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THE CYCLONE METHOD FOR ECONOMICAL NODULAR IRON PRODUCTION USING COMMERCIALLY PURE LIQUID MAGNESIUM

By

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ABSTRACT

The cyclone method inoculates grey iron with commercially pure liquid magnesium to make nodular iron at less than half the total alloy cost normally experienced in using the sandwich technique.

Magnesium recoveries of greater than 30 percent were experienced using the new technique which inoculates a small amount of the base iron with a small amount of the magnesium on a continuous basis as the ladle is filled. The design forces the magnesium to the center of the ladle, excluding contact of the magnesium with refractory interfaces.

A synopsis of the conception, initial design, fabrication, and testing of equipment used in the process illustrates the development of the cyclone method of producing nodular iron.

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INTRODUCTION

Definition of Nodular Iron

Nodular iron is an increasingly important engineering material which combines such exceptional cast iron founding properties as high fluidity and a low melting point, with such good mechanical properties of steel, as ductility and strength.

Both cast iron and nodular iron have a steel matrix in which are suspended particles of free graphite that act as voids in the material. In cast iron the graphite particles take the shape of curved surfaces wide in two directions and very narrow in the third, almost like corn flakes. The sharp edges of the particles act as internal notches in the material and make it brittle.

In nodular iron the graphite assumes a spherical shape by an unknown mechanism. Although the spheres still act as voids in the metal matrix, there are no sharp edges, and thus no internal notches or cracks, and the metal can deform plastically without fracturing.

While nodular iron is not as ductile as low carbon steel having no voids in the matrix structure, elongations as high as 10 percent are easily obtainable in nodular iron. This, plus better founding properties, make it competitive with steel castings. While the strength of nodular iron is lower than that of steel for a given matrix composition because of the graphite voids in the matrix, the presence of free graphite is often desirable.

In addition, the strength advantage of steel is often offset in castings by the high fluidity and lower melting point of nodular iron. This is especially true when a casting has thin sections, or when mold erosion due to high temperature steel becomes a problem. The pouring temperature of steel ranges from 2850F to 3200F. Also, cheaper refractory materials can be used to line both the furnace and the ladles, and a lower quality sand can be used for the molds with equivalent or longer life expectancy because of the lower pouring temperature of nodular iron (2400F to 2600F).

Nodular iron was made accidentally as far back as the early 1940's, but the process was not sufficiently understood or controlled to become patentable until the early 1950's. Since the expiration of the International Nickel Co. patent, U.S. nodular iron production has grown rapidly.

Necessary Conditions for Making Nodular Iron

Nodular iron is produced when the following two conditions are satisfied:

1. Iron containing approximately 2.5 percent to 3.5 percent carbon and 2.0 percent to 4.0 percent silicon is inoculated with magnesium in some form until a residual level of 0.035 percent to 0.06 percent is reached.

2. A graphitizer such as silicon, nickel, or copper must be added to the melt either with or after the magnesium, but not before. Nodular iron can be made in either way, but the best iron, with small well-dispersed nodules, is made when silicon is added after the magnesium, and as close to the time the metal solidifies as possible. NON-EQUILIBRIUM CONDITIONS with the silicon dissolving into the iron promote very small nodule size and random nodule distribution. A rapid cooling rate also helps.

Rare earth elements, such as cerium and yttrium, coupled with a graphitizer also promote nodular iron, but the nodules are never as well-formed as with the magnesium inoculant. Graphite nodules induced by either rare earths or an extremely rapid cooling rate appear ragged and are almost never perfectly formed spheres.

Several theories exist on the mechanism of nodular iron formation. The two most widely publicized are the undercooling theory of H. Morrogh (1947), and the nucleation site theory of A. L. DeSy (1949). Since neither of these theories explain all the observed facts, they will not be mentioned further.

All that is presently important is the fact that nodular iron is an important engineering material, and can be made under certain conditions. Present production methods, however, are all either uneconomical or very inefficient.

The introduction of magnesium into iron is inefficient for at least the following four reasons:

1. Magnesium is only slightly soluble in iron. Equilibrium diagram data for iron in magnesium in iron does not exist. All that Schunk (1969) says about the solubility of magnesium in iron is that the upper limit of solubility is 0.1 weight percent or 0.2 atomic percent in nearly pure liquid iron in the presence of magnesium and 25 atmospheres argon.

2. Magnesium melts at 1200F and boils at 2024F, and since the minimum inoculation temperature is usually 2500F, the magnesium shows a marked tendency to vaporize and boil off.

3. The 1.74 density of magnesium is approximately one-fifth that of iron at 7.86. Magnesium in any concentration tends to float on top of the iron, boil, and combine with any oxygen present to form a brilliant white flare and MgO smoke.

4. The first magnesium that dissolves into the iron breaks up existing sulphur compounds such as manganese sulphide, ties up this sulphur probably as magnesium sulphide, and is then unavailable to participate in the reaction of reactions which produce nodular iron (Rehder, 1950).

Rehder (1950) metallographically analyzed sulphur compounds in nodular iron produced by the sandwich technique, which is described later. He observed that manganese sulphide inclusions decreased to a minimum at a residual sulphur level of 0.02 percent, and that the magnesium level would not increase above 0.02 percent until the 0.02 percent sulphur level was reached. Also, no graphite nodules were observed until the magnesium level exceeded 0.02 percent, after which the nodule count increased with increasing magnesium concentration.

The magnesium seems to remove the sulphur on a one to one ratio, or as MgS. If the magnesium recovery is 30 percent, and the initial sulphur content is 0.05 percent, then an additional (0.05-0.02)/0.3 percent or 0.1 percent magnesium must be added to the total amount of inoculant in order to achieve a sulphur level low enough to produce nodular iron. If 0.04 percent is the minimum magnesium residual needed to produce a fully nodular structure, and 0.05 percent is the initial sulphur level, then the amount of magnesium actually needed to assure a fully nodular structure or the equivalent magnesium residual is computed as (0.04 + (0.05-0.02)) or 0.07 percent. The amount of magnesium that must be added for a 30 percent magnesium recovery is 0.07/0.3 or 0.203 percent.

Old Methods of Making Nodular Iron

Three successful methods for inoculating the iron are:

Nickel Magnesium Method

1. A magnesium bearing alloy denser than the iron, such as nickel magnesium, is placed on the bottom of the ladle, and the iron is tapped directly on top of the alloy. The alloy does not float and releases the magnesium as it dissolves at a slow rate, achieving good recovery.

Sandwich Technique

2. A less dense magnesium-bearing alloy such as magnesium ferro-silicon, is sandwiched between the ladle bottom and the steel plate, and the iron is then tapped onto the steel plate. The alloy is not released until the plate dissolves, at which time the alloy begins to float to the surface, dissolving and releasing magnesium into the melt as it rises.

Air is trapped beneath the steel among the pieces of alloy, and as it expands under the molten iron, it increases the violence of the reaction, sometimes creating a safety hazard by throwing iron completely out of the ladle. In addition, there is usually an insufficient delay in the start of the reaction because of too little steel cover over the alloy. This results in increased violence of the reaction and decreased recovery.

Plunger Technique

3. A MgFeSi alloy is enclosed in a perforated ceramic cage at the end of a refractory rod which is plunged to the bottom of a tall narrow ladle and held there until the alloy dissolves.

Of the three methods, the nickel magnesium method is the most efficient, although it has two major drawbacks:

1. Nickel is so expensive that even with increased efficiency, the alloy cannot compete with MgFeSi alloys;

2. The alloy serves as heterogeneous nucleation sites for magnesium vapor.

The sandwich method is the most widely used because it is simple and dependable, requiring less equipment and maintenance than the plunger technique. However, it also has several drawbacks:

1. The magnesium recovery is low, usually between 20 percent and 40 percent depending on the magnesium content of the alloy and on the inoculation temperature. Efficiency increases with decreasing magnesium content and decreasing inoculation temperature.

2. The high silicon content of the inoculating alloy, usually 40 percent to 50 percent, requires a low base-iron silicon content, and this can cause considerable melting problems, depending on the type of furnace used.

3. The alloy still serves as heterogeneous nucleation sites for magnesium vapor.

The plunger technique is only slightly more efficient than the sandwich technique and has the same problems of entrapped air in the alloy, and heterogeneous nucleation sites, plus maintenance problems with the refractory plunger, rod, and lid.

The equipment used in the sandwich and plunger techniques is illustrated in figures 1 and 2.

All three methods share the advantage of the metal cleansing action caused by the rising magnesium vapor which tends to attract impurities and carry them to the surface, where they can be removed as slag.

New Methods of Making Nodular Iron Using Pure Magnesium

At least two new methods of making nodular iron have evolved recently, the high pressure method and the cyclone method proposed in this thesis.

High Pressure Technique

The high pressure method is a batch type operation in which the base iron is poured into a refractory-lined steel

