dots$. A linear regression equation of X_1 on X_2 and X_3 is given in equation (1).

$$X_1 = a + b X_2 + c X_3 \quad (1)$$

where a, b, c are constants.

The curve represented by equation (1) is a plane in a three dimensional rectangular coordinate system. The constants a, b, c are determined by solving simultaneously the normal equations given by equations (2), (3) and (4).

$$\sum X_1 = aN + b \sum X_2 + c \sum X_3 \quad (2)$$

$$\sum X_1 X_2 = a \sum X_2 + b \sum X_2^2 + c \sum X_2 X_3 \quad (3)$$

$$\sum X_1 X_3 = a \sum X_3 + b \sum X_2 X_3 + c \sum X_3^2 \quad (4)$$

where N represents the number of data points.

The standard error of estimate of X_1 on X_2 and X_3 is given by equation (5)

$$s_{1.23} = \sqrt{\frac{\sum (X_1 - X_{1\text{est}})^2}{N}} \quad (5)$$

where $X_{1\text{est}}$ indicates the estimated values of X_1 as calculated from the regression equation.

The coefficient of multiple determination is defined by equation (6) as

$$R_{1.23} = \sqrt{1 - \frac{s_{1.23}^2}{s_1^2}} \quad (6)$$

where s_1 is the standard deviation of the variable X_1 and is defined by equation (7) and $s_{1.23}$ is given by equation (5).

$$s_1 = \frac{\sum (x - \bar{x})^2}{N} \quad (7)$$

The coefficient of multiple determination lies between 0 and 1. The closer it is to 1 the better is the relationship between the variables and the closer it is to 0 the worse the relationship between the variables. In this case it can be concluded that the relationship that was assumed between the variables is not correct and some other kind of relationship probably exists.

Design of experiments

Two levels of four processing variables (% pig iron in the charge, superheat, holding time, and pouring temperature) were used in this study. This implies that 16 experiments must be conducted for a full factorial Taguchi experiment. The levels of the variables and their combination are given in Tables 1 and 2.

Table 1 Variable levels studied

Variable letter	Variable name	Level 1 value	Level 2 value
A	% pig iron	80 %	40 %
B	Superheating temperature	1540 °C	1580 °C
C	Holding time	0 minutes	10 minutes
D	Pouring temperature	1400 °C	1330 °C

Table 2 Experimental matrix employed in the statistical design

Trial No.	A level	B level	C level	D level
1	1	1	1	1
2	1	1	1	2
3	1	1	2	1
4	1	1	2	2
5	1	2	1	1
6	1	2	1	2
7	1	2	2	1
8	1	2	2	2
9	2	1	1	1
10	2	1	1	2
11	2	1	2	1
12	2	1	2	2
13	2	2	1	1
14	2	2	1	2
15	2	2	2	1
16	2	2	2	2

4.0 Experimental Technique

4.1 Melt Preparation

Charges weighing 40 lbs each were melted in an induction furnace. Each charge had known quantities of pig iron and scrap as fixed by the statistical design. The composition was adjusted at temperatures around 1350 °C by pouring samples into tellurium coated

ElectroNite cups which gave the %C, %Si and carbon equivalent values instantaneously from the white iron cooling curve. Silicon was added by using 75% FeSi and carbon was added by using graphite. The charge was then heated to the desired superheat temperature and held at that temperature as required by the experimental design. To spheroidize the melt it was then poured into a ladle containing 425g FeSiMg (5% Mg, 45% Si, rest Fe). After stirring the melt in the ladle, the melt was poured at the desired pouring temperature into ElectroNite sand cups which had a K type thermocouple embedded into them. These cups were placed over stands which were connected to a PC-XT through an IBM Dash-8 interface. The temperature in the middle of the cup was recorded as a function of time. One chill depth measurement sample was also poured at every pouring temperature. Hence one cooling curve sample, one chill depth sample and one spectrometer sample was poured at each pouring temperature. The experimental flow chart is given in Figure 4.

Figure 4. Experimental flow chart for the designed experiment.

