Casting Emission Reduction Program

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Carbon Monoxide and Carbon Dioxide Emissions in Metalcasting Pouring, Cooling and Shakeout Operations

1413-211 HT

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This report has been reviewed for completeness and accuracy and approved for release by the following:

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The data contained in this report were developed to assess the relative emissions profile of the product or process being evaluated. You may not obtain the same results in your facility. Data were not collected to assess casting quality, cost, or producibility

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EXECUTIVE SUMMARY

Carbon monoxide (CO) and carbon dioxide (CO_2) have recently been discovered to be emitted during pouring, cooling, and shakeout (PCS) operations from metalcasting. Carbon monoxide is classified as a criteria pollutant, and as such can trigger major source permitting and other requirements. Carbon dioxide is not currently regulated as a pollutant, but federal and state initiatives are being considered that could result in future regulatory compliance and control. This report provides a summary of recent CERP studies at Technikon to quantify CO and CO_2 emissions from different metals and molding processes. In addition, the contribution of known carbon sources potentially responsible for forming CO and CO_2 emissions from metal foundry PCS operations is discussed.

Emission results from the testing performed and described herein are not suitable for use as emission factors or for purposes other than evaluating the relative emissions associated with the use of alternative materials, equipment, or processes. The emissions measurements are unique to the specific castings produced, materials used, and testing methodology associated with these tests. These measurements should not be used as the basis for estimating emissions from actual commercial foundry applications.

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1.0 Introduction

1.1. Background

Carbon monoxide (CO) is classified by the USEPA as a criteria pollutant. If a facility has the potential to emit (PTE) 100 tons of CO or more per year, it is considered a major source and is subject to Title V air permitting requirements, and possibly can be considered a major source for New Source Review. Major source status under Prevention of Significant Deterioration (PSD) is triggered at either 100 tons or 250 tons of CO emissions per year, and is dependant on a facility's use of different types of metallic charge materials.

Carbon dioxide (CO_2) is currently not regulated by either state or federal governments, although attempts are being made to do so because it is a potent greenhouse gas associated with global climate change. Initiatives are being developed to limit emissions through several methods, including setting quantitative and qualitative emission reduction targets, cap and trade policies, or sequestration.

Emissions from industrial PCS processes are very difficult to capture and quantify. Many production foundries do not have capture and collection systems in place and molding processes themselves are widely variable. Historical research in foundry emissions has focused mainly on hazardous air pollutants (HAPs) as a response to federal and state regulations.

Metalcasting facilities have recently broadened their scope to also look for CO emissions, especially from iron greensand PCS operations. The results have shown slightly variable emission rates (ranging from a low of 3.5 to over 5.0 pounds per ton of metal). No attempts have been made to correlate emissions to process variables, and the incomplete available data set did not lend itself to determining process emission factors due to small sample size and limited process information. Existing EPA databases and reference documents are of little help, as they do not quantify CO emissions from pouring, cooling, and shakeout operations from metalcasting facilities.

To remedy the lack of gas emission data, stand-alone real-time monitoring instruments were installed at Technikon, LLC enabling accurate measurement of several criteria pollutants including CO, and CO_2 from PCS processes.

Technikon, LLC is a privately held contract research organization located in McClellan, California, a suburb of Sacramento. Technikon offers emissions research services to industrial and government clients specializing in the metal casting and point source emissions areas. Technikon operates the Casting Emission Reduction Program (CERP). CERP is a cooperative initiative between the Department of Defense (US Army) and the United States Council for Automotive Research (USCAR). The parties to the CERP Cooperative Research and Development Agreement (CRADA) include The Environmental Leadership Council of USCAR, a Michigan partnership of DaimlerChrysler Corporation, Ford Motor Company, and General Motors Corporation; the U.S. Army Research, Development, and Engineering Command (RDECOM-ARDEC); the American Foundry Society (AFS); and the Casting Industry Suppliers Association (CISA). The US Environmental Protection Agency (US EPA) and the California Air Resources Board (CARB) also have been participants in the CERP program and rely on CERP published reports for regulatory compliance data. All published reports are available on the CERP web site at www.cerp-us.org. The CERP facility is designed to capture and measure emissions from different PCS processes while maintaining very tight process control. The emission testing equipment is designed into the process to improve test results.