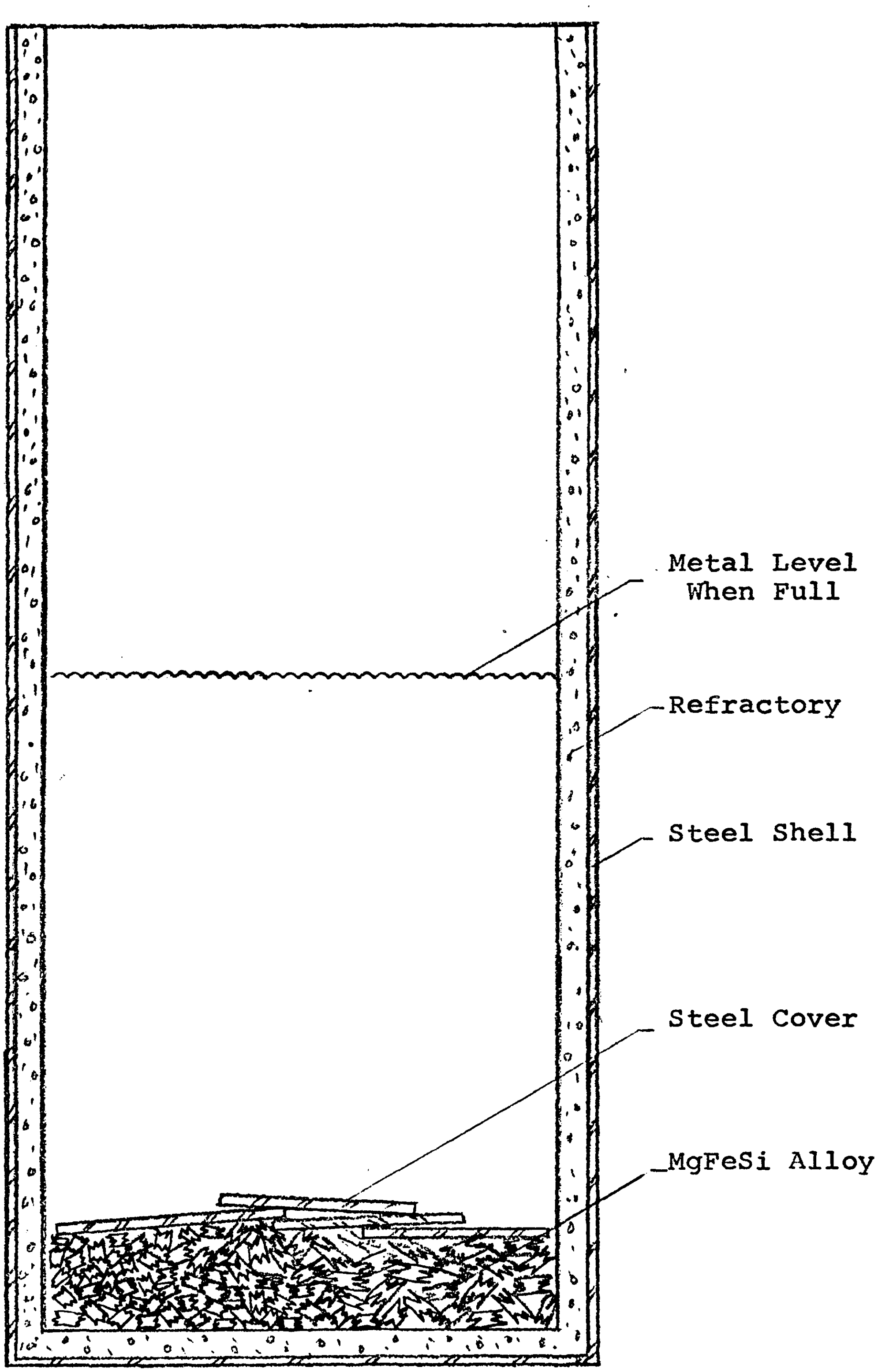


Figure 1 - Equipment used in sandwich technique

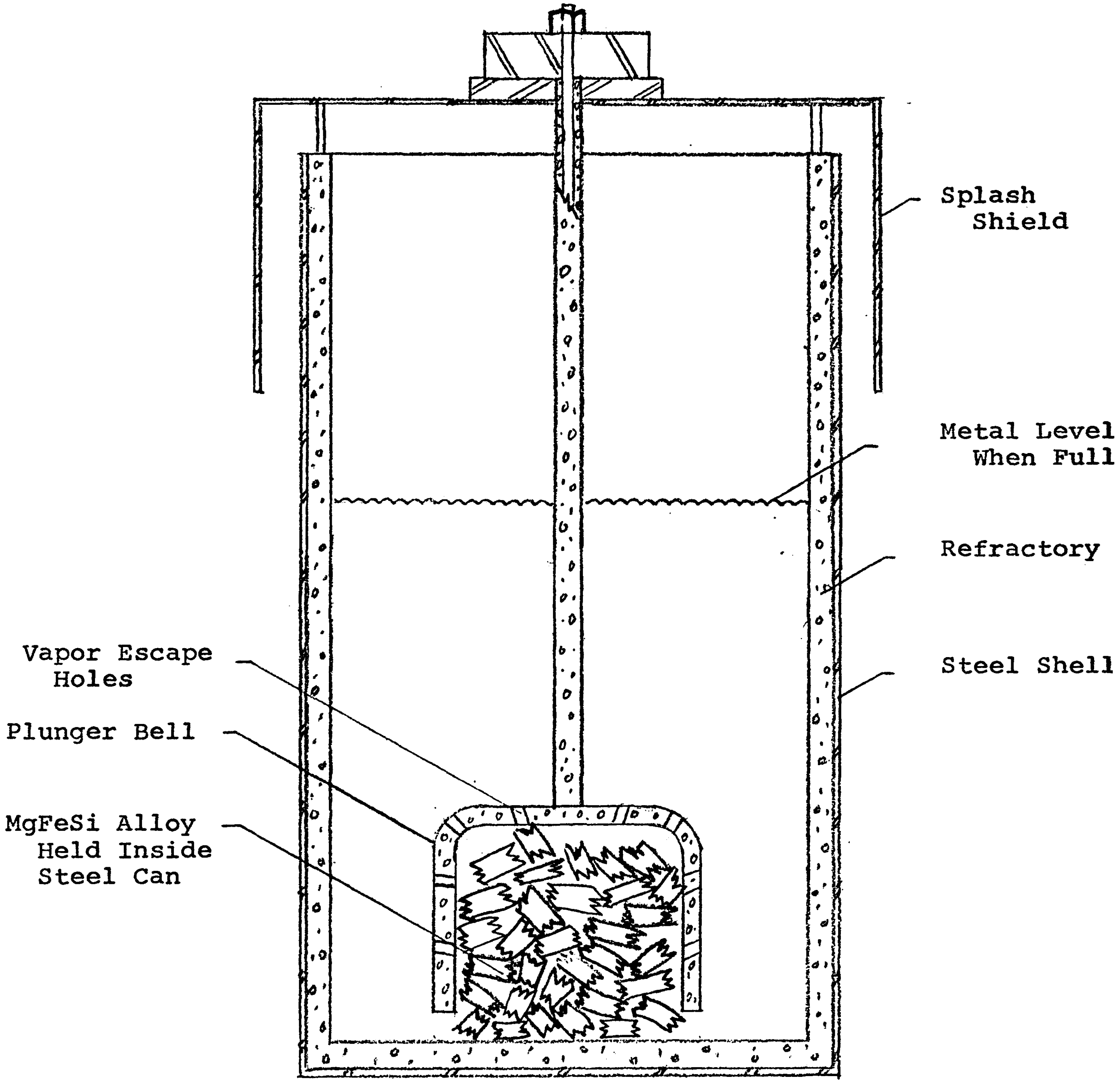


Figure 2 - Equipment used with plunger technique.

pressure vessel. A steel lid with a mechanism for lowering the magnesium into the iron is then placed on top. The system is pressurized with an inert gas such as nitrogen, and pure magnesium is then dropped on top of the metal bath.

The partial pressure of magnesium vapor increases over the iron until the magnesium is forced to dissolve rather than boil off. Treatment time is approximately 7 minutes for a 1000 lb. batch.

The high pressure method uses a solid commercially-pure magnesium bar as the inoculant, thus lowering the inoculant cost considerably. However, this method also has some disadvantages, some of which are:

1. The high pressure required necessitates an enclosed pressure vessel, making the process a batch type.

2. The system requires considerable support equipment and maintenance. Gas storage and pressurization equipment, the mechanical gear for controlling the lid and emptying the ladle, plus the instrumentation, must all be maintained.

3. No cleansing action occurs in the melt, since magnesium diffuses into the melt rather than bubbling through it. Inclusions from sulphur compounds may or may not be detrimental to the resulting iron structure.

Cyclone Technique

The cyclone method for producing nodular iron with pure magnesium is the basis for this thesis. The ladle used in the process operates at atmospheric pressure on a batch basis, but could easily be adapted to a continuous operation.

The mechanical equipment consists of a pouring basin and downspout feeding fresh base iron tangentially into the ladle, which simulates a cyclone separator, and a magnesium injection device that mixes pure liquid magnesium with the fresh iron as it enters the cyclone.

The cyclone takes advantage of the iron surface tension to retard magnesium vapor formation, since magnesium seeks the center of rotation of the cyclone and thus moves away from iron-refractory interfaces that could act as heterogeneous nucleation sites for magnesium vapor formation. Also, the mixing action of the cyclone should optimize the conditions for diffusion of the magnesium into the iron.

The new process is neither as complicated nor the equipment as massive as the high pressure system simply because it does not have to withstand high pressure. The mechanical equipment used for the injector was fairly complicated and required considerable maintenance, but the possibilities for different and better types of injectors are unlimited. The time for inoculation using the new process is essentially zero, the reaction being complete within 1 minute after the ladle is filled.

SYNOPSIS OF THE INITIAL EQUIPMENT DESIGN

Following is a synopsis of the thoughts and calculations that went into the original theoretical design of the ladle.

A 300 lb. iron heat was decided upon as roughly representative of an industrial process. Smaller experiments would have been easier; however, they might have been unrealistic because of temperature losses, and such mechanical problems as iron freezing up in a one-quarter inch diameter downspout.

One minute was chosen as a reasonable filling time for 300 lb. of iron, allowing sufficient time for technicians to perform tasks that would have to be automatically controlled if the experiment lasted for considerably less than 1 minute.

Certain basic restrictions were incorporated into the design as much as possible in order to achieve contact between the magnesium and iron for a maximum amount of time. They are:

1. Maximum metal depth is maintained in the cyclone consistent with the 300 lb. maximum limit of metal, and with the cyclone analysis.

2. The ratio of the vertical velocity to the radial velocity of a one-sixteenth inch diameter magnesium sphere should be equal to the ratio of the average metal height to the cyclone radius. This will insure that the magnesium will neither shoot directly to the iron surface and burn, nor shoot to the center of rotation and then float to the surface without further mixing. Instead, the magnesium should ascend along a line between the injector nozzle and the point where the center of rotation intersects the iron surface.

Rigorous theoretical calculations were not attempted, because many assumptions were made, tending to make the system unrealistic. Instead, rough calculations were made to ascertain the cyclone and downspout dimensions that most closely satisfied the above restrictions.

By trial and error calculations which are summarized in appendix 1, the optimum cyclone diameter was selected as 12 inch, the flow rate and inlet velocity through a one-half inch diameter nozzle was 5.7 lb/sec. and 8.7 ft/sec., the downspout diameter was 1 inch with a smooth 4 inch radius bend at the bottom leading into a one-half inch diameter nozzle. Also, the radial and vertical velocity component of a one-sixteenth inch diameter magnesium sphere is 9.3 in/sec. and 7.9 in/sec.

The ratio of the vertical to radial velocity components is equal to 7.9/9.3 or 0.85, which compares favorably with the ratio of the average metal height to the cyclone diameter, 0.83. A second significant figure is not justified. Friction considerations would lower the radial component but would not affect the vertical component of the velocity. A lower radial component would increase the velocity ratio, and the average metal head would have to increase in order to maintain an equivalent length ratio. The average metal head could be increased by delaying the start of magnesium injection until the metal level reaches a given point.

INITIAL TESTING

The magnesium injector was the first unit of the ladle to be constructed and tested. After several injector problems were resolved, the ladle itself was constructed, the injector assembly was attached, and a magnesia refractory slurry was poured into the ladle.

Magnesium Injector

Injector Body

The magnesium injector was turned out of a single piece of 3 inch diameter 1042 steel bar (fig. 3). Originally two gas inlet ports were provided. One fed into the cavity at the bottom of the bore to keep the nozzle clear both during magnesium melting and after the iron had been inoculated and was still in the ladle. A secondary gas port entered near the flange end to keep the steel behind the piston as it moved inward from oxidizing, and to extinguish any magnesium which for unforeseen reasons might come around the piston.

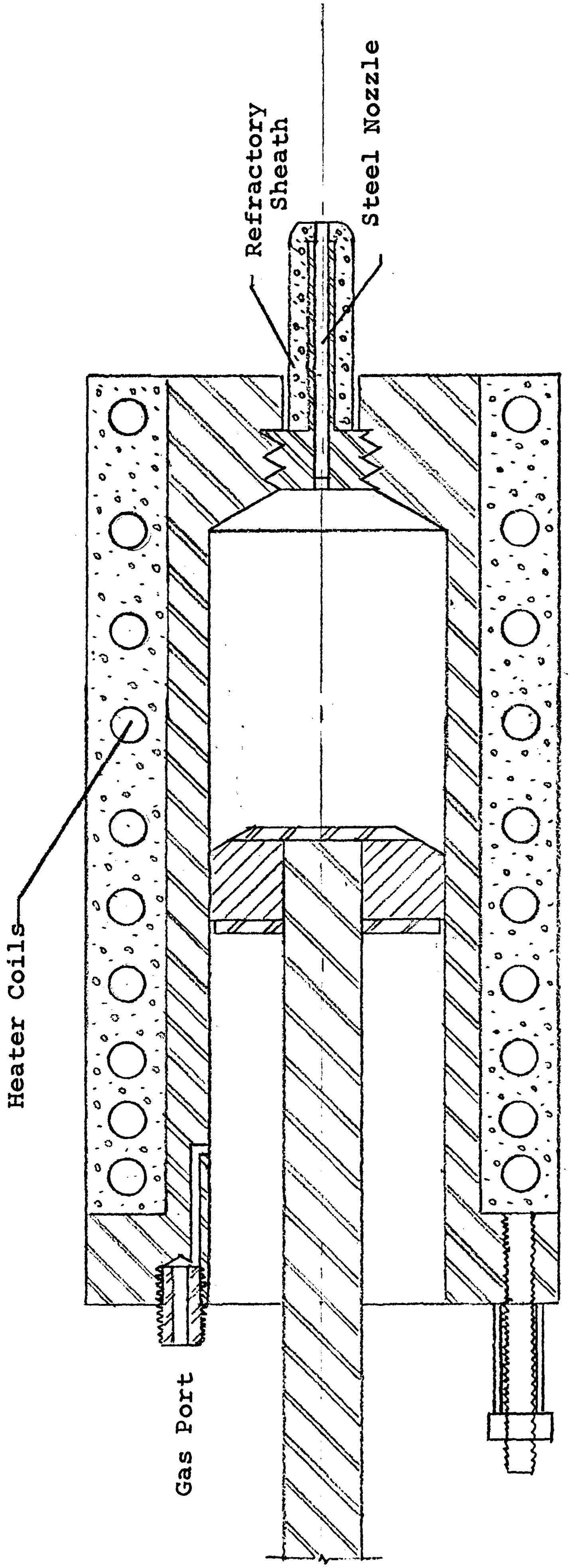


Figure 3 - Magnesium Injector

Piston

The original extruder utilized a hand-driven close-fitting steel piston which was unlubricated. From room temperature to about 400F this arrangement was fine, but at higher temperatures galling of the piston occurred with subsequent seizure inside the extruder tube. A graphite powder lubricant was tried unsuccessfully, together with a very long and a very short piston. All combinations failed with piston seizure.

The answer to the problem was a graphite piston sandwiched between two pieces of steel. The steel pusher was 0.010 inch smaller than the inside diameter of the cylinder in order to minimize the amount of graphite not supported by the steel when a maximum load of 3100 lb. was applied.

The puller part of the piston was arbitrarily made 1 inch in diameter and would only function when the piston was being removed.

A threaded piece of graphite was screwed into the narrow piston as a first attempt to use a combination graphite and steel piston. Due to friction between the graphite and the cylinder wall, the graphite fractured at the threads as the piston was being removed, leaving the piston face at the bottom of the cylinder. At this point the idea of a sandwich piston with steel on both sides of the graphite was conceived.

Figures 4A to 4E summarize by illustration the five different piston designs that were tested before the graphite-steel-sandwich piston was finally developed.

Magnesium Heater

Heat transfer problems manifested themselves during the early, steel piston phase of extruder testing. This problem was particularly nebulous since anything short of actually testing the assembly in the ladle would not be representative of the experimental operating conditions. Nonsteady state conditions complicated the problem until it was felt that theoretical calculations would be exceedingly difficult and not worth the effort.

The main flange and the refractory surrounding the heater was wrapped with five layers of one-sixteenth inch thick asbestos, and the nozzle end of the extruder was also covered with three layers of one-sixteenth inch asbestos. The sealer plate and the pusher rod and handle were left exposed, as they would be in actual practice.