4.2 Sample Characterization

All the samples were sectioned just below the thermocouple location and were polished for to determine nodule counts, shape factors and nodularity. They were evaluated by using an Olympus 2 image analysis system. The data was collected at a microscope magnification of 100X. An average of three readings taken across the diagonal of each sample was used for evaluation of nodule count, shape factor and nodularity. The system determines the nodule count by counting the number of nodules present in a fixed area at 100X. The shape factor is determined by dividing the area of each nodule with the square of its perimeter times 4π and averaging over all the nodules present in the screen. This means that the shape factor is very low for flake graphite and is equal to one when the nodules are perfectly spherical. Hence the determination of the shape factor gives an idea of how close the nodule is to a perfect sphere. Nodularity was defined as the ratio between the number of nodular graphite counts to the total number of graphite counts in 100X. The reader is referred to a chart⁷ for the differences between nodular and non-nodular graphite.

5.0 Results

5.1 Experimental nomenclature

In Table 3, P = % pig iron used in the charge (multiply by 10), S = superheating temperature ($^{\circ}\text{C}$), H = holding time (minutes), and Po = pouring temperature ($^{\circ}\text{C}$). So, for example, P8S1540H10Po1330 would indicate that the processing condition for the melt involved using 80 per cent pig iron in the charge, superheating to 1540 C, holding at that temperature for 10 minutes, and then pouring at 1330C.

Table 3

Processing conditions	Sample no.
P8S1540H0Po1400	S11
P8S1540H0Po1330	S12
P8S1540H10Po1400	S13
P8S1540H10Po1330	S14
P8S1580H0Po1400	S15
P8S1580H0Po1330	S16
P8S1580H10Po1400	S17
P8S1580H10Po1330	S18
P4S1540H0Po1400	S21
P4S1540H0Po1330	S22
P4S1540H10Po1400	S23
P4S1540H10Po1330	S24
P4S1580H0Po1400	S25
P4S1580H0Po1330	S26
P4S1580H10Po1400	S27
P4S1580H10Po1330	S28

5.2 Results of experimental trials

Table 4 shows the chemical analysis of the samples.

Table 4 Chemical composition, wt%.

Sample	%C	%Si	%Mn	%P	%S	%Mg	C.E.
S11	3.20	2.85	0.062	0.027	0.014	0.030	4.13
S12	3.20	2.85	0.062	0.027	0.014	0.030	4.13
S13	3.43	2.68	0.089	0.026	0.014	0.030	4.43
S14	3.43	2.68	0.089	0.026	0.014	0.030	4.43
S15	3.48	2.63	0.073	0.023	0.014	0.029	4.36
S16	3.48	2.63	0.073	0.023	0.014	0.029	4.36
S17	3.84	2.41	0.072	0.026	0.012	0.032	4.65
S18	3.84	2.41	0.072	0.026	0.012	0.032	4.65
S21	3.16	2.91	0.108	0.023	0.016	0.031	4.14
S22	3.16	2.91	0.108	0.023	0.016	0.031	4.14
S23	3.39	2.58	0.156	0.022	0.019	0.044	4.26
S24	3.39	2.58	0.156	0.022	0.019	0.044	4.26
S25	3.36	2.43	0.107	0.022	0.019	0.031	4.18
S26	3.36	2.43	0.107	0.022	0.019	0.031	4.18
S27	3.29	3.00	0.131	0.022	0.017	0.030	4.30
S28	3.29	3.00	0.131	0.022	0.017	0.030	4.30

The average nodule count and shape factor obtained is given in Table 5

Table 5

Sample No.	Nodule Count, N (mm ⁻²)	Shape factor SF	Nodularity NOD
S11	209	0.763	86
S12	229	0.785	79
S13	161	0.745	76
S14	181	0.765	75
S15	105	0.734	61
S16	144	0.736	55
S17	122	0.760	58
S18	127	0.824	56
S12	110	0.800	88
S22	179	0.815	89
S23	170	0.862	85
S24	205	0.809	96
S25	111	0.821	77
S26	99	0.766	73
S27	112	0.802	80
S28	123	0.756	78

Figure 5 shows a typical cooling curve obtained from the experiments.

Figure 5. Cooling curve and first derivative for sample S14

Selected cooling curve parameters for the samples studied are given in Table 6.