1.2. Discussion

The formation of both CO and CO_2 from metal foundry PCS processes requires a carbon source, oxygen and energy. Energy is supplied in the form of heat from molten metal. Different metals have different pouring temperatures and melting energy requirements, so the metal itself can be influential in the production of these gases.

Sources of carbon and the availability of oxygen are also important to CO and CO_2 formation. Potential sources of carbon available to form CO and CO_2 originate from materials inherent to PCS metalcasting and include seacoal and other carbon based greensand mold additives, organic core materials, molten metal, Southern clays, Western clays, and inorganic additives

Emission testing conducted through CERP is configured to either isolate core emissions from mold emissions, or to determine combined core and mold emissions. Core emissions are quantified by placing test cores in molds that contain little to no carbonaceous materials. Conversely, to quantify emissions of mold material, cores containing little to no carbon containing materials are used. A cored mold emission profile can then be determined by addition of the independent core emissions to the independent mold emissions. The additive nature of emissions was proven for HAPs through this method. Results indicated that the carbonaceous sand additives and organic components present in the core and mold materials are the only measurable HAP emission sources.

Core emission tests use the American Foundry Society's (AFS) step core configuration to simulate an "average" casting. Determination of emission profiles of greensand molds use a coreless 4-on star pattern. The star pattern has a much higher surface area than the step core pattern. Both patterns are designed to reproducibly affect overall emission rates. HAP emissions from greensand molds were found to be proportional to the surface area of the casting exposed to the molding sand, but no determination had been made for criteria pollutants such as CO.

Emission tests run for the purposes of generating emission data generally include 9 to 12 individual discrete replicate pours. Results from individual pours that have undergone rigorous data and statistical validation are computed as an average for each test.

Emissions data presented in this report have been background subtracted to provide more accurate reporting of results for the materials undergoing investigation. Process emissions can be significantly overestimated without background correction, especially in the case of CO_2. The background concentrations of CO_2 generally are much higher than the CO_2 emissions emanating from PCS processes. Without removal of the background CO_2 levels, process CO_2 emissions would appear to be much higher than they actually are. By contrast, background levels of CO are quite low in comparison to process emissions. This seldom affects overall CO emission results for iron PCS processes. However, for lighter metals such as aluminum, the higher increased stack volumes required to obtain an equivalent metal mass to iron could potentially influence results.

Data has also been corrected for any non-detect (ND) values and for outliers. Individual pour data that were determined to be below the practical quantitation limit (PQL) after data validation and verification were considered to be non-detects. If any datum were found to be non-detect after the application of calculated detection limits, they were not included in the averaged result for a test. This procedure was effected to eliminate potential discrepancies introduced by the numerous approved methods for the handling of non-detects in a data set.

1.3. CO and CO_2 Emissions from Iron Pouring, Cooling and Shakeout Operations

1.3.1. Effect of Core and Mold Configuration

Historical CO and CO_2 data from CERP emission tests of iron PCS processes are summarized in Table 1 and grouped by process. Core tests and mold configurations such as No-Bake binders and Shell (Novolac) molds are also included.

Table 1. CO and CO_2 Emissions from Iron Pouring, Cooling and Shakeout Stack Tests

	Published and Draft Tests / CERP Test Designation	Process Description#	lbs/ton metal CO	lbs/ton metal CO_2
Core Tests	GZ	SS Cores	1.4	4.1
	FR	PU Cores	1.8	NA
	FQ	PU Coated Cores	2.0	NA
	GG,FT,FR	PU Anti-viening	2.1	NA
	GE	Coated Ecotech CO_2	1.6	4.9
	FU	Shell	2.5	4.5
	GH	Hot Box	1.9	5.2
	GJ	Furan Warm Box	2.0	4.3
	GW	Iso-Set	2.1	NA
	GM	Oil Sand	2.4	6.7
	GX	Acrylic/Epoxy	1.9	3.8
	HD	Beach Box	1.3	2.1
Other Tests	DG, DL, FP, DP	PU NB	4.8	NA
	DW,DX,GI,EB	FN NB	5.3	NA
	DZ	ES NB	4.3	NA
	HT	SS with Ester Part 2 NB	3.2	4.1
	GN (Two Tests)	Shell Molds	10.8	0.0
Greensand Tests	GB	GS Coated PU	4.2	10.0
	EA	GS & Repl with PU Cores	5.3	NA
	GU,DR,DS,DT,DU	GS SS	4.7	NA
	GQ	GS Stars	5.5	12.9
	GL	GS Stars, Graphite Parting	2.8	NA
	FV	GS Stars, Graphite Parting	1.4	3.1