The injector was originally bored straight to within ± 0.0005 of 1.435 inches. The heat transfer problem became evident when the piston, which had heated up while next to the large rear flange, would slide in and out freely if moved rapidly, but would gall and seize inside the cylinder when pushed to the bottom and left for 5 seconds and then pulled back out. Enough of a thermal gradient existed that when the piston equilibrated with the higher temperature

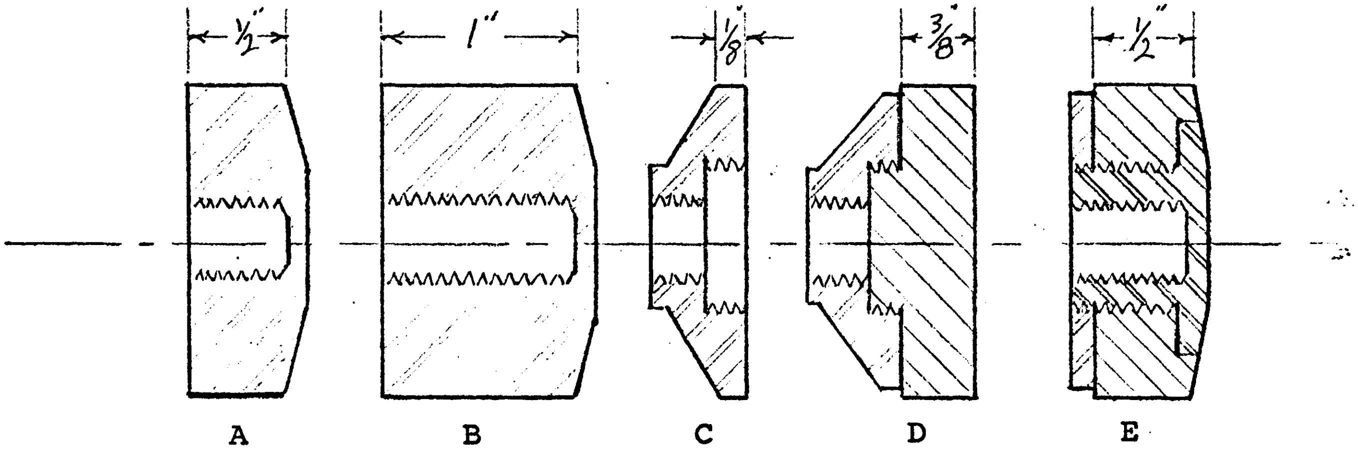


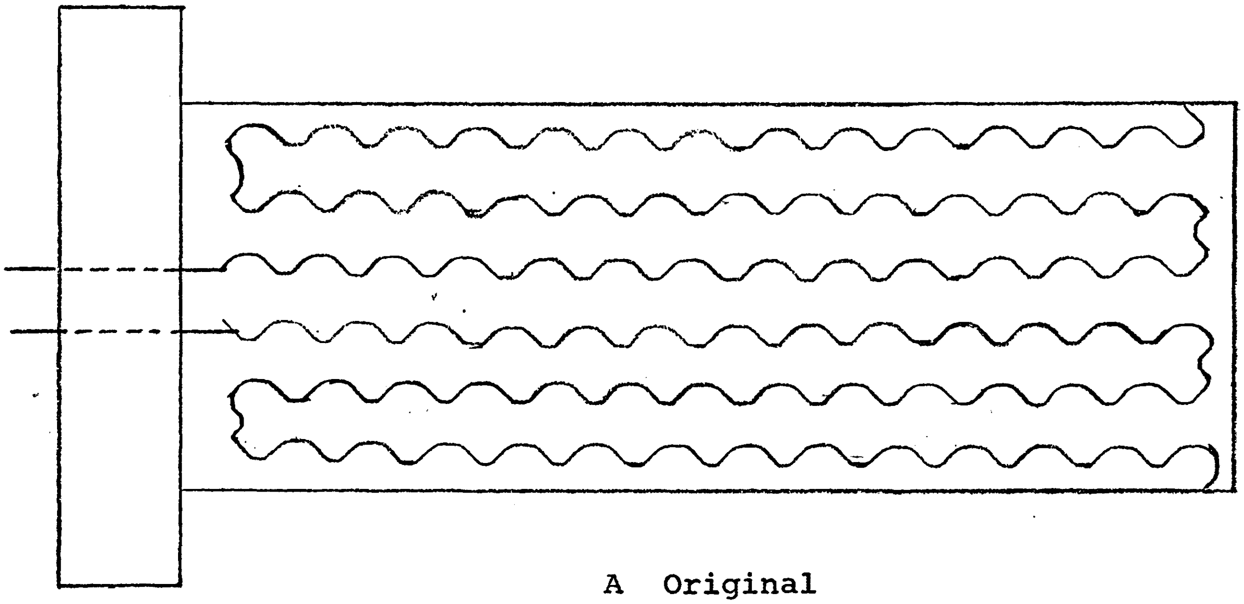
Figure 4 - Summary of injector piston designs

conditions present at the bottom of the cylinder, it would expand and not clear the contracted cooler portion of the cylinder near the flange. The problem was alleviated somewhat by honing the cylinder until a 0.004 inch taper with the large end at the flange was obtained. The metal pistons, however, still seized at high temperatures as they were withdrawn.

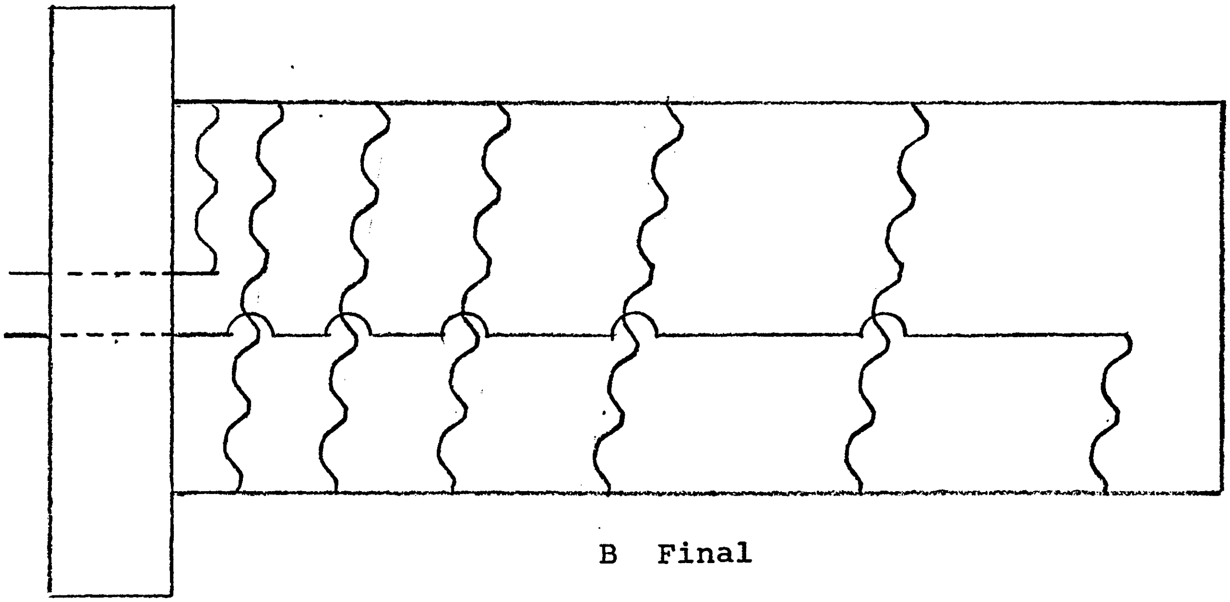
The magnesium-heater wiring pattern used during the first tests was a simple s pattern with the wire coil running parallel to the centerline of the extruder. The temperature gradient inside the extruder was somewhere between 280F and 475F with the higher gradient occurring at higher test temperatures (1050F) (fig. 5A).

The heater wire configuration was also changed at the same time the hydraulic system was being made so that the heating wire was wrapped around the extruder with more turns of wire near the flange end than near the nozzle end. This new heater configuration would help alleviate the thermal gradient from flange to nozzle (fig. 5B).

Magnesium was melted and extruded once, using the metal piston and the s heater configuration. The results were discouraging. Magnesium came out around the nozzle threads and around the piston. Twenty-two grams out of a 183 gram sample, or 12 percent of the magnesium, went around the piston. The piston seized as it was being withdrawn. It was decided at this point to install a hydraulic system



A Original



B Final

Figure 5 - Initial and final heater wire configurations.

to operate the piston, so that more uniform feeding and more pressure could be applied when necessary. The graphite piston was also deemed necessary at this point to eliminate galling.

Hydraulic System

The hydraulic system was constructed out of an automotive power steering unit by welding a flange and spacer onto the neck of the hydraulic cylinder around the shaft which drives the piston (fig. 6).

The valving arrangement which was selected is illustrated in figure 7, and has a total of five valves in it. While the same result could have been obtained using a single automotive power steering control valve, it was felt at the time that a single control valve would not provide sufficient piston travel control. Looking back, the single control valve might well have been simpler to operate and control. If such a thing as a hydraulic flow meter exists, it would be useful for accurately judging inward piston travel.

A 0 to 2000 psi gauge with 20 pound scale divisions was used to measure the pressure between the positive displacement pump and the inlet side of the control valves. The force capability of the hydraulic piston was then calibrated as a function of valve position and pressure reading for both inward and outward pull.

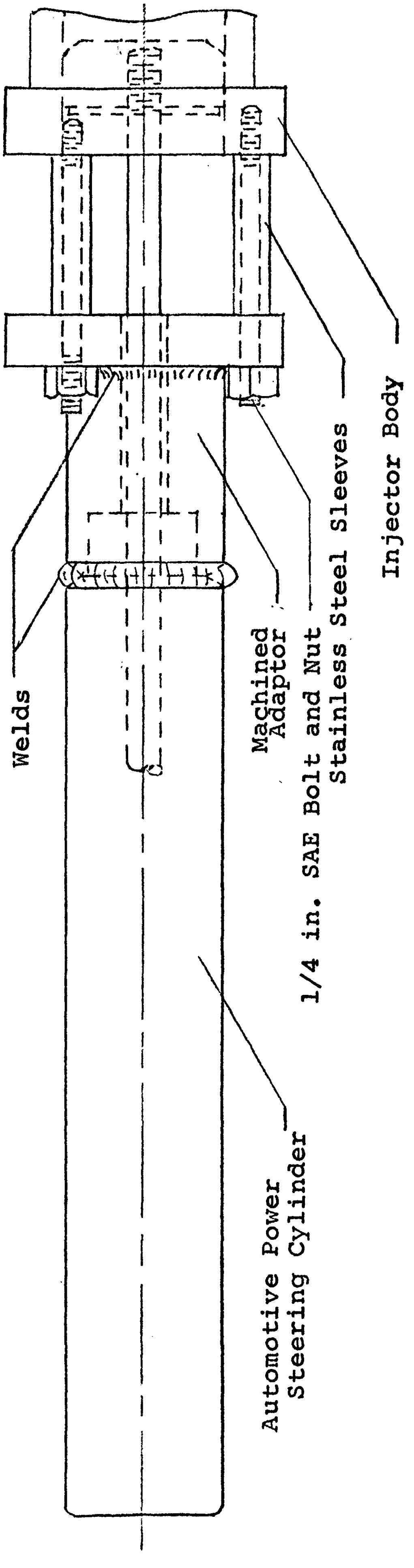


Figure 6 - Hydraulic cylinder for piston movement and control

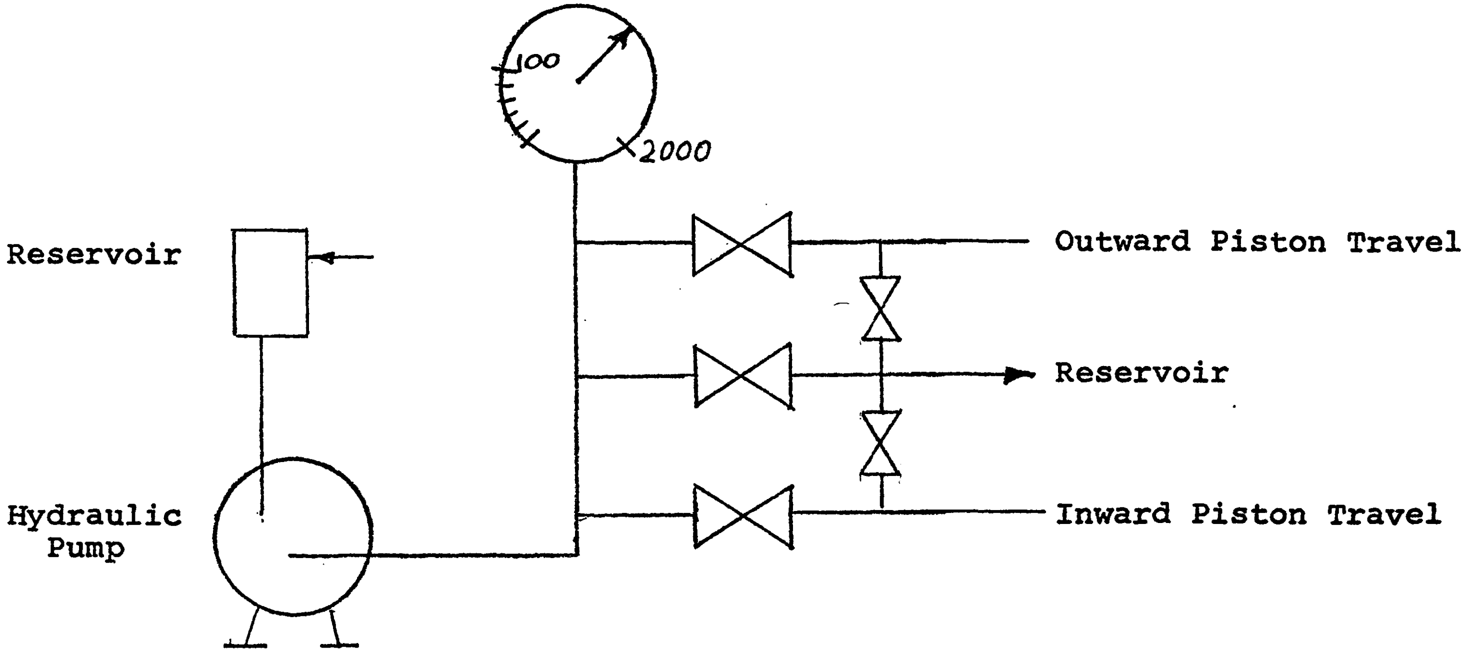


Figure 7 - Schematic of hydraulic controls

Although the system was only tested to 550 psi hydraulic pressure, the total force capability of the hydraulic system then was 1800 psi (1.73 in^2) or 3110 lb. while pushing the magnesium in, and 1800 (1.53 in^2) or 2750 lb. while extracting the piston. It is worthwhile to note here that after the inoculation of heat 5, when some magnesium was allowed to solidify between the piston face and the side, and the extruder wall, the bond was sufficiently strong to withstand the 2750 lb. force developed. The extruder, magnesium, and piston had to be reheated to approximately 600F before the bond broke and the piston could be withdrawn.