Table 6 Cooling curve parameters

Sample No.	T_{LA}	T_{ES}	T_{EU}	T_{ER}	T_{EE}	AP	MXCR	NPPE
S11	NA	1141	1138	1140	1116	NA	0.36	-1.27
S12	NA	1165	1133	1138	1108	NA	0.32	-2.56
S13	1167	1158	1144	1144	1100	-0.75	0.31	-2.47
S14	1190	1182	1141	1141	1088	-0.82	0.27	-2.09
S15	1196	1146	1140	1144	1102	-2.59	0.25	-2.35
S16	1183	1137	1132	1139	1107	-4.00	0.54	-2.50
S17	1176	1169	1135	1135	1089	-2.17	0.15	-2.23
S18	1141	1135	1133	1133	1096	-0.55	0.20	-2.70
S21	1159	1154	1141	1147	1108	-0.11	0.33	-2.22
S22	1159	1151	1138	1143	1100	-0.15	0.30	-2.22
S23	NA	1158	1136	1147	1089	NA	0.35	-2.23
S24	NA	1167	1137	1142	1096	NA	0.35	-2.52
S25	1161	1154	1140	1144	1084	-0.21	0.33	-2.05
S26	1160	1152	1138	1149	1088	-0.26	0/47	-2.05
S27	NA	1137	1132	1135	1088	NA	0.34	-2.25
S28	NA	1134	1131	1139	1081	NA	0.33	-2.30

NA = Not apparent from the cooling curve

where

T_{LA} = Temperature of austenitic arrest ($^{\circ}\text{C}$)
 T_{ES} = Eutectic start temperature ($^{\circ}\text{C}$)
 T_{EU} = Eutectic undercooling temperature ($^{\circ}\text{C}$)
 T_{ER} = Temperature of eutectic recalescence ($^{\circ}\text{C}$)
 T_{EE} = Temperature at end of eutectic solidification ($^{\circ}\text{C}$)
 AP = Austenitic peak ($^{\circ}\text{C}/\text{sec}$)
 $MXCR$ = Maximum recalescence rate ($^{\circ}\text{C}/\text{sec}$)
 $NPEE$ = Negative peak at eutectic end ($^{\circ}\text{C}/\text{sec}$)

Table 7 shows the nodule count obtained for different variable levels.

Table 7

Variable	Level	Nodule Count
B(1)	Superheat 1540 $^{\circ}\text{C}$	131
B(2)	Superheat 1580 $^{\circ}\text{C}$	114
C(1)	Holding 0 min.	124
C(2)	Holding 10 min.	122
D(1)	Pouring 1400 $^{\circ}\text{C}$	108
D(2)	Pouring 1330 $^{\circ}\text{C}$	136

5.3 Statistical Analysis of Results

To find the effect of a particular variable on the final microstructural parameter, and average of the parameter obtained at different levels was determined. For example, to determine the effect of percent pig iron in the charge on the nodule count, an average of the nodule counts obtained by using 80% pig and those obtained using 40% pig was determined. A graph of nodule count vs. % pig iron in the charge using average values was thereby representative of the variation of nodule count with % pig iron in the charge.

A direct comparison between the effect of different parameters cannot be made because of the dimensional differences between them. A common method to alleviate this problem is to center and scale (CS) the data.⁸ CS is a linear transformation that converts the data points to dimensionless parameters. This method involves centering the data about the mean and scaling it to its standard deviation. The CS data hence have a mean value of zero and a standard deviation of one. Mathematically this technique takes the form as shown in equation 8.

$$CS = \frac{x - \bar{x}}{\sigma} \quad (8)$$

where

x is the data point to be transformed
 $\bar{x}$ is the average of the data
 σ is the standard deviation of the data.

Center and scaling does not alter the statistical significance of a particular model. It just gives the direction of the variable's influence (positive or negative) and the magnitude of this influence.

Tables 8 and 9 illustrate the concept by showing the CS values for the processing and cooling curve parameters respectively.

Table 8. CS Values for Processing Parameters

Sample No.	Superheating temperature	Pouring temperature	Holding time
S11	-0.9354732	0.9354135	-0.9354553
S12	-0.9354732	-0.9354135	-0.9354553
S13	-0.9354732	0.9354135	0.9354553
S14	-0.9354732	-0.9354135	0.9354553
S15	0.9354732	0.9354135	-0.9354553
S16	0.9354732	-0.9354135	-0.9354553
S17	0.9354732	0.9354135	0.9354553
S18	0.9354732	-0.9354135	0.9354553

Table 9. CS Values for Cooling Curve Parameters

Sample No.	TES	TEU	TER	TEE
S11	-0.8579	0.1786	-0.04170	1.5831
S12	0.6260	-1.0118	-0.70904	0.7527
S13	0.1932	1.6070	1.29290	-0.0778
S14	1.6772	0.8927	0.29296	-1.3236
S15	-0.5488	0.6547	1.29295	0.1297
S16	-1.1053	-1.2499	-0.37537	0.6488
S17	0.8734	-0.5357	-1.71003	-1.2199
S18	-0.8579	-0.5357	-0.04171	-0.4931

The nodule count, shape factor and nodularity obtained in the first set of analysis were correlated with the processing and cooling curve parameters. The statistical software package SAS was used for obtaining a regression equation between the variables.