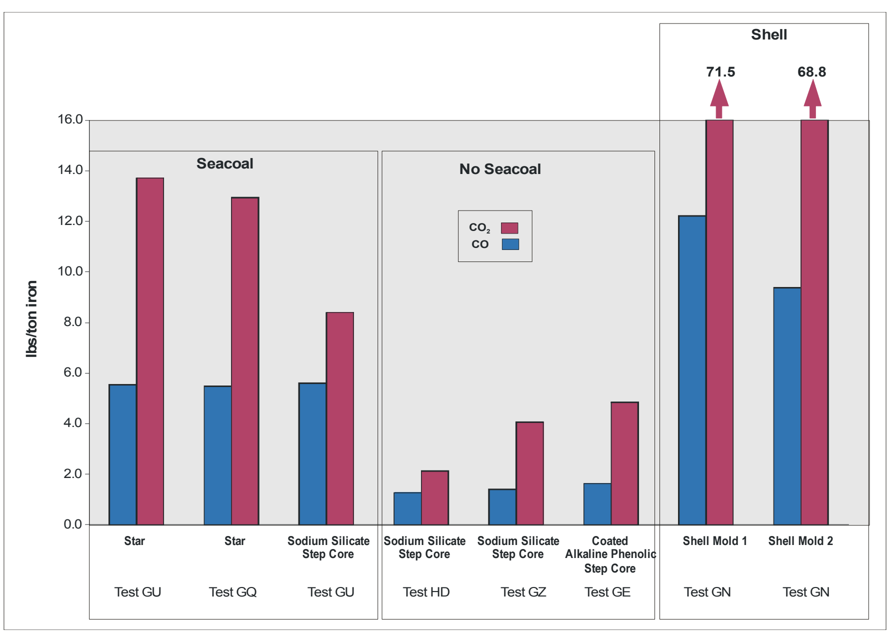
#SS=Sodium Silicate
PU=Phenolic Urethane
FN=Furan
ES=Ester
GS=Greensand
NB=No-Bake

The core emission testing showed CO levels averaging between 1.3 and 2.5 pounds of CO per ton of iron poured. The CO_2 ranged between a low of 2.1 for Beach Box, to a high of 6.7 pounds per ton of metal for oil sand cores. The most commonly used core binder is based on phenolic urethane (PU) chemistry. PU core tests averaged approximately 2 pounds of CO per ton of metal poured. Greensand molds, either using the star pattern or containing step cores, emitted between 4.2 and 5.5 pounds of CO per ton of metal. Results from No-Bake molds averaged between 3.2 to 5.3 pounds of CO per ton of metal.

With the exception of shell molds, the CO emission range seems relatively narrow. The two shell mold emission tests resulted in values of 9.4 and 12.2 pounds of CO per ton of metal. Although these tests were conducted on a standard shell resin mix and a low free phenol proprietary resin, the molds were not the standard test pattern but were supplied by an operating foundry.

Selected emission results taken from Table 1 are shown in Figure 1. The first two tests shown (Test GU and Test GQ) were from the star pattern in greensand molds that contained seacoal. This combination of materials was expected to have the highest emissions. The third test shown was also a greensand test with seacoal, but contained sodium silicate cores, which were expected to have minimal contribution to the overall emission profile. The reduction in exposed surface area through the use of cores instead of stars was also predicted to reduce emissions. Expected results were observed somewhat for CO_2, although the CO concentration was observed to be somewhat invariant.