Downspout

The original downspout design was easy to analyze from a theoretical standpoint, but was not too functional from a practical standpoint. First, it was a constant diameter pipe with a smooth 4 inch radius bend leading into a one-half inch diameter nozzle which then exited tangentially into the ladle 1 inch above the bottom. Since metal falling into a constant diameter pipe tends to aspirate air, the modified downspout was tapered with decreasing cross sectional area toward the bottom of the downpipe. The final design was a 3 inch diameter pipe at the top decreasing to a 2 inch diameter 3 inches below the top that acted as a pouring basin, and finally decreasing to a 1 inch diameter 15 inches below the top of the ladle.

Second, due to previous experience with spouts on teapot ladles freezing up when they were insulated with over 1 inch of refractory, the decision was made to scrap the smooth radius bend in the downspout and go to the right angle bend, which would allow the downspout to be within one-half inch of the ladle center rather than 2 inches, as with the smooth radius bend. With less than one-half inch of refractory separating the bulk of the metal in the ladle from the metal in the downspout, experience indicated that the metal would retain enough heat, even when the metal was standing before pouring the castings, to keep the metal fluid in the downspout, thus allowing it to drain as the ladle was emptied.

The right angle turn would increase metal turbulence and decrease the tangential inlet velocity, but the tapered design of the downspout should correct for this decrease.

During later tests using the entire ladle and iron, the downspout still plugged up twice after an otherwise successful run. The solidified metal had to be remelted and cleaned out with an oxygen and steel lance, which would not have been possible with the smooth radius bend and constant diameter pipe.

The initial and final designs of the downspout are shown in figures 8A and 8B.

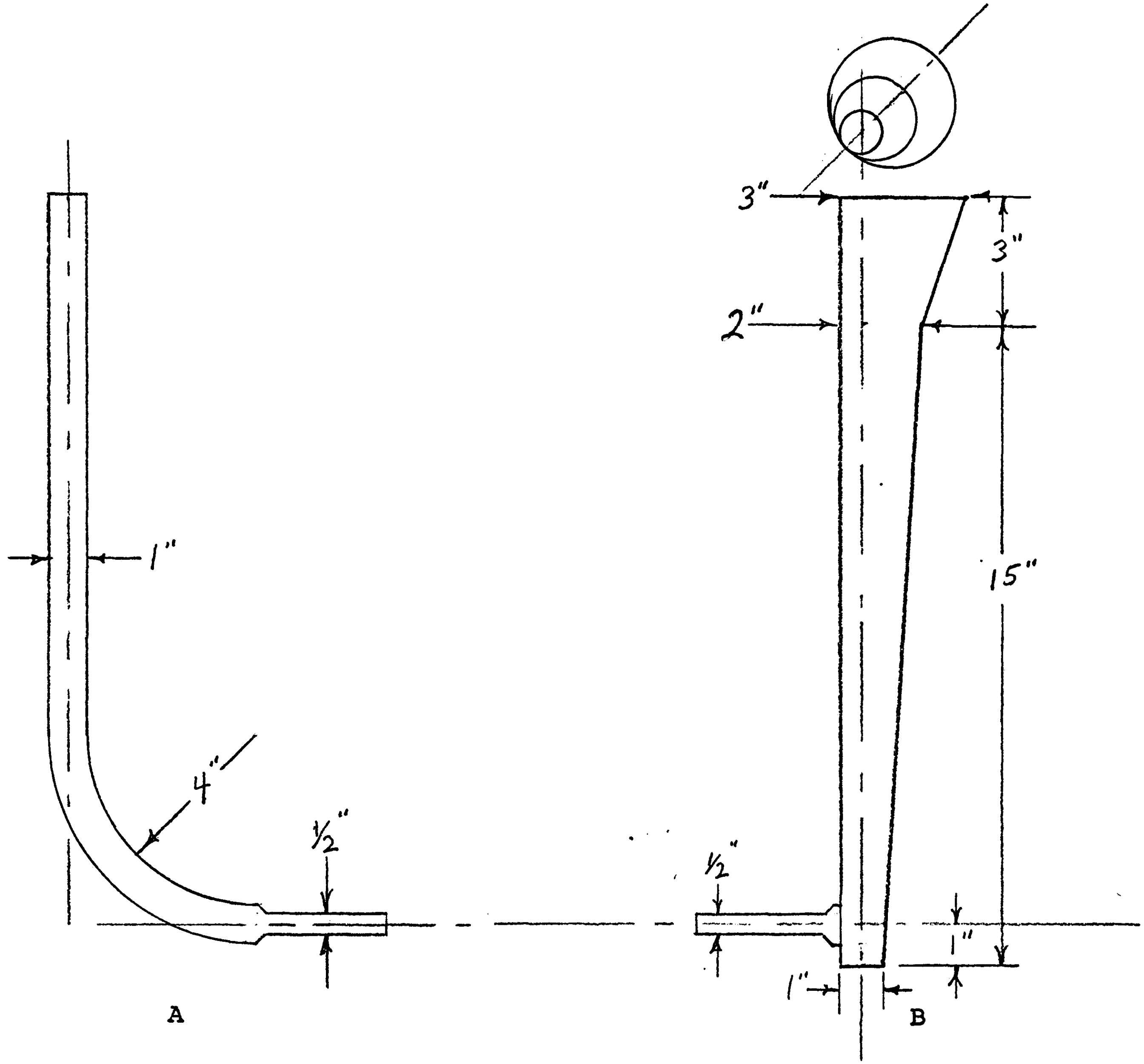


Figure 8 - Initial and final downspout designs

EXPERIMENTAL WORK INVOLVING ENTIRE SYSTEM

Fabrication and Final Assembly of the Ladle

The ladle was constructed by the General Iron Works out of one-eighth inch steel plate, according to figure 9. A smaller steel shell was made to form the inside of the ladle, the nozzle was welded on tangentially, the wooden downspout was wired onto the nozzle, and the whole assembly was tack welded onto the outer shell. The injector and heater assemblies were then mounted and the ladle filled with a magnesia refractory slurry.

Runs Using Built-in Pouring Basin

Two initial runs were made to burn out the steel nozzle and inner shell, to test the downspout, and to determine if an auxiliary pouring basin would be necessary. No magnesium was injected during these runs. The two initial runs were followed by six heats during which magnesium was injected into the iron in various degrees. Test bars were poured and chemical samples were taken for analysis after each heat. Following is a synopsis of the two initial runs and six heats that were made.

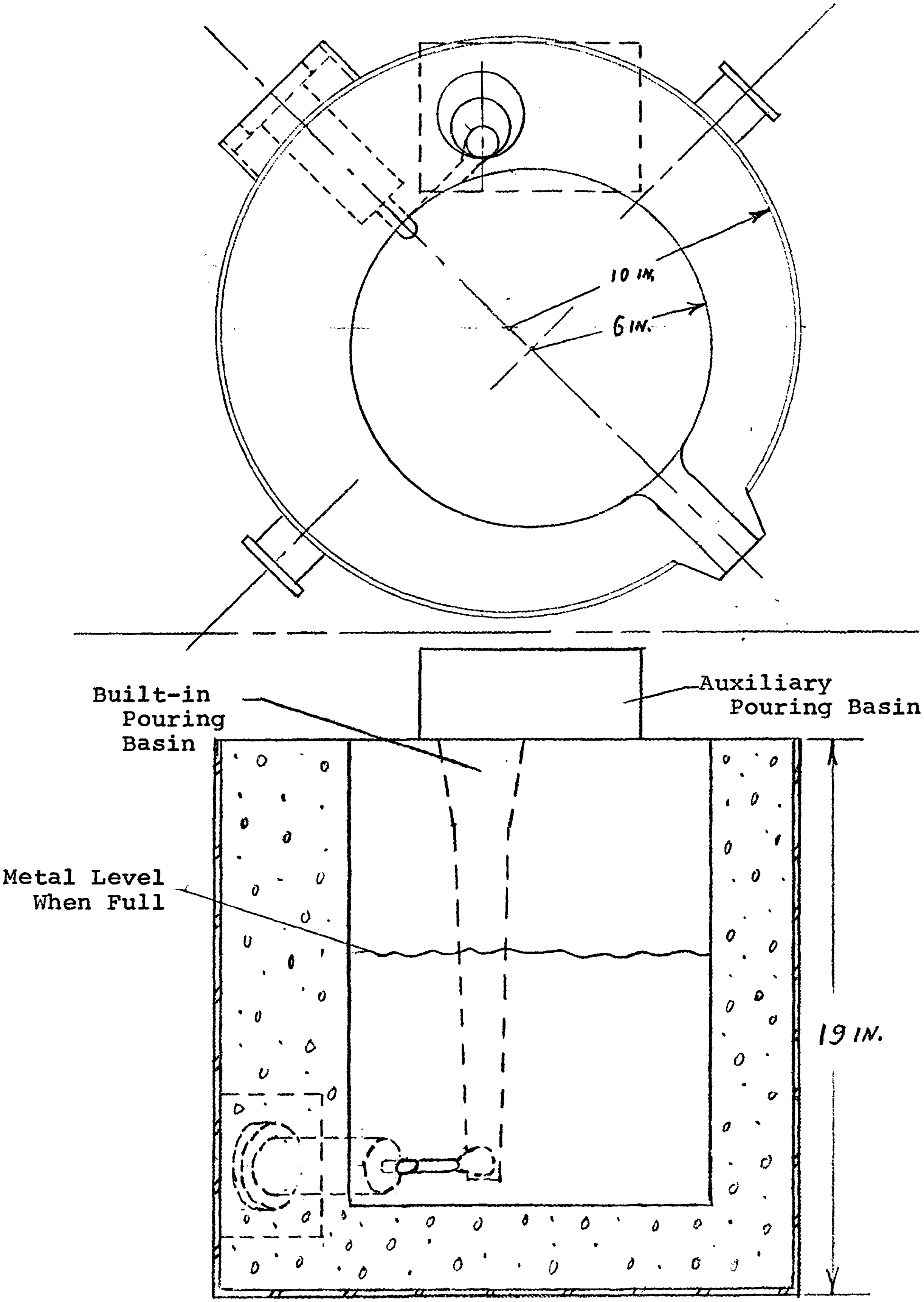


Figure 9 - Ladle downspout and injector configuration.

The ladle was preheated to between 1500F and 2000F with a large natural gas and air torch prior to all experimental runs that were made.

In the first run metal was tapped directly out of the furnace so as to obtain the hottest possible metal for burning out the steel nozzle and inner shell. The built-in pouring basin was used, and this proved to be a mistake. The ladle was so small compared to the 150,000 lb. channel induction furnace, that trying to hit a 3 inch diameter hole and accurately control the flow rate was like trying to fill a thimble from a 5 gallon can of water.

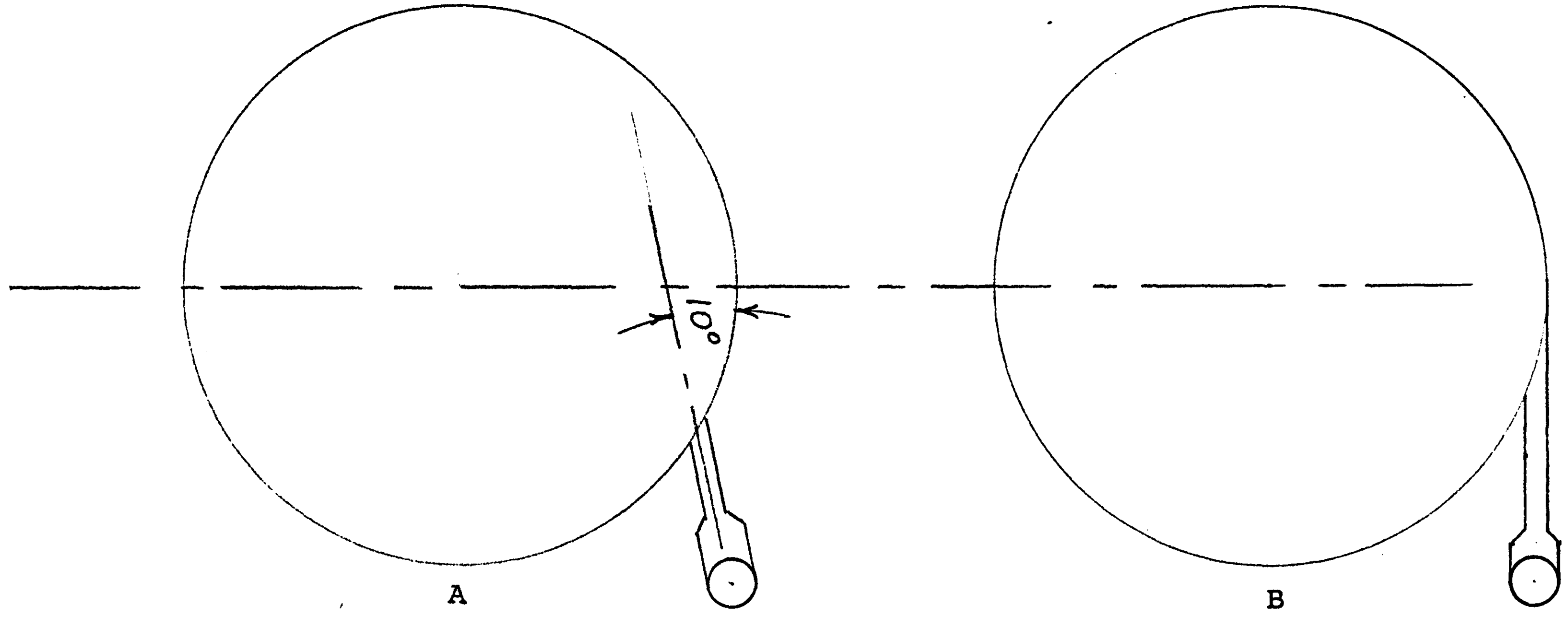
The first metal out of the drum-type furnace was a very small stream which dribbled over the furnace lip and over the ladle. Only part of the metal hit the downspout and since there was not enough metal to maintain the flow through the downspout, it promptly froze up. As the bulk of the metal entered the frozen downspout, it simply filled up and then began to run over the side of the ladle and either onto the floor or into the center of the ladle. At this point it was decided to continue filling the ladle by pouring down the center. This would melt the steel liner and get it out of the way for future runs, the heat from the metal bulk perhaps opening the frozen downspout. Although the liner did melt out, the downspout remained frozen and had to be reopened with a steel and oxygen lance. The lance consisted of a piece of low carbon steel pipe with oxygen flowing through it under 5 to 10 psi pressure. The tip of the lance is molten and reacts with the oxygen to give off considerable heat. The heat remelts the frozen metal in the downspout, which is also partially oxidized by the oxygen giving off more heat. The metal, which is not oxidized, is superheated enough to flow out. This type of lance generates enough heat to melt refractory as well as metal and care had to be taken not to damage the refractory.