5.4 Results of Experiments

5.4.1 Nodule Count vs. Processing Parameters

The effect of superheating and pouring temperatures on nodule count is shown in Figure 6.

The graph shows that increasing the superheating and pouring temperatures decreases the nodule count. This is because increasing the temperature annihilates potential nuclei. The higher superheating temperatures may also be related to increased Mg loss, which would decrease its effect. Also, increasing the holding temperature leads to a loss of carbon from the melt, which also lowers nodule count.

Figure 7 shows the effect of % pig iron in the charge and holding time on nodule count.

The graph shows that increasing the amount of pig iron in the charge increases the nodule count. This is because larger amounts of undissolved graphite are present in the melt when higher amounts of pig iron are used. This increases the nucleation potential of the melt leading to higher nodule counts. There seems to be little effect of holding time on the nodule count.

Figure 6. Effect of superheat and pouring temperatures on nodule count.

Figure 7. Effect of percent pig iron in the charge and holding time on nodule count.

Figures 8 and 9 show that higher superheating temperatures result in lower values for nodularity. This is believed to be the result of magnesium loss at higher temperatures, which leads to lower nodularity. Pouring temperature and holding time have little effect on

nodularity. However, a higher percentage of pig iron in the charge decreases nodularity, perhaps because of the presence of deleterious elements in the charge.

Figure 8. Nodularity as a function of superheat temperature and pouring temperature

Figure 9. Nodularity vs. % pig iron in charge and holding time at superheat temperature.

Figure 10. Shape factor vs. superheat temperature and pouring temperature

As shown in Figure 10, increasing the superheat and pouring temperatures lowers the shape factor. Also, as was previously shown, high superheat temperatures result in a lower nodule count and nodularity. This implies that as the superheating temperature increases, the chance of forming degenerate graphite shapes also increases, resulting in a lower shape factor. Higher pouring temperatures result in a lower cooling rate, which increases the solidification time, which, in turn, promotes graphite diffusion from the nodules, also leading to a lower shape factor.

In Figure 11 it is seen that higher percent pig iron in the charge leads to a lower shape factor and the reverse is true. This effect could be related to the higher nodularity obtained with lower percent pig iron in the charge. The effect of holding time does not appear to be significant, although the shape factor does increase marginally with time.

Figure 11. Shape factor vs. % pig iron in the charge and holding time at superheat temperature.

5.4.2 Regression Equations

5.4.2.1 Nodule Count vs. Processing Parameters

The regression equations obtained were with the centered and scaled data:

$$\begin{aligned}
 N = & 149.19 + 10.91 \% \text{ pig} - 32.34 T_{\text{sup}} + 0.968 t_{\text{hold}} - 12.07 T_{\text{pour}} \\
 & + 2.33 t_{\text{hold}} T_{\text{sup}} + 6.73 T_{\text{pour}} T_{\text{sup}} + 3.00 T_{\text{pour}} t_{\text{hold}} - 4.20 \% \text{ pig } T_{\text{sup}} \\
 & + 1.27 \% \text{ pig } T_{\text{pour}} - 13.80 \% \text{ pig } t_{\text{hold}} \quad (9)
 \end{aligned}$$

with $R^2=0.8911$.

In equation (9) N stands for the nodule count, T_{sup} for the superheating temperature, t_{hold} for the holding time at the superheating temperature and T_{pour} for the pouring temperature. Equation (9) suggests that the superheating temperature is the single most important processing parameter that influences the nodule count (coefficient is -32.34). The negative sign preceding the coefficient implies that the nodule count decreases with increasing superheating temperature. As previously indicated, this results from the annihilation of potential nuclei as the superheating temperature increases. Also, higher pouring temperatures decrease the nodule count. In principle, a higher pouring temperature is associated with a lower cooling rate and hence a lower undercooling which results in a smaller number of nuclei. This results in a decrease in nodule count as pouring temperature is increased.