Figure 1. Iron PCS CO and CO_2 Results



The next three sets of data in Figure 1 are for seacoal-free molds. The core material used for these tests was also expected to contribute little to emissions. Similar to the first three tests in Figure 1, results showed minimally varying levels of CO with fluctuating concentrations of CO_2. The last two data sets shown in Figure 1 are from a shell mold test, Test GN. Results from the two shell materials used exhibited comparatively very high levels of both CO and CO_2. The CO_2 levels are in the range of 70 pounds per ton of metal. The test with the highest binder level resulted in the highest CO level.

1.3.2. Effect of Surface Area

The dissimilar surface areas and exposure to molten metal between the star pattern and sodium silicate step core pattern were used to determine their effect on emissions from greensand molds containing seacoal. Detailed emission results from this test (CERP Test GU) are listed in Table 2. Cores were made using a non-carbon containing sodium silicate binder. As shown in the table, the exposed surface area of the star pattern that contacts the molten metal is 113% higher than that of the step core. HAP emissions were higher by 107%, a proportion similar to that of the surface area. Emissions of CO_2 were also somewhat higher for the star pattern, but not by the surface area proportion. The CO emissions differed by only 1%.

Table 2. Greensand Surface Area Comparison

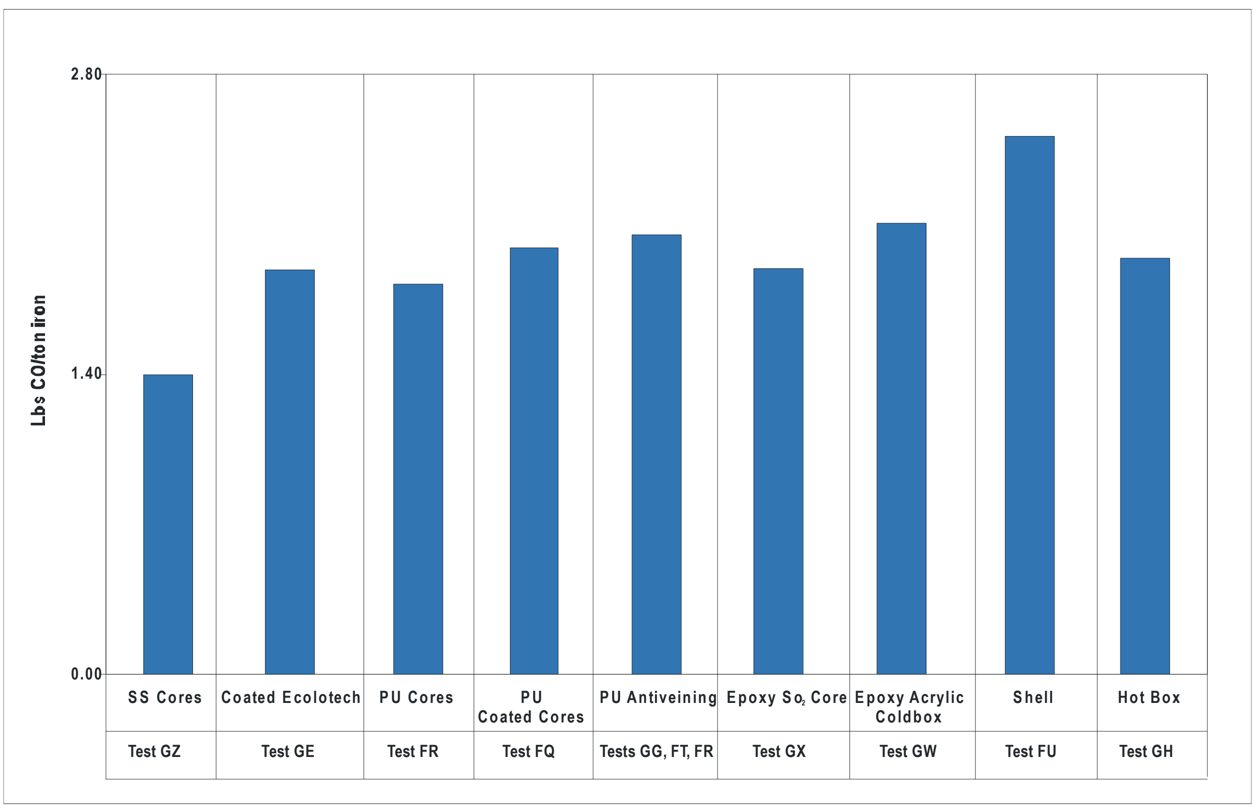
Test GU

Greensand Molds Containing Seacoal			
	Cores	Stars	Difference
Surface Area in^2	682	1,455	113%
Analyte	Concentration lb/ton		
CO	5.6	5.5	-1%
CO_2	8.4	13.7	63%
SO_2	0.01	0.03	149%
NOx	0.005	0.01	17%
HAPs	0.2	0.4	107%

The relationship between CO emissions and core binder chemistry is illustrated in Figure 2, where several of the core tests from Table 1 are graphed. It was expected that molds with low carbon containing cores would yield low to non-detectable emissions. As shown in Figure 2, this was not the case. The lowest emission of approximately 1.3 pounds of CO per ton of metal was generated with sodium silicate cores in molding sand without seacoal. The highest emission was for shell step cores at 2.5 pounds of CO per ton of metal poured.

On a per ton of metal basis, carbon containing core chemistries added about 0.5 to 0.75 pounds of CO to mold emissions, with shell cores adding just over 1.24 pounds of CO per ton of metal poured. The use of shell cores added about 0.5 pounds per ton of iron to the most commonly used PU core technology. The reasons for the unusually high shell mold CO emissions are unexplained at this time.

Figure 2. CO Emissions from Low Carbon Cores Poured with Iron in Seacoal-less Molds



2.0 SOURCES OF CARBON