A second run was made immediately after the ladle was cleaned out. This time, however, the metal was tapped into the center of the ladle until an even flow was established out of the furnace, at which time the ladle was moved with hooks so that the metal stream entered the downspout.

Once again there was so much spillage that it was impossible to determine if the ladle was being filled by the downspout or by metal that was splashing over the top of the refractory and into the ladle.

The downspout did plug up when pouring was stopped, but it is impossible to say whether or not the downspout was plugged during the pour. Though the downspout was cleared with the oxygen lance, this time the nozzle also had to be cleared, and in so doing the refractory was modified enough to change the tangential entry of the iron (fig. 10B). Tangential entry of the iron was re-established prior to heat 4 (fig. 10A).

The built-in pouring basin was declared a failure at this point, and all further experiments utilized a large



Modified Configuration
Heats 1, 2, and 3

Original Configuration
Heats 4 and 5

Figure 10 - Modification of tangential metal entry by oxygen lance

auxiliary pouring basin plus a steel plug which was removed only after the pouring basin was completely full of iron. A moldable plastic refractory material was used to seal the gap between the pouring basin and the ladle.

Heats Involving Magnesium Injection

Heat One

No changes were made to the treatment ladle for heat 1. A procedure change was made, however, and the metal was poured into the pouring basin from a 1 ton ladle rather than from the furnace.

A 130 gm. billet of pure magnesium was used for the inoculant. The injector nozzle size was one-sixteenth inch. A high density alumina sheath was used to protect the injector nozzle tip from the iron stream entering the ladle.

The silicon shock consisted of 0.75 percent of 85 percent ferro-silicon material which was greater than five-sixteenth inch in size. The shock was stirred into the ladle after filling was complete and the magnesium reaction had died down.

Heat 1 began when the magnesium was placed in the injector followed by the piston to seal air out of the system. The magnesium melted in the extruder under a gas flow rate of 6 cf/hr. to inhibit magnesium burning and keep the nozzle open. Magnesium temperature was measured with a chromel alumel thermocouple which was placed at the bottom of the threaded hole in the piston (fig. 4E).

Iron was poured into the auxiliary basin until the metal level was 1 inch below the top, at which time the plug was pulled and the ladle began to fill. This method for choking the downspout worked very well, and the downspout did not plug up again as the ladle was filled.

Magnesium injection failed, due to a plugged nozzle tip, and the magnesium came around the injector piston to relieve the applied pressure. Also, the inlet gas port was plugged with magnesium to within 1 inch of the shutoff valve.

A small amount of magnesium did get into the iron during heat 1, but it was after the ladle was filled that a very small and mild magnesium flare appeared. The flare lasted no more than 10 seconds.

The valves on the hydraulic system were set so that the piston would travel 1 inch in 15 seconds. Since the magnesium billet was 4 inches long, the total injection time was 1 minute. To obtain the slow piston travel, the inlet valve was opened one-eighth turn, which in itself was difficult. Piston behavior under these conditions was unstable. The valve was set in an equilibrium position, and if the valve were closed just slightly, the piston would move inward, but any slight resistance would stop the motion, and the valve would have to be reopened before the piston would see the pressure available on the inlet side of the control valve and begin to move.

Either a more sensitive needle valve should have been used to control the inward piston travel, or two hand pumps in parallel should have been used to accurately control piston travel and maintain forward motion.

Heat 1 did not work because the carbon dioxide gas flow was shut off immediately before iron entered the ladle, and before the piston had started to move. The nozzle tip became plugged with iron and could not be reopened. Essentially zero magnesium got into the iron.

Heat Two

No modifications were made to the equipment used in heat 2. The injector nozzle had to be replaced and the gas ports reopened by drilling out the magnesium, but this was all that was done to the equipment.

A 4 inch by 1.25 inch diameter piece of magnesium bar was used for the inoculant.

The silicon shock again consisted of 2-1/4 lb. of 85 percent ferro-silicon with a minimum particle size of five-sixteenth inch which was stirred into the ladle after magnesium treatment.

Heat 2 also began with the insertion of solid magnesium into the injector. The magnesium melted and some was forced out the nozzle by the volumetric expansion which accompanies the solid liquid transformation.

The temperature measured inside the piston, however, was only 775F. Since magnesium melts near 1200F, there was at least a 425F thermal gradient between the magnesium and the thermocouple. The thermocouple definitely was not contaminated. It was decided that this thermal gradient would not hurt the procedure as long as it was constant and the magnesium melting point could be predicted. Time temperature data from heats 2 and 3 indicated that the thermal gradient was not constant but varied with piston location in the injector tube. A larger thermal gradient was observed when the piston was near the flange than when the piston was one-half inch inside the flange. In heat 5 a dummy piston was used with a nine-sixty-fourths inch hole drilled through the piston face. The thermocouple could then extend into the injector cavity, thus making accurate magnesium temperature control possible. Time vs. magnesium temperature data was obtained using the dummy piston, and when the magnesium temperature neared the melting point, the dummy piston was removed and the regular piston with the hydraulic cylinder was installed. The magnesium treatment of the iron began when the magnesium temperature, as predicted from the time temperature data, reached 1250F.

The downspout and removable plug worked as planned and the ladle filled smoothly. The magnesium injection, however, did not go as well. The gas inlet port was left open while the piston was started inward, since magnesium had backed into the gas port on all prior runs in spite of the shutoff valve. Initially the piston moved in rapidly, but as soon as the flare appeared the injection controls were set so that slight forward movement would be maintained. Due to instability of the equipment, the piston stopped moving and the nozzle plugged up. Further attempts to open it failed.

An undetermined amount of magnesium was lost when the piston was removed from the injector, but undoubtedly some of the 50 gram difference got into the iron initially. The magnesium flare observed was much less violent than flares observed in later heats, but the magnesium was coming out of a one-sixteenth inch nozzle rather than a one-eighth inch nozzle. Magnesium spheres one-sixteenth inch in diameter would contain only one-quarter as much magnesium as one-eighth inch spheres; thus the reaction should be much less violent.

Heat 2 failed when the nozzle plugged up after the gas was shut off with no concurrent forward piston movement. Approximately 50 gm. of magnesium entered the iron. The pouring temperature was 2620F.

Heat Three

The nozzle size was enlarged to one-eighth inch for heat 3, and the same procedure was followed to get the magnesium moving out of the nozzle rapidly at the start, and then to slow it down after it was certain that the nozzle was open.

Gas leakage of 3 cf/hr. was observed with the brass control valve in the closed position before the run. The gas flow was increased to 12 cf/hr. to keep the nozzle open.

A 4 inch by 1.25 inch diameter magnesium bar weighing 139 gm. was used as the inoculant. The usual 2-1/2 lb. silicon shock was stirred into the ladle after filling was completed and the magnesium flare had died down.

The run started with the iron filling the ladle smoothly and with gas bubbles coming out of the injector nozzle. After the iron was 2 to 3 inches above the injector nozzle, the hydraulic inlet valve was opened a full one-half turn to get the piston moving rapidly until all slack and trapped gas was out of the injector. The valve was closed to near equilibrium as soon as the magnesium flare signified the nozzle was open.

Though the new method worked well, there was considerable turbulence and a brilliant white flare as the first magnesium bubbles broke the iron surface. Splattering metal startled the man pouring the iron, and he stopped pouring momentarily. At the same time the magnesium injection was shut down until the iron flow could be restored, and during the interim of about 5 to 10 seconds, the nozzle froze up and could not be reopened.

The injector nozzle plugged up when piston movement temporarily stopped. The sulphur content decreased from

0.034 - 0.019, while the residual magnesium content increased from 0 - 0.006 percent. The pouring temperature was 2560F, and 89 gm. of magnesium were injected. Metal depth in the ladle was 8.8 inch, from which the weight was calculated as 270 lb.

Heat Four

During injector maintenance after heat 3, a drill bit broke off in the long gas port as the magnesium was being drilled out of it. A new gas inlet hole was drilled into the plugged gas port behind the broken drill bit about 1-1/2 inch from the rear flange of the injector. Also, a straight stainless steel fitting was installed in place of the brass valve, since the threads on the brass valve may have been leaking.

A new technique for introducing the silicon shock was tried. Eighty-five percent ferro-silicon material smaller than 0.13 inch was poured into the downspout with the last 50 lb. of iron into the ladle.

Both high density alumina injector nozzle sheaths supplied by the Coors Porcelain Co. had broken while attempting to remove solidified iron from them, and a substitute nozzle was molded out of plastic refractory material used for patching ladles. This nozzle, shaped like a volcano around the one-eighth inch metal nozzle, worked very satisfactorily.

Magnesium temperature was measured through a nine-sixty-fourth inch hole drilled in the center of a dummy piston inserted in the extruder during melt-down of the magnesium. The dummy piston, an extra piston modified to allow the thermocouple to pass through into the injector cavity, provided much more sensitive temperature control of the magnesium.

The run began as the magnesium was put into the injector and power was applied to the heater. During magnesium melting the thermocouple pushed the billet against the front of the injector, and as the magnesium melted, some of it was pushed out of the nozzle by the solid-to-liquid volume expansion. The nozzle did not plug up, but about 5 gm. of magnesium were lost before the run began.

The ladle filled smoothly, and the magnesium was injected almost completely. Less than 5 gm. of magnesium was reclaimed from the injector following the run. The total amount injected then was between 142 gm. and 132 gm. of magnesium.

The finely divided silicon shock material entered the downspout with the metal stream; however, the ferro-silicon that was near the upper size limit floated on top of the pouring basin and did not enter the downspout until the last metal started down. This last metal solidified, plugging up the downspout, but it caused no harm other than the inconvenience of having to clean out the downspout with the oxygen lance.

An additional one-half lb. of 85 percent ferro-silicon was stirred into the ladle to make up for the spillage loss encountered at the start of the heat, and the ferro-silicon trapped in the downspout.

Heat 4 was the first mechanically successful heat. It failed to produce nodular iron for two reasons: first, the sulphur content of the base iron was not allowed for in figuring the magnesium which would be required for a residual of 0.04 percent; secondly, the ladle was overfilled by 50 lb. A magnesium residual of 0.007 percent was obtained, but this was insufficient to produce nodular iron.

The metal was poured at 2610F, and 135 gm. of magnesium were injected into 350 lb. of iron. The sulphur content decreased from the base of 0.034 percent to 0.002 percent and the magnesium residual increased from zero to 0.007 percent. The equivalent magnesium residual, or the actual magnesium residual plus the decrease in sulphur content, was 0.041 percent, and if the base iron had been desulphurized with calcium carbide prior to magnesium treatment, nodular iron would have been made.

Heat Five

The weight of iron poured into the treatment ladle was measured from the metal depth by a rod cut to length from the top surface of the ladle. This method was used because the small crane scale used in the other heats proved to be only within 50 lb., even though the smallest scale divisions were 10 lb..

Calcium was added to the magnesium billet in order to retard the violence of the reaction. The composition of the magnesium billet then was 1.7 percent calcium, 1 percent manganese, 3 percent aluminum, and 94.3 percent magnesium. The physical dimensions of the billet were 4 inches long, 1.43 inches in diameter, and a one-quarter inch diameter hole was drilled one-half inch deep into the rear face of the billet as a thermocouple receptacle.

The ladle filled smoothly with iron, and 75 percent of the magnesium went in as planned. The metal level could not be judged accurately, however, because of the magnesium flare and the pour was stopped early. After the flare died down one-half minute later, the metal level was observed to be considerably low. Unfortunately no pin samples were taken and no test bars were poured before the metal level was adjusted to the 260 lb. level without further magnesium addition.