The effect of holding time is less significant (coefficient is 0.968). In addition, as seen in equation (9), there is a significant interaction between the percent pig iron in the charge and the holding time (the coefficient is - 13.80), and between superheating and pouring temperatures (the coefficient is 6.73). This means that, considering a simple linear regression equation, these second order coefficients might get added to the first order coefficients and hence lower the significance of the model.

5.4.2.2 Shape factor vs. Processing Parameters

The regression equation obtained with scaled and centered data was:

$$\begin{aligned} \text{SF} = & 0.788 - 0.024 \% \text{ pig} - 0.013 T_{\text{sup}} + 0.011 t_{\text{hold}} - 0.0018 T_{\text{pour}} \\ & + 0.0005 t_{\text{hold}} T_{\text{sup}} + 0.007 T_{\text{pour}} T_{\text{sup}} - 0.004 T_{\text{pour}} t_{\text{hold}} \\ & + 0.001 \% \text{ pig} T_{\text{sup}} - 0.012 \% \text{ pig} T_{\text{pour}} - 0.0007 \% \text{ pig} t_{\text{hold}} \end{aligned} \quad (10)$$

with $R^2=0.7112$

Equation (10) suggests that for a higher shape factor the holding time should be increased (+0.011). The effect of an increase in superheating temperature is to reduce the shape factor (0.013 coefficient). The effect pouring temperature is not very significant (-0.0018). The interaction term involving the percent pig iron in the charge and the pouring temperature may be significant (0.012). The other interaction terms are not significant (see their coefficients).

5.4.2.3 Nodularity vs. Processing Parameters

The regression equation obtained with the centered and scaled data was:

$$\begin{aligned} \text{NOD} = & 75.75 - 7.75 \% \text{ pig} - 8.78 T_{\text{sup}} - 0.258 t_{\text{hold}} + 0.646 T_{\text{pour}} \\ & + 1.07 t_{\text{hold}} T_{\text{sup}} + 1.20 T_{\text{pour}} T_{\text{sup}} - 1.47 T_{\text{pour}} t_{\text{hold}} \\ & - 2.40 \% \text{ pig} T_{\text{sup}} + 1.47 \% \text{ pig} T_{\text{pour}} - 1.87 \% \text{ pig} t_{\text{hold}} \end{aligned} \quad (11)$$

with $R^2=0.9858$.

Equation (11) suggests that the superheating temperature has the largest influence on nodularity (-8.78). As previously explained, this can be attributed to some loss of magnesium with increasing superheat temperature. Hence an increase in the superheating temperature decreases the nodularity and the nodule count (equation 9). An increase in the percent pig iron in the charge decreases the nodularity (-7.75). The effect of pouring temperature and the holding time on the nodularity is not very significant. Increased pouring temperature seems to increase the nodularity marginally.

5.4.2.4 Nodule Count vs. Cooling Curve Parameters

The cooling curve parameters obtained were correlated with the nodule count. The cooling curve parameters used were T_{ES} , T_{EU} , T_{ER} and T_{EE} . The regression equation obtained for the nodule count with the centered and scaled data was:

$$N = 149.19 + 26.81 T_{\text{ES}} + 24.83 T_{\text{EE}} - 15.91 T_{\text{EU}} - 0.513 T_{\text{ER}} \quad (12)$$

with $R^2 = 0.5249$

Equation (12) shows that the nodule count depends strongly on the eutectic solidification interval. Higher eutectic start and eutectic end temperatures reduce the eutectic solidification interval. This would thus increase the amount of free graphite and hence the nodule count so there would be fewer intercellular carbides. An increase in the temperature of eutectic undercooling would decrease the nodule count (the temperature is - 15.91). The temperature of eutectic recalescence seems to be less significant (-0.513). Nevertheless, there is a decrease in nodule count with an increase in the temperature of eutectic recalescence.

5.4.2.5 Shape Factor vs. Cooling Curve Parameters

The regression equation obtained for the shape factor with the centered and scaled data was:

$$SF = 0.787 + 0.0145 T_{ES} + 0.004 T_{EE} - 0.0290 T_{EU} - 0.020 T_{ER} \quad (13)$$

with $R^2 = 0.2078$.

Equation (13) indicates that higher eutectic start and end temperatures lead to higher shape factors (0.0145 and 0.004). Increasing the eutectic undercooling temperature results in a reduction of shape factor (-0.020). Higher eutectic recalescence temperature decreases the shape factor (-0.020). However, the correlation coefficients can be seen to be very small.