CERP tests have shown that seacoal is a major source of carbon for CO and CO_2 production from iron pouring/cooling/shakeout processes. Additional potential sources of carbon were identified as core material, additives (such as Southern and Western clays in molding sand), and the molten metal used for the casting. Molten aluminum, for example, has no measurable carbon, while iron can contain up to 3.5%.

2.1. Carbon in Molten Metal

Emissions from the production of aluminum castings in No-Bake molds have yielded CO and CO_2 emissions close to background levels. The lack of emissions from aluminum can be attributed to two potential possibilities. One is the comparatively low pouring temperature, which also corresponds to the available amount of energy released during solidification and cooling (melt energy). The other possibility for the absence of emissions is the lack of carbon in the casting alloy.

Iron contains sufficient carbon levels to produce most of the CO and CO_2 emissions determined from CERP testing. This is illustrated by example in Table 3 for CERP Test GZ. This test determined emissions from uncoated sodium silicate cold box cores contained in greensand without seacoal. The core binder was activated with CO_2.

Table 3. CO and CO_2 Carbon Requirements

	Test GZ Results lbs/ton	CO MW lb/lb mole	C MW lb/lb mole	% C	C Emissions lb/ton metal
CO	1.4	28	12	43%	0.6
CO_2	4.1	44	12	27%	1.1
Total C					1.7

Typical gray iron castings have a carbon level of 3.25%, which is equivalent to 65 pounds of carbon per ton of iron. From Table 3, the total carbon required to produce all of the CO and CO_2 from Test GZ is 1.7 pounds – or 2.6% of the carbon available from the gray iron castings. This 2.6% change would be equivalent to losing 0.09% of the 3.25% total carbon level, which is equivalent to a molten metal carbon content of 3.16%. It is common for iron foundries to experience small amounts of carbon fade during the casting process. A level of carbon fade from 3.25% to 3.16% would not be unexpected.

Not all alloys have carbon in the molten metal available to contribute to CO and CO_2 emissions. Steel has very low carbon levels compared to iron, and would have very low potential to contribute to the overall availability of carbon to form CO and CO_2 emissions. Aluminum and copper alloys have no measurable metal carbon.

Comparing CO and CO_2 emissions from an intermediate melting point metal such as copper could fill in the data gaps, but little is known currently about emissions from copper based castings.

2.2. Carbon in Southern and Western Clays

Most foundries that pour iron into greensand molds utilize a pre-blend as the method for introducing bentonite clays (Southern and/or Western), fireclay, carbon, and inorganic additives into the molding sand. The emissions of CO and/or CO_2 during PCS metal casting processes could be affected by the selection of greensand additives.