Measuring the metal depth from the top of the ladle with a rod proved unfeasible because the magnesium flare shrouded the rod. Either some sort of low density material should have been attached to the rod tip so that the metal surface could be detected when the rod began to float, or the rod should have been longer than necessary so that it would have time to heat to a dull red while the metal level rose to the proper height.

Only 75 percent of the magnesium got into the iron. For some reason the last inch of the billet would not go through the nozzle even under maximum pressure. The temperature was high enough to melt the magnesium; however, during the melting phase the thermocouple has been removed from the dummy piston when the magnesium was molten, and a small button of magnesium came out the hole and was exposed to the air. Since the button was not protected by flux, it probably acted like a wick for oxygen to diffuse into the reactive magnesium, duplicating the phenomenon of internal burning in the temperature range where magnesium is usually stable.

The phenomenon of internal burning in magnesium protected by flux is common to magnesium die casters, and occurs whenever the temperature of the magnesium exceeds 1350F. Fluid, stable, molten magnesium will react to form a viscous, chunky mass when internal burning occurs, even under the protective cover of a flux. If the protective flux is not present, as is the case in the injector, then internal burning could easily occur at lower temperatures.

The amount of metal originally treated, and the amount of metal added, could be calculated both from the base and final sulphur content, and from the measured pouring time during which the magnesium was added. The weighted average of the results is 115 lb. of iron (appendix C).

The inoculation reaction was much more violent in heat 5 than in heat 4, but this is reasonable, since

32 percent more magnesium was added to one-half the iron in a shorter period of time than normal. This also indicates that more metal depth in the cyclone is desirable for decreased violence and its counterpart, increased magnesium recovery.

Nodular iron would have been made, according to appendix C, had the iron originally treated not been diluted. However, several things were observed accidentally because of the iron dilution which would not have been observed otherwise.

The sulphur content in heat 4 decreased from the base of 0.034 percent to 0.002 percent, when all of the iron was treated with magnesium. In heat 5 the sulphur content decreased from 0.034 percent to 0.019 percent. As the sulphur balance in appendix B show, none of the sulphur added in the diluting iron was removed by residual magnesium in the treated iron.

The sulphur in the diluting iron may or may not have combined with the residual magnesium, but if it did combine, then the magnesium sulphide particles remained suspended in the iron. This indicates that one function of the magnesium that boils out of the iron is to attract and physically remove sulphur in one form or another to the air-metal surface where it can be removed in the slag.

Pin samples were taken from the surface of the ladle immediately after the ladle was full, before the surface was slagged, and before the ferro-silicon was added. The sulphur content was 0.045 percent and the magnesium content was 0.090 percent in these pin samples, further evidence that magnesium removes sulphur as it boils through the melt.

Seventy-five percent of the magnesium, or 137 gm., were injected into 115 lb. of iron. The sulphur content probably decreased for 0.034 to 0.002 or less, and the magnesium residual was 0.043 percent. The iron was diluted to the planned treatment weight of 260 lb.. The final sulphur and magnesium residual concentrations were both 0.019 percent which is unfavorable for good nodular iron production. Microstructure photographs of test bars that were poured from the diluted iron show a tendency toward nodular iron. Nodular iron would have been produced if the iron originally treated had not been diluted. The pouring temperature in heat 5 was 2625F.

Heat Six

The only modification planned on heat 6 was the addition of 1 percent calcium carbide to the carbon and silicon, which had to be boiled into the base iron with nitrogen to adjust the chemistry. The calcium carbide would remove some sulphur from the base iron, allowing more iron to be treated in the ladle with the fixed maximum amount of magnesium that could be placed in the injector.

A one-eighth inch nozzle was used in the injector, and the magnesium billet weighed 201 gm.. The usual 2-1/4 lb. of 85 percent ferro-silicon, 0.28 inch and +0.13 inch in size, was prepared for the silicon shock.

The run started more smoothly than any other run, but during the initial pour iron splashed on the hydraulic lines, causing the input line to rupture, aborting the experiment.

Castings were poured and pin samples were taken, but they were not analyzed, because almost no magnesium got into the iron.

This completed the developmental work agreed to by General Iron Co.

RESULTS

The chemical analysis, conventional magnesium recovery, magnesium recovery considering desulphurization, pouring temperature, approximate treatment temperature, weight of iron treated, initial magnesium weight, weight of magnesium recovered after each run, weight of magnesium injected by difference, and the tensile strength of a sample bar taken from each heat is tabulated for iron heats one through five.

A representative microstructure photo from heats 1 and 5 follows the Table of Results.

Table of Results

HEAT NO.		1	2	3	4	5	5 Before Dilution
Initial Mg Wt. gms		130	134	139	142	188	188
Wt. Mg Recovered From Injector		?	77?	50	7	51	51
Mg Injected into Iron gms*		0*	57?*	89*	135*	137*	137*
Base S		0.034	0.034	0.034	.034	.034	.034
Final S		0.034	not determined	0.019	.002	.019	.002 assumed
S Removed		0*	0*	0.015*	.032*	.015*	.032*
Mg Residual		0.000	0.003	0.006	0.008	0.019	0.043*
Conv. Mg Recovery*	%	—	—	8*	9*	16*	17*
Mg. Recovery Sulphur Adjusted*	%	—	—	29*	47*	29*	30*
Cause of Failure		Nozzle Plugged	Nozzle Plugged	Insuff. Mag.	Insuff. Mag.	Metal Dilution	Good Iron
Tensile Strength		29,000	32,000	24,000	25,000	41,000	—
Elongation	%	<1	<1	<1	<1	<1	—
No. Bars Pulled		1	1	2	3	2	—
Chem. Comp. Base Iron							
C		3.56	3.55	3.59	3.50	3.50	—
S		0.034	0.034	0.034	0.034	0.034	—
MN		.65	.68	.80	.66	.65	—

* Denotes Calculated Values

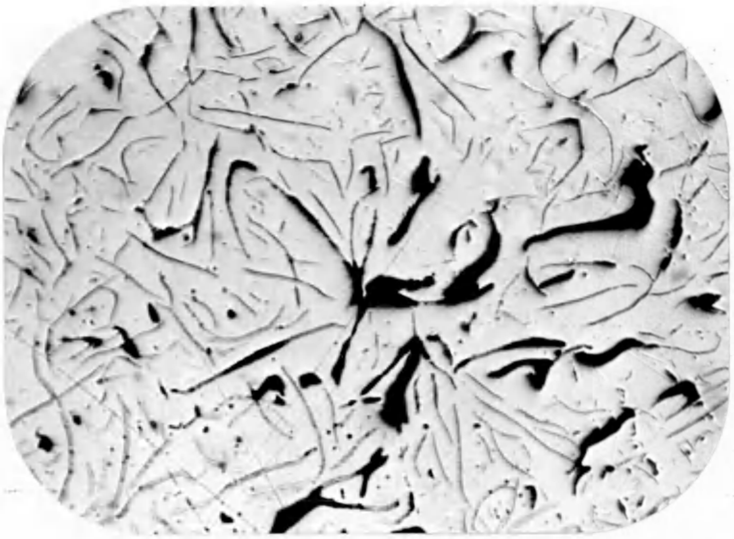
Table of Results (cont.)

HEAT NO.	1	2	3	4	5	5 Before Dilution
Chem. Comp. (cont.)						
Iron After Treatment but Before Casting						
S	.034	not determined	.019	.002	.019	—
Mg	0.000	0.000	0.006	0.008	0.019	0.043*
Ca	0.000	0.000	0.004	0.002	0.002	—
Si	2.29	not determined	2.61	2.34	1.83	—
Iron After Casting						
Mg	—	—	0.005	0.007	0.015	—
Ca	—	—	0.004	0.000	0.000	—
Pouring Time	—	—	1.55 min.	—	—	—
Wt. Iron Treated lb.	300	300	270	350	260	115
Nozzle Size	1/16 in.	1/16 in.	1/8 in.	1/8 in.	1/8 in.	—
CO_2 Flow Rate cf/hr.	6	6	12	6	6	—
Pour Temp. (Meas.)	—	2620F	2560F	2610F	2625F	—

* Denotes Calculated Values

MICROSTRUCTURE PHOTOS

Heat 1

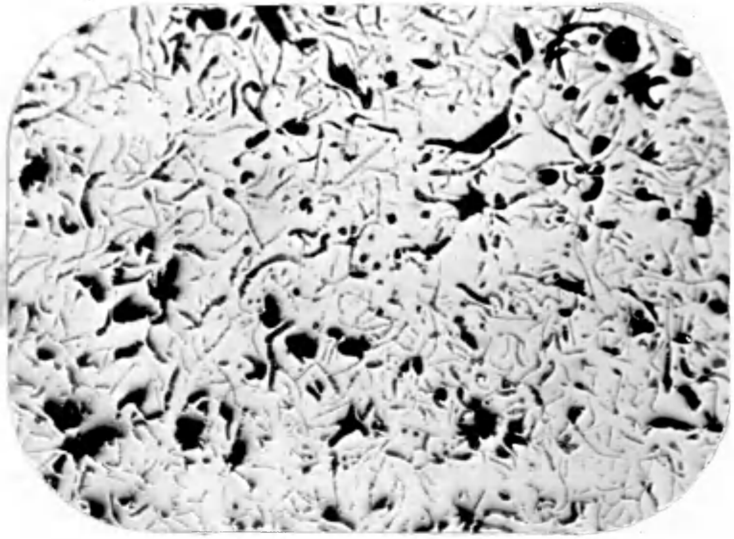


Unetched

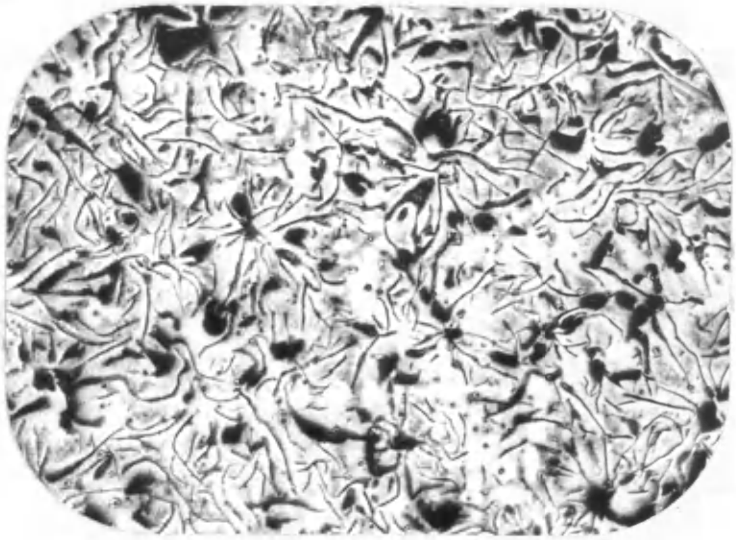
Etched

MICROSTRUCTURE PHOTOS

Heat 5



Unetched



Etched

Explanation of Table of Results

Following is a synopsis of how the different items in the table of results were obtained, and how large the errors are in them.

1. Pouring Time: was obtained in only one of the six heats, although it was supposed to be obtained from each heat. Time was measured with a stop watch calibrated in hundredths of a minute, accurate to 0.01 minute.

2. Weight of Metal Treated: was measured several different ways, as different methods tried were found unacceptable. They are described in detail in the synopsis of each heat.

3. Nozzle size: was not measured except by the size of the drill used to make the hole. Nozzle size is ± one-sixty-fourth inch.

4. Initial Magnesium Weight: was measured on a 2000 gm., double-pan balance accurate to ± 0.03 gm.

5. Final Magnesium Weight: measurement was complicated by incomplete magnesium recovery in some instances. Magnesium was lost in machining chips, lost into the gas ports, extruded around the piston and lost as the piston was withdrawn, or converted to powdery, brittle compounds that crumbled and were blown away. In different heats different complications were present and thus the limits of accuracy are different. In all cases the remaining material was

reweighed on the same balance to within 0.03 gr., but the results are reported based on how much magnesium was lost to the above items.

6. Carbon Dioxide Flow Rate: was measured with a National Cylinder Gas, Carbon Dioxide Flometer, model number 5668 accurate to ± 1 cf/hr.

7. Iron Temperature: going into treatment ladle was measured with consumable "Temtip" thermocouples accurate to ± 10F before the pouring ladle was transferred from the furnace to the treatment ladle. No facilities for measuring iron temperature were available at the treatment ladle.

8. Temperature after treatment was measured visually by the furnace foreman to ± 100F.

9. Tensile Strength and Microstructure: specimens were taken from a single bar or bars poured after each heat. The bars cast were 6 inches long by 1 inch diameter. From this bar a standard 0.505 inch diameter ductile iron test bar was machined, and a 1 inch long sample for metallographic examination was machined 1 inch from the risered end of the bar. Actual tensile strength was obtained on an Olsen balance-type, tensile test machine accurate to ± 10 lb. force. Since the standard area was 0.200 square inches, the strength was within ± 50 psi.

10. Elongation: was essentially zero, since all specimens tested were grey iron. A mechanical strain gauge was not used for fear of damaging it when fracture occurred before the yield point.

Chemical Analysis: was obtained from outside sources, General Iron Works Analytical Laboratory, and Colorado Analytical Laboratory.

1. Carbon: was determined by General Iron on a Leco Carbon analyzer to within ± 0.03 percent. The sample was first burned in an induction furnace, and the CO_2 gas formed from carbon and clean oxygen was absorbed, giving the percent carbon in the sample.

2. Silicon: was determined by General Iron by solution of the iron in perchloric acid, filtering and charring the residue to yield percent silicon within ± .05 percent.