5.4.2.6 Nodularity vs. Cooling Curve Parameters

The regression equation obtained with the centered and scaled data was:

$$NOD = 75.75 + 2.825 T_{ES} + 1.40 T_{EE} - 1.594 T_{EU} - 4.43 T_{ER} \quad (14)$$

with $R^2 = 0.1334$.

Although equation (14) seems to suggest that nodularity increases with increasing eutectic start and eutectic end temperatures, and that it decreases with increasing eutectic undercooling and eutectic recalescence temperatures, the correlation coefficient is so low that no statistically significant conclusion can be drawn from the equation.

5.4.3 Evaluation of the Statistical Design

The success of conducting the statistical experiments lies in controlling the composition of all the samples within very narrow limits to preclude the effect of composition as one of the variables. However, as seen in Table 4 there is scatter in the composition. Because of limitations inherent in foundry practice, constant composition could not be obtained consistently. Also, as is apparent from the previous discussion, no correlation was obtained between shape factor, nodularity and CCA parameters. This could be because of the assumption in the statistical design that composition was completely constant in the experiments.

To find the effect of composition on the nodule count, shape factor and nodularity, graphs were drawn between the microstructure (Table 5) and carbon equivalent and percent Mg (Table 4). These are shown in Figures 12 to 17.

Figure 12. Variation of nodularity with magnesium levels.

Figure 13. Variation of shape factor with magnesium level

It can be seen from Figures 12 - 14 that the nodularity, shape factor and nodule count increase for increasing percentages of residual magnesium. This increase is seen to be rapid at lower levels of magnesium but becomes slower as the level of magnesium increases. A good ductile iron is characterized by higher nodule count, shape factor and nodularity. Since the above parameters increase with increasing percentages of magnesium, this indicates the importance of controlling the magnesium content to obtain good quality

ductile iron. The scatter at the same levels of magnesium is because of the different pouring temperatures employed.

Figure 14. Variation of nodule count with residual magnesium

Figure 15. Variation of nodularity with carbon equivalent.

It can be seen from Figures 15 - 17 that the effect of higher carbon equivalent is to reduce the nodularity, shape factor and nodule count. As the carbon equivalent of the melt increases, the amount of free carbon also increases. This should increase the nodule count. This means that the processing conditions play an important role in dictating the microstructure at each level of carbon equivalent. Strongly hyper-eutectic compositions are

also associated with graphite flotation. This in turn could reduce the nodularity and shape factor (Figures 15 and 16) resulting in a poor quality iron. This argument means that an attempt to correlate the microstructural parameters with cooling curve parameters would introduce substantial error because of the normal fluctuations in cast iron composition.

The melt was treated with Mg in the ladle. Before that the composition of the melt was adjusted and the melt was heated to the desired superheating temperature and was held at that temperature. This fixed the number of available nuclei in the melt for the nucleation of spheroidal graphite. Then the melt was poured into the mold at two different pouring temperatures. The different cooling rates introduced by the above procedure resulted in different microstructures (nodule count, shape factor and nodularity).

Figure 16. Variation of shape factor with carbon equivalent.

The poor correlations obtained between the nodularity and CCA parameters could also be explained from Figure 18. Here the y axis could be replaced with percent nodularity. As Illustrated, there is scatter in the values of nodularity when the residual magnesium is around 0.03%. In all of our experiments there was little scatter in the residual magnesium content. A Mg content of around 0.03% was obtained consistently except for two samples; this is the marginal lower limit of Mg for ductile iron. Also, at this level of Mg, there is a substantial scatter in the nodularity, as the figure shows. Hence, any attempt to correlate nodularity with CCA parameters should not be expected to be successful.

Figure 17. Variation of nodule count with carbon equivalent.

Figure 18. Influence of residual magnesium on nodularity.⁹

5.4.4 Correlations of Cooling Curve Data for Hypo- and Hyper-eutectic Irons

In considering the data, it appears that improvement in the correlation coefficients might be found if the statistical design were divided into two groups:

I. Hypo-eutectic, and II. Hyper-eutectic.

Cooling curve parameters are quite different for hypo- and hyper-eutectic iron. However, within either group, the effect of composition on microstructure might be reduced. Hence the nodule count, shape factor and nodularity have been correlated with cooling curve parameters within each group.