The clays used in the bonding mechanisms and the inorganic additives that are used to modify the performance of the clays are not considered a primary contributor to CO and CO_2 emission, but their emission characteristics require review as they may include carbon containing constituents.

The major source of carbon in bentonite clays comes from the naturally occurring carbonates in the geological deposits. The quantity of carbonates in Western (sodium) bentonites and Southern (calcium) bentonite mined in North America was determined by analysis of actual clay samples. Samples were randomly selected from several bentonite clays and sent to the University of Kentucky for analysis. It was determined that the concentration of the carbonates in the samples tested from both deposits was 0.7% or less. This concentration of carbonate in clays is sufficient to provide carbon for CO and CO_2 formation.

The most likely carbonate to be present is sodium carbonate. The following theoretical calculations are therefore based on sodium carbonate.

The decomposition of sodium carbonate at elevated temperatures in the metal casting process is as follows:

$$Na_2CO_3 \rightarrow Na_2O + CO_2$$

The following calculations determine the potential emissions of CO_2 during the metal casting process at PCS assuming 0.7% carbonates from the bentonite clays:

Na_2CO_3 = MW of 106

Na_2O = MW of 62 or 58% of Na_2CO_3

CO_2 = MW of 44 or 42% of Na_2CO_3

Therefore:

100 lbs of bentonite clays consumed = 0.7 lbs x 42% of Na_2CO_3 = 0.29 lbs of CO_2

Sodium carbonate is also the primary additive used in pre-blend technology in North America. In addition to the potential for natural carbonates contained in bentonites, traditional pre-blends consumed in iron foundries sometimes contain added soda ash (sodium carbonate). Soda ash levels added to pre-blend formulations in North America are typically 0 to 2%. Since there is a greater quantity of "carbonates" added to greensand systems through pre-blend formulations containing soda ash, all the carbonates found in the bentonite clays and the soda ash additions into the pre-blends must be taken into consideration when calculating the total potential emissions of CO and CO_2 at PCS.

Typical iron foundry pre-blend = 75% Clay and 25% Carbon (such as seacoal)

75% Clay x 0.7% carbonates (max.) = 0.53% of pre-blend is carbonates

Typical soda ash, when used, is 0.5% of pre-blend (some blends higher)

Potential Carbonates = 0.5% from pre-blend + 0.53% from bentonites = 1.03% carbonates

The potential to emit CO_2 from the carbonates in 100 pounds of pre-blend, which is typically added to produce one ton of iron castings, is therefore:

Potential to Emit CO_2 = 1.03% carbonates available x 0.42 CO_2 = 0.43 lbs of CO_2

Table 4 contains a comparison of the addition levels of soda ash and the potential to emit CO_2.

Table 4. Comparison of Soda Ash addition and Potential to Emit CO_2

Percent Soda Ash Added to Premix	0	0.5	1	2
Pounds CO_2 Potential to Emit per ton of metal poured	0.22	0.43	0.64	1.06

The potential emission levels from sand system carbonates cannot fully be attained in actual foundry operations since some of the clay and soda ash added to greensand systems in the form of pre-blend additions is not actually consumed in the PCS process. Much of the carbonate additions are removed from the sand system with excess system sand and recycled off site or disposed of in landfills. Lesser amounts of carbonates are also picked up by ventilation systems and removed as fines in baghouse catch. Nevertheless, carbonates can potentially produce measurable levels CO and CO_2 from PCS operations.

2.3. Quantification and Identification of Carbon Sources

Better understanding of the sources of CO and CO_2 emissions can assist metalcasting facilities to develop emission factors for their individual processes for permitting purposes, and provide information for potentially reducing CO and CO_2 levels.

Supplemental tests (CERP Test HT) were recommended and designed to specifically identify and quantify the identified potential sources of carbon (including iron fade), and to further understand the effect of metals and pouring temperature, and to a lesser extent, the carbon containing constituents of sands on CO and CO_2 emissions. The contributions of carbonates in the preblend are a secondary concern, but funds have not available to specifically investigate their contribution as a potential carbon source.