3. Manganese: was determined by General Iron, using the standard ASTM test.

4. Sulphur: was determined by General Iron, using hydrochloric acid and starch solution, plus potassium iodide. Titrant turns the solution blue, the sulphur dioxide gas from the burning furnace clears it up again. The titration is complete when blue color returns (ASTM test, accuracy ± 0.001 percent).

5. Magnesium: was determined by Colorado Analytical by Atomic Absorbtion and interpolation between standard solutions, accurate to 0.001 percent.

6. Calcium: was determined by Colorado Analytical by Atomic Absorbtion accurate to within 0.001 percent.

ECONOMIC ANALYSIS OF THE CYCLONE AND SANDWICH METHODS

An economic analysis of the alloy cost for treating iron must take into account the original cost of the alloy and the recovery expected when using that alloy, which would in turn depend on the method of introducing the alloy into the melt, and such other variables as the temperature at which the alloy is introduced. Once the primary cost and the recovery have been established, the economic analysis may be carried out.

Total alloy costs are computed for a fixed 25 percent Mg recovery and the recoveries experienced for both the sandwich method using 9 percent magnesium ferro-silicon and 0.5 percent silicon shock, and the cyclone method using 96 percent magnesium with 0.5 percent silicon shock, plus sufficient silicon in the form of 50 percent ferro-silicon to equal the silicon added with the magnesium in the sandwich method. Eighty-five percent ferro-silicon was arbitrarily chosen as the shock material since this material is normally used by foundries, and since the same cost will be added to both alloy totals. The only reason it is even included in the analysis is to give a better overall picture of the total alloy cost per ton.

Data on cost of alloys is taken from the January 2, 1970, price sheet published by the Union Carbide Corporation, Ferroalloys Division. The price for magnesium was obtained from Iron Age, February 1970 issue.

Material	Bulk price less transportation and pkg. costs
magnesium ingot	36¢/lb.
50 percent ferro-silicon	14.7¢/lb. of silicon
85 percent ferro-silicon	18.2¢/lb. of silicon
9 percent magnesium ferro-silicon	21.8¢/lb. of alloy (usually 40 percent silicon)

The alloy cost will be calculated two ways: first, by assuming equal 25 percent recoveries for both methods, and second, by using 20 percent magnesium recovery for the sandwich technique, and 30 percent magnesium recovery for the cyclone technique. The General Iron Works Co. usually gets 20 percent magnesium recovery using the sandwich technique (9% MgFeSi). The weighted-average magnesium recovery was 30 percent in heats 3, 4, and 5 using the cyclone technique.

Assuming a 25 percent recovery for both methods, a negligible sulphur content in the base iron, and a magnesium residual of 0.04 percent:

Cost of sandwich technique (25% Mg recovery)

$$\text{Mg needed/ton iron} = \frac{(0.0004\text{Mg})(2000\text{ lb.})}{0.25\text{ recovery}} = 3.2\text{ lb. Mg}$$

MgFeSi cost = $\frac{3.2 \text{ lb Mg}}{0.109 \text{ Mg}}$ X 21.8¢/lb. alloy = $7.75/ton iron

Si shock cost = (0.005 Si)(2000 lb.)(18.2¢/lb. Si) = $1.82/ton iron

Total alloy cost = $9.57/ton iron

Cost of pure mag. technique (25% Mg recovery)
Additional silicon which must be added as 50 percent FeSi to equal silicon
Added in MgFeSi in sandwich method
35.5 lb. MgFeSi (.40 Si)(14.7¢/lb. Si) = $2.09/ton
Mg cost (3.2 lb. Mg)(36¢/lb. Mg) = $1.15/ton
Si shock cost = $1.82/ton
Total alloy cost = $5.06/ton iron

Percent reduction in cost using pure mag. technique =

$$\frac{\$9.57-\$5.06}{\$9.57} \times 100 = 47.2\%$$

$$\text{Cost ratio} \quad \frac{\text{Sandwich method}}{\text{Pure mag. method}} = \frac{\$9.57}{\$5.06} = 1.89$$

Total alloy cost is cut approximately in half.

Cost comparison using observed mag. recoveries

Sandwich technique using 20 percent recovery:

Cost of silicon shock will remain constant at = $1.82/ton iron treated

Magnesium ferro-silicon cost will increase by the ratio of the recoveries: $7.75 (0.25 / 0.20) = $9.70/ton iron treated

Total cost of alloys per ton of iron $11.52

Pure mag. technique with 30 percent recovery:

Cost of silicon shock = $1.82/ton
Magnesium cost $1.15 (.25 / .30) = $0.96/ton

50 percent ferro-silicon cost

$$\frac{4 \text{ lb. Mg}}{0.109 \text{ Mg factor}} \text{ X } .40 \text{ Si factor X } 14.7¢/\text{lb. Si} = \underline{\$2.62/\text{ton}}$$

$$\text{Total alloy cost/ton iron} = \$5.40/\text{ton iron}$$

$$\text{Percent reduction in cost } \frac{11.52 - 5.40}{11.52} \text{ X } 100 =$$

$$\frac{6.12}{11.52} \text{ X } 100 = 53\%$$

$$\text{Cost ratio sandwich/pure mag} = \frac{11.52}{5.40} = 2.14$$

Economics definitely favors the pure magnesium inoculation technique by a factor of two in the total alloy cost per ton of iron.

If the silicon content of the base iron could be increased by using high silicon scrap rather than ferro-silicon alloys, the cost ratio would increase to \$11.52/\$2.78 = 4.2

Alloys for the new process could cost less than one-fourth of the sandwich technique alloy cost and have the additional advantage of using base metal with a much higher silicon content. Taking the 20 percent recovery calculations as an example,

$$100\% \left(\frac{4 \text{ lb. Mg}}{109 \text{ Mg factor}} \text{ X } 0.4 \text{ Si factor}\right)/2000 \text{ lb. iron} =$$

0.89 % Si added with magnesium in MgFeSi alloy.

The recovery of the silicon is nearly 100 percent; it is unfortunate that the magnesium recovery is not as good. This means that the base metal could be 0.89 percent higher in silicon and still make good nodular iron with the cyclone method.

DISCUSSION AND CONCLUSIONS

Overall Evaluation of the Cyclone Process

The main point of the thesis has been verified, even though good nodular iron was not made. Magnesium recoveries as good as or better than those obtained using magnesium ferro-silicon can be obtained using commercially pure magnesium if a small amount of the iron is treated with a small amount of the magnesium.

Evaluation of the Sandwich Method

The sandwich technique, which heavily inoculates the first metal into the ladle and then simply dilutes the inoculated metal with fresh metal, while effective and simple, is too simple. It is unrealistic to expect several tons of iron to equilibrate with several hundred pounds of magnesium alloy instantaneously, which must happen if good magnesium recovery is to be achieved.

Economics: Cyclone vs. Sandwich Methods

The economic analysis shows that the total alloy cost using the pure cyclone technique is between one-half and one-fifth (depending on how the Si in the MgFeSi is taken into account) of the total alloy cost using the sandwich technique. Alloy cost drops from $11.42/ton to between $5.40/ton and $2.78/ton.

Miscellaneous

A higher base silicon content, or a higher silicon shock, or both, can be used with the cyclone technique of injection, since no silicon pick-up occurs with the magnesium inoculation. The higher silicon content of the base iron would have the added advantage of allowing both grey iron and ductile iron to be made, without gross chemical composition changes, from a single melting furnace. This will simplify melting practice greatly in smaller job shop foundries with only a single furnace.

A metal cleansing action together with lower magnesium recovery occurs using the new process; however, as more experimental work is done on optimizing the ladle dimensions and other process variables, the magnesium recovery can probably be increased considerably while still allowing sufficient magnesium boiling for optimum metal cleanliness.

Evaluation of the Mechanical Equipment

The proposed experimental equipment works well in inoculating a small amount of the iron with a small amount of magnesium on a continuous basis as the ladle is filled. However, the equipment cannot be used, without modification, in foundries at the present time because of plugging problems with the magnesium injection nozzle and gas ports.

Pouring Basin, Stopper, and Downspout

The auxiliary pouring basin was absolutely necessary in order to maintain a continuous, well-controlled flow of iron in the downspout. The pouring basin plug prevented metal from entering the downspout until the pouring basin was full, thus minimizing the possibility of metal freezing up in the downspout and the filling time of the pouring basin.

Metal leakage in heat 4 between the pouring basin and downspout proved that the tapered downspout maintained positive metal pressure throughout the downspout and nozzle, thus preventing air aspiration which would decrease the magnesium recovery.

The tapered downspout was easy to reopen with the steel-oxygen lance.

Cyclone

Considerable stirring occurred in the ladle, even though the tangential iron velocity was only 3.3 ft/sec.

instead of the design velocity of 8.6 ft/sec. While it was impossible to observe where most of the magnesium bubbles broke the iron surface because of the intensely bright flare, after the reaction had almost died out, small bubbles were observed midway between the ladle wall and the center of rotation. The radial-to-vertical velocity ratio for one-eighth inch magnesium spheres was 2.2 instead of the theoretical 1.2, thus one-eighth inch magnesium spheres should not have reached the center of rotation (appendix A). Magnesium definitely came up through the iron and not along the iron-refractory interfaces. The turbulence undoubtedly helped mix the magnesium into the iron.

A much less violent reaction occurred with the one-sixteenth inch nozzle than with the one-eighth inch nozzle. This difference would be mostly due to the factor of 4 difference in volume between a one-eighth inch and one-sixteenth inch diameter magnesium sphere. The magnesium entrance velocity with the one-sixteenth inch nozzle was 4 times larger than the magnesium velocity with the one-eighth inch nozzle, which would also help achieve better mixing between iron and magnesium.

Injector

The final magnesium injector design satisfactorily injects magnesium into the iron, but maintenance would have to be performed to clear the nozzle after every run, and this would not be feasible on a production basis.

Piston: The sandwich piston design works very well. The graphite seals tightly during magnesium injection, although a very thin film is left inside the extruder after injection and piston removal. It is unknown whether or not this film actually has to be removed after each run. Quite possibly it would be removed as the piston moved in during the next run. The film was removed between heats for fear the film might further hinder piston travel and cause an experiment to abort.

Nozzle: The one-sixteenth inch diameter injector nozzle worked satisfactorily in the initial test phase when the injector was not mounted in the ladle. In both cases where it was tried in the ladle, it plugged up. It will probably work as the injection nozzle in the ladle if gas flow is sufficient to keep the nozzle open until the magnesium flow starts. The one-sixteenth inch nozzle will definitely plug up if for any reason iron is allowed to enter the nozzle. The one-eighth inch nozzle did not seem to be as easy to plug up.

The one-eighth inch nozzle was used during all three semi-successful runs in which an appreciable amount of magnesium got into the iron.

Steady gas flow during magnesium melting keeps the nozzle both open and cool. Gas flow should be increased from 6 to 9 cf/hr. for one-eighth inch nozzle, as the iron treatment begins to insure that no iron gets into the nozzle before magnesium injection begins.

Magnesium Burning: The injector nozzle is in contact with molten iron, and a considerable thermal gradient exists between the nozzle entrance and the nozzle tip where the magnesium meets the iron. When the magnesium is flowing rapidly out the nozzle, the high temperature presents no real problem, since the magnesium is not in contact with the nozzle long enough to heat up above 1350F. However, when magnesium injection is complete, the magnesium still in the nozzle begins to heat up quickly, leading to plugging of the nozzle. Internal burning of the last magnesium trapped in the injection nozzle is what ruined most of the nozzles that were lost. The material formed by the burning could not be drilled out, making nozzle replacement necessary.

The Process as a Desulphurizer

As heat 4 indicates, when all of the metal is effectively treated with magnesium, the residual sulphur content will tend toward 0.002 percent, but any desired sulphur residual between 0.002 percent and the base could be obtained by inoculating only part of the ladle, and then mixing base metal with it, as was unintentionally done in heat 5.

Nodular iron with a base sulphur content greater than 0.002 percent could probably be obtained, if desired, by heavily inoculating the first metal into the ladle and then diluting it by shutting off the magnesium flow as the last metal is added. This would simulate the sandwich process of making nodular iron.

The base sulphur content of 0.034 percent was lowered an order of magnitude in heat 4. Since 0.002 percent is the limit of sulphur removal as noted by Rehder (1950), the desulphurizing efficiency of heat 4 was 100 percent, with 45 percent magnesium recovery. It is impossible to estimate what the efficiency would be if the base sulphur content were higher than 0.035 percent, but probably it would increase, and probably the same low sulphur level of 0.002 percent could be obtained (Rehder, 1950).

Some magnesium loss seems to be necessary to cleanse the metal of sulphur, either as sulphur compounds attached to the rising magnesium vapor, or as free sulphur dissolved in the magnesium vapor. The mechanism is not presently known.

RECOMMENDATIONS FOR FURTHER WORK

A cost saving of from \$6.12 to \$8.74 per ton of nodular iron produced is a strong economic incentive to improve and perfect the cyclone technique of producing nodular iron.

Injector

The magnesium injector will have to be perfected, or at least modified, to keep the nozzle open so that more than one run per nozzle can be made. The process will not be feasible until this maintenance problem is solved.

Heats 1, 2, and 3 might have been successful if some mechanical means of opening a plugged nozzle during the run had been available. A mechanical nozzle opener capable of operating on stream would be desirable, if not mandatory.

Important System Parameters

Next in importance are the process variables which should be evaluated statistically to determine the conditions for optimum magnesium recovery and optimum metal cleanliness. These variables are: inlet velocity of the iron, velocity of the magnesium, percent calcium or other reaction-suppressing material in the magnesium, size of the magnesium inlet nozzle, depth of the metal being treated, temperature of the metal being treated, and possibly the sulphur content of the metal being treated.