5.4.4.1 Group I Correlations (Hypo-eutectic Irons)

Nodule Count vs. Cooling Curve Parameters

The cooling curve parameters obtained in the first set of analyses were correlated with the nodule count for hypo-eutectic irons. The regression equation using scaled and centered values now becomes:

$$N = 156.177 + 10.162 T_{ES} + 13.587 T_{EE} - 23.395 T_{EU} - 30.870 T_{ER} \quad (15)$$

with $R^2 = 0.9765$.

This equation shows that with an increase in eutectic start and end temperatures the nodule count increases, with the temperature of the eutectic end temperature being slightly more significant. As the temperatures at the end of the eutectic increases, solidification is forced to be completed between the stable and metastable temperature regions. Hence, there should be smaller amount of intercellular carbides. This should increase the amount of free graphite and therefore the nodule count. An increase in the temperatures of eutectic undercooling and recalescence is shown to decrease the nodule count substantially.

Shape Factor vs. Cooling Curve Parameters

The regression equation using scaled and centered data is now:

$$SF = 0.792 + 0.017 T_{ES} + 0.0106 T_{EE} + 0.029 T_{EU} - 0.0225 T_{ER} \quad (16)$$

with $R^2 = 0.7578$.

Equation (16) indicates that higher eutectic start, end and undercooling temperatures lead to higher shape factors, while a higher eutectic recalescence temperature will decrease the shape factor.

Nodularity vs. Cooling Curve Parameters

For hypo-eutectic irons, the regression equation obtained with scaled and centered data was:

$$NOD = 82.00 + 0.7868 T_{ES} + 4.765 T_{EE} + 4.774 T_{EU} - 2.000 T_{ER} \quad (17)$$

with $R^2 = 0.714$.

This equation suggests that nodularity will increase with increasing eutectic start, end and undercooling temperatures. The eutectic end and undercooling temperatures seem to be more significant. An increase in the eutectic undercooling temperature increases the nodularity, but also decreases the nodule count, as shown in equation (15). Increasing the eutectic recalescence temperature decreases the nodularity.

5.4.4.2 Group II Correlations (Hyper-eutectic Iron)

Nodule Count vs. Cooling Curve Parameters

For hyper-eutectic iron the regression equation with the scaled and centered values was:

$$N = 144.79 + 27.678 T_{ES} + 2.413 T_{EE} - 15.950 T_{EU} - 18.685 T_{ER} \quad (18)$$

with $R^2 = 0.6235$.

This equation suggests that higher eutectic start and end temperatures will yield a high nodule count, while high eutectic undercooling and recalescence temperatures will lower it. The eutectic start temperature appears to be most dominant.

Shape Factor vs. Cooling Curve Parameters

The regression equation for shape factor for hyper-eutectic iron was:

$$SF = 0.7853 + 0.028 T_{ES} + 0.0069 T_{EE} - 0.041 T_{EU} - 0.0321 T_{ER} \quad (19)$$

with $R^2 = 0.4124$.

The coefficients are so small, and the R^2 value so low that no significant conclusions can be drawn.

Nodularity vs. Cooling Curve Parameters

The regression equation for hyper-eutectic iron, using scaled and centered data was:

$$NOD = 72.00 + 3.641 T_{ES} + 7.258 T_{EE} - 2.028 T_{EU} - 5.882 T_{ER} \quad (20)$$

with $R^2 = 0.4671$.

This equation predicts that an increase in the eutectic start and end temperatures will result in a higher nodularity, while an increase in eutectic undercooling and recalescence temperatures will result in a reduction in the shape factor.

Comparison of R^2 values between the original analysis and those based on dividing the data into hypo- and hyper-eutectic irons shows that, while such a division is helpful, the correlations are still below the value required to approach conclusions with high confidence. It appears that more work is required to control the experiments so that more meaningful conclusions can be drawn.

Correlation Between the Shape Factor and Nodularity

To ascertain which of the microstructural features is more useful (shape factor or nodularity) a graph (see Figure 19) was plotted between the shape factor and the nodularity. The data was randomly obtained at different positions in the sample.

While there is significant scatter in the graph, a general pattern can be seen. Nodularity increases with an increasing shape factor. Nodularity might be more accurate as a quantifying tool for microstructure because it varies between larger values. The values over

which shape factor varies are rather small. Also, the image analysis system determines nodularity and shape factor by using color contrast input into the image of the microstructure by adjusting threshold values. Small variations in the threshold values do not affect nodularity, but change the shape factor substantially. For this reason, evaluation of shape factors as a quantifying tool is disadvantageous because human bias is presently unavoidable.