APPENDIX A

Initial Design of Equipment

The rough original design calculations for the cyclone inoculation ladle can be divided into three parts:

1. Determination of the rate at which a magnesium sphere one-sixteenth inch in diameter will rise through molten iron.

2. Determination of a downspout size which will give a total fill time of approximately 1 minute, and the nozzle size at the tip of the downspout that will give tangential velocity to the cyclone such that a one-sixteenth inch diameter magnesium sphere will rise through the iron on a diagonal from the injector nozzle to the intersection of the center of rotation and the cyclone and the metal-air surface.

3. Determination of cyclone dimensions such that the ratio of the vertical velocity to the radial velocity of a one-sixteenth inch magnesium sphere will be equal to the ratio of the average metal height to the radius of the cyclone.

Vertical Velocity of Magnesium Spheres in Liquid Iron

The rate at which a magnesium sphere will rise in iron is calculated, based on the assumption that turbulent conditions will exist, and that terminal velocity is reached instantaneously.

At terminal velocity the summation of all vertical forces = 0; thus the bouyant force is equal to the resistance of the fluid to the movement of the magnesium spheres.

The bouyant force is equal to (volume of iron displaced) (density difference between iron and magnesium) (gravity) = $(\frac{D^3}{6})$ $(\rho \text{ iron} - \rho \text{ mag.})$ g.

The resistance force has been determined for cubic sands in various liquids and was found to be proportional to the (particle velocity^2) (the density of the liquid) and (the cross-sectional area of the particle). Mathematically, $R = V_r^2 \rho_{iron} A$, the constant of proportionality was defined as Q/2 and experimentally determined. Q would be constant for any geometrically similar particle.

Data for Q for cubic sands was used in the analysis for the magnesium spheres in iron due to the lack of data for magnesium spheres rising in iron. Because the assumption that magnesium is in spherical form may or may not be accurate, the use of the cubic sand data is justifiable.

The rising velocity of a magnesium sphere is determined by equating the bouyant and resistance forces:

$$V_r^2 \frac{Q}{2} \rho_{iron} \left(\frac{\pi D^2}{4}\right) = \left(\frac{\pi D^3}{6}\right)(\rho_{iron} - \rho_{mag})\, g$$

$$V_r = \sqrt{\frac{4}{3}\, \frac{(\rho_{iron} - \rho_{mag})\, g D}{\rho_{iron}\, Q}}$$

For Reynolds numbers greater than 1000, Q is constant at 0.4; thus as a first approximation say Q = 0.4.

For a one-sixteenth inch diameter sphere

$$\underline{V_r} = \sqrt{\frac{4}{3}\, \frac{(7.6 - 1.7)}{7.6 \times 0.4}\, (32.2 \times 12)\frac{1}{16}} = \sqrt{62.5\, \frac{in^2}{sec^2}} =$$

<u>7.9 in/sec</u>.

Reynolds Number

$$\underline{N_R} = \frac{\rho_L V_r D}{\mu} = \frac{7.6\ (7.9 \times 2.54\ cm)\ (\frac{1}{16} \times 2.54\ cm)}{0.02} =$$

<u>1210</u> thus Q = .4 is correct.

For a one-eighth inch diameter sphere

$\underline{V_r} = \underline{11.2}$ in/sec.

The Reynolds number for a one-eighth inch particle is larger than 1,210. Thus the assumption that Q = 0.4 is valid for both one-sixteenth and one-eighth inch magnesium spheres. The vertical velocity of an one-eighth inch and one-sixteenth inch diameter magnesium sphere in iron is 11 and 8 in/sec..

Determination of Initial Downspout and Nozzle Dimensions

The flow rate in the downspout and nozzle was calculated by trial and error to yield a filling time for 300 lb. of iron of approximately 1 minute.

The average head loss that had to be dissipated in the downspout was 21 inches minus the average metal depth of 6 inches, or 15 inches (h_L = 15 in.).

The surface roughness ϵ of the magnesia refractory was arbitrarily taken as 0.02 inches, equivalent to an ϵ value for concrete.

The Reynolds number was assumed to be large and a value of friction coefficient f was then obtained for an $\frac{\epsilon}{D}$ value of 0.02 as 0.049.

The actual length of 19 inches of 1 inch diameter pipe was lengthened by 27 x diameter or 27 inches for a total length of 46 inches because of the medium radius bend at the bottom of the downspout.

The metal velocity in the 1 inch diameter pipe was then calculated from the friction equation as follows:

$$f = \frac{2h_L\ Dg}{\rho\ LV^2} \text{ from which } v = \sqrt{\frac{(\frac{15}{12})\ (\frac{1}{46})\ 32.2}{0.049\ 7.6}} =$$

$$\sqrt{4.7\ \frac{ft^2}{sec^2}} = 2.18 \text{ ft/sec.}$$

The Reynolds number = N_R = 7.6 (2.18x12x2.54)(2.54)/ .02 = 64,000. Thus, f of 0.049 is correct.

The volumetric flow rate is thus:

$$2.18 \text{ ft/sec.} \times \frac{\pi}{4} \left(\frac{1}{12} \text{ ft}\right)^2 = 0.0119 \text{ ft}^3\text{/sec. or}$$

$$0.715 \text{ ft}^3\text{/ min.}$$

and the fill time for 300 lb. $= \dfrac{300 \text{ lb.}}{480 \frac{\text{lb.}}{\text{ft}^3}} \times \dfrac{60 \text{ sec.}}{0.715} = 53$ sec.

The inlet velocity into the cyclone being too low, a one-half inch diameter, 30°-tapered nozzle was installed at the lower end of the downspout to increase the velocity by a factor of 4 from 2.18 ft/sec. to 8.7 ft/sec.

Determination of Cyclone Dimensions

Determination of cyclone radius, subsequent metal height for 300 lb. iron, inlet velocity to the cyclone, and the radial component of velocity for a one-sixteenth inch diameter magnesium sphere was determined by analyzing a table of values computed for each of the parameters and selecting those parameters that most closely satisfied the restrictions described in the initial design synopsis. Sample calculations are presented only for the parameters chosen.

Based on an inlet velocity of 8.7 ft/sec. and a vertical velocity of 8 in/sec. for a one-sixteenth inch diameter magnesium sphere, the cyclone dimensions were calculated as follows:

The radial acceleration experienced by a magnesium particle is equal to the (tangential velocity)^2 divided by the (distance of the particle from the center of rotation), or radial acceleration = V_t^2/R_O.

At terminal velocity in the radial direction, the force due to radial acceleration equals the resistance of iron to magnesium movement. The resistance force in the radial direction is determined as in the analysis of the vertical velocity.

$$\sum F_R = 0 = \left(\frac{D^3}{6}\right)\left(\frac{\rho\,\text{mag}}{g}\right)\left(\frac{V_t^2}{R_0}\right)-\left(\frac{D^2}{4}\right)\left(\frac{Q}{2}\right)\left(\frac{\rho\,\text{iron}}{g}\right)V_r^2$$

$$V_r^2 = \frac{V_t^2}{R_0}\left(\frac{\rho\,\text{mag}}{\rho\,\text{iron}} \times \frac{D}{Q} \times \frac{4}{3}\right).$$

From inspection, the radial velocity will increase with increasing particle size, with decreasing radius R_0 from the center of the cyclone, and with decreasing Q. For Reynolds numbers greater than 1000, however, Q = 0.4; therefore, assume Ry will always be greater than 1000 to start.

For R_o = 6 in., V_r =

$$\sqrt{\frac{(8.7\ \text{ft/sec.})^2}{6\ \text{in.}} \times \frac{1.7}{7.6} \times \frac{1}{16}\ \text{in.} \times \frac{1}{0.4} \times \frac{4}{3}} =$$

$$\sqrt{.59} = 0.768\ \text{ft/sec.} = \underline{9.2\ \frac{\text{in.}}{\text{sec.}}}$$

Reynolds Number = $(7.6 \times 9.2 \times 2.54 \times \frac{1}{16} \times 2.54)/.02$ = <u>1410</u>. Thus Q = 0.4 is valid. The average metal height in the 12 inch dia. ladle is 5 inches. Thus the ratio of radial to vertical velocity = $\frac{9.2}{7.9} \simeq 1.2 = \frac{6\ \text{in.}}{5\ \text{in.}}\ \frac{(\text{cyclone diameter})}{(\text{av. metal height})}$.

APPENDIX B

Sample Calculations for Magnesium Recoveries

Calculation of magnesium recovery in conventional way not adjusted for sulphur removal by magnesium.

Heat no. 5 Data: Mg injected = 137 grams

Before dilution Weight iron treated = 115 lb.

Final Mg concentration ==0.043%

Let R = recovery factor

using magnesium balance

$$\frac{\frac{137\text{ gm}}{454\text{ gm/lb.}} \times R}{120\text{ lb.}} = 0.00043$$

$$R = \frac{(0.00043)(120)(454)}{137} = 0.17$$

Mg recovery = .17 or 17%.

Calculation of Mg recovery considering sulphur removal. Assumption: Sulphur is removed as MgS and therefore the decrease in sulphur concentration must be added to residual Mg concentration to get an equivalent Mg concentration this is especially important if decrease$[S] \geq$ Mg residual.

Sulphur concentration removed = 0.032

<u>Mg residual</u> = <u>0.043</u>

Equiv. Mg residual = 0.075

$$R = \frac{(0.00075)(120)(454)}{137} = 0.296$$

Recovery = 0.296 = 30%

APPENDIX C

Calculated Chemical Composition Before Dilution in Heat 5

In heat 5, the iron which was originally treated was not properly weighed into the ladle as the magnesium treatment was taking place because the measuring rod was obscured by the magnesium flare.

The original plan was to treat 260 lb. of iron; however only about 100 lb. were actually treated before the pour was stopped for fear of overfilling the ladle. The magnesium flare did not die down for approximately one-half minute after pouring was stopped, at which time the metal level was observed to be considerably short of the 260 lb. mark.

Unfortunately, the exact metal depth was not measured, and the metal level was mistakenly judged to be only two inches short of the proper level. No chemical sample pins were taken, and no test bars were poured.

The metal level was simply adjusted, without considering the sulphur being added, to the 260 lb. mark, under the reasoning that the first metal was so heavily inoculated that it would have to be diluted in order to achieve good nodular iron.

Because of the shallow depth of the metal being treated, the short treatment time during which considerable magnesium was added, and the possible deleterious effects of the sulphur being added in the diluting iron, not only was <u>good</u> nodular iron not made but it is debatable whether <u>bad</u> nodular iron was made.

The microstructure of one of the test bars poured using this bad nodular iron indicates that the structure is definitely not that of a normal flake-grey iron. The graphite is definitely not the perfect spheroidal shape associated with good nodular iron but because it is chunky and closer to spheroidal than to any type of flake, it will be called poor nodular iron.

The sulphur content of the final iron obtained in heat 5 was 0.019 percent, at the upper limit usually specified for ductile iron. The magnesium residual was also 0.019 percent, which is considerably below the usual minimum specification of 0.030 percent; thus, nodular iron was not made from a composition viewpoint.

The only definite data taken on the iron treated with magnesium was the pouring time = 0.54 minutes. The total pouring time was not measured in heat 5, but was measured in heat 4. One estimate of the amount of iron treated can be obtained, then, from the ratio of pouring time to weight of metal poured in heats 4 and 5, letting X represent the weight of metal originally treated in heat 5.

$$\frac{0.54}{X} = \frac{1.55}{270} \qquad X = 94 \text{ lb. metal.}$$

Since all of the iron originally treated was heavily inoculated with magnesium, it is reasonable to assume that the sulphur content of this iron was as low as that obtained in heat 4, 0.002 percent. Knowing the base sulphur content was 0.034 percent, and the final sulphur content was 0.019 percent, and assuming that no sulphur was removed by the residual magnesium concentration in the treated iron, then the weight of the original iron treated can be calculated from a sulphur balance as follows:

Y=initial weight of iron treated	0.002%=sulphur concentration in Y
Z=weight of iron added	0.034%=sulphur concentration in Z
Y + Z = 260 lb.	0.019%=sulphur concentration in Y+Z

then, $Y(0.002) + Z(0.034) = 260(0.019)$

$$Y(0.002) + (260 - Y)(0.034) = 260(0.019)$$

$$-0.032Y = -3.89 \text{ or } Y = 121 \text{ lb.}$$

From inspection, Y can get smaller only if the sulphur concentration in Y gets smaller, and if the sulphur concentration in Y is allowed to go to zero, Y goes to a minimum of 115 lb., which is still larger than the 95 lb. calculated from the pouring time. The discrepancy between the two is roughly 20 percent.

The chemical analyses were all double checked and found to be correct as reported. The only other possibility is that the nozzle opening was modified appreciably betwen heats 4 and 5, which is very likely since the downspout had to be reopened with the oxygen lance after the silicon shock and iron froze up the downspout in heat 4.

The best estimate of the iron originally treated in heat 4 then, is a weighted average of 95 and 121 lb. or 115 lb..

Calculation of the Magnesium Concentration in the 115 lb. of Iron Originally Treated

Assuming the original magnesium concentration in the base iron to be zero, and knowing the final magnesium concentration to be 0.019 percent, the magnesium concentration in the iron originally treated can be calculated as follows:

$X\ (115\ \text{lb.}) = 0.019(260) \qquad X = 0.043\%$

Had the iron originally treated been given the silicon shock and been poured, good nodular iron almost certainly would have been made.

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