Figure 19. Variation of nodularity with shape factor.

6.0 Conclusions

The results of this investigation underscored the practice most foundries use daily. Lower superheating temperatures and holding times are essential to produce good quality (i.e., high nodularity) ductile iron. Raw materials also affect the final microstructure. Lower percentages of pig iron in the charge yielded higher nodularity; this was attributed to the presence of deleterious elements in the pig iron.

Nodule count was strongly dependent on the percent pig iron in the charge and superheating and pouring temperatures. Higher percent pig iron in the charge yielded higher nodule counts. This was attributed to the presence of larger amounts of undissolved graphite in the melt when a higher percentage of pig iron was used. Higher superheating and pouring temperatures resulted in lower nodule counts because of the annihilation of potential nuclei at higher temperatures.

The shape factor was found to be strongly dependent upon all the processing parameters studied. Higher superheating and pouring temperatures resulted in lower shape factors, while higher percent pig iron in the charge yielded higher shape factors.

Attempts to correlate the microstructure with cooling curve parameters did not yield statistically significant models in some cases because of fluctuations in the composition of the iron used in the experiments, and the sensitivity of the experiments to compositional fluctuations. The scatter in the carbon equivalents and the residual magnesium contents clearly affected the validity of the statistical design, and thereby resulted in poor correlations in some cases.

The cooling curve of a hypo-eutectic and a hyper-eutectic iron are different. These differences were treated by analyzing the data (correlating the microstructural with the

cooling curve parameters) in two groups, hypo-eutectic and hyper-eutectic, depending on the composition of the iron.

It was found that all the microstructural parameters (nodule count, shape factor, and nodularity) improved with higher eutectic start and end temperatures. These temperatures determine the solidification interval of the particular sample. Whenever the interval falls in the gray iron solidification range, optimum microstructure is observed, with a minimum of intercellular carbides. Higher eutectic recalescence lowered the nodule count, shape factor and nodularity in each group. The strongest correlation was observed when the cooling curve parameters were correlated with the nodule count for hypo-eutectic iron.

An attempt was also made to ascertain which microstructural feature, nodularity of shape factor, was a better tool for quantifying the microstructure of ductile iron. In general, nodularity was found to increase with increasing shape factor. Because shape factor is heavily dependent on human judgment, nodularity was judged to be a more accurate quantifying tool.

In summary the results validate the concept that a definite correlation exists between ductile iron microstructure and molten metal processing. Further investigation of this relationship is recommended.

References

- ¹J. Smothers, and Y. Chang, *Handbook of Differential Thermal Analysis*, Chemical Publ. Co., 1966.
- ²P.D. Garn, *Thermoanalytical Methods of Investigation*, Academic Press, Inc., 1965.
- ³M.D. Chaudhari, "Principles Involved in the Use of Cooling Curves in Ductile Iron Process Control," *AFS Transactions*, vol. 82 (1974), p. 431.
- ⁴J.M. Frost, "Melt Quality Assessment of Spheroidal Graphite Cast Iron through Computer-Aided Cooling Curve Analysis," M.S. Thesis, The University of Alabama, 1992.
- ⁵E.F. Ryntz *et alia*, "Prediction of Nodular Microstructure Using Thermal Analysis," *AFS Transactions*, vol. 78 (1971), p. 141.
- ⁶K.G. Upadhyay *et alia*, "Computer Aided Cooling Curve Analysis: Principles and Applications in Metal Casting," *AFS Transactions*, vol. 97 (1989), p. 61.
- ⁷D.M. Stefanescu, "Solidification of Flake, Compacted/Vermicular and Spheroidal Graphite Cast Irons as Revealed by Thermal Analysis and Directional Solidification," *MRS Symposium Proceedings*, vol. 34 (1985), Elsevier Science Publishing Co.
- ⁸F.J. Bradley *et alia*, "On the Application of Thermal Analysis to the Control of Molten Metal Processing of Ductile Iron," *Physical Metallurgy of Cast Iron IV*, Materials Research Society, 1990, p. 485.
- ⁹R. Barton, "Magnesium Content Required to Produce Nodular Graphite Structures in Heavy Section Iron Castings," *BCIRA Journal*, No. 5 (Sept., 1961), p. 668.