The effect of temperature was determined by pouring aluminum, brass, and steel in No-Bake sodium silicate molds using an ester Part 2 resin. These three metals were poured at their appropriate temperatures: Aluminum was poured at 1280°F, brass at 2217°F, iron at 2630 °F and steel at 3023°F.

The effect of carbon content in molten iron was investigated by comparing CO and CO_2 emissions from iron and steel in seacoal-free greensand molds containing inorganic cores. A summary of results from Test HT are shown in Table 5. The results from Test GZ were used for the iron comparison and are also given in Table 5.

Table 5. Selected CO and CO_2 Results

CERP Test Designation	Description	Metal	CO	CO_2
			lb/ton of Metal Poured	
GZ	Greensand No Seacoal, SS Core	Iron	1.3975	4.06
HT	Greensand No Seacoal, SS Core	Steel	0.51	1.93
HT	No-Bake SS with Ester Part 2	Iron	3.2	4.08
HT	No-Bake SS with Ester Part 2	Brass	0.49	2.07
HT	No-Bake SS with Ester Part 2	Aluminum	ND	ND
HT	No-Bake SS with Ester Part 2	Steel	2.31	5

Steel greensand and greensand cored emissions fundamentally will be much different than those from cast iron. Steel greensand cored molds contain organic cores, bentonite clays, and cereals. But greensand pre-blends for steel do not contain significant sources of carbon. They have the potential to form CO and CO_2, but at much lower levels than cast iron, due to the differences in additive formulations and metal chemistries. CO emission levels would be approximately 1.09 pounds per ton of metal. This is 3.39 pounds per ton less for steel than for cast iron if these components did not contribute to emissions.

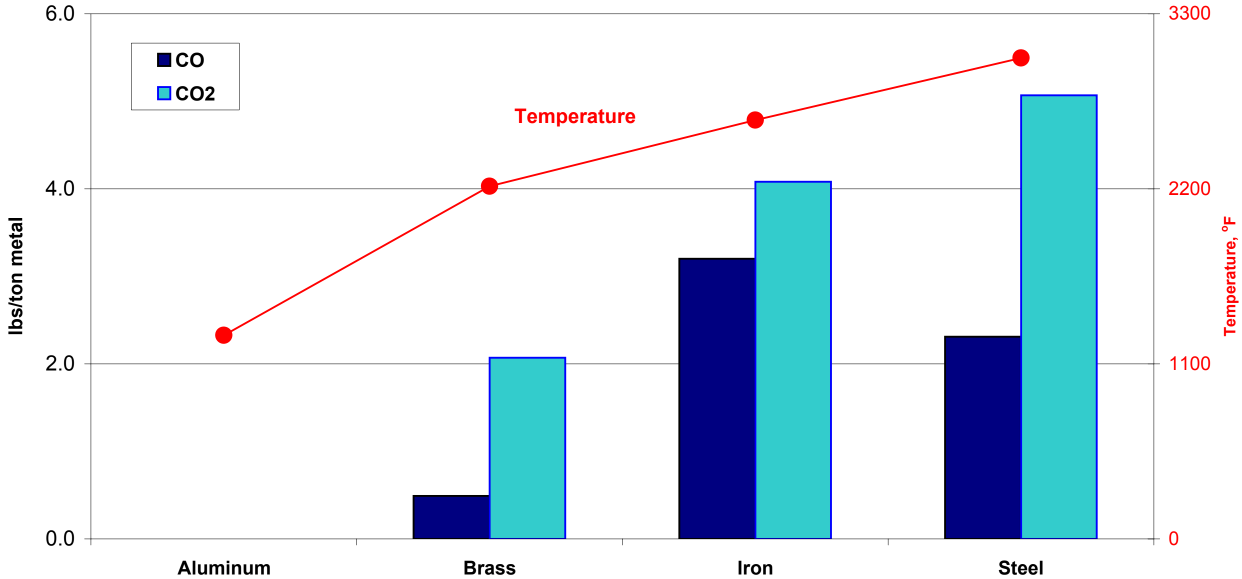
Brass CO and CO_2 emissions were found to be much lower than those of steel and iron in the No-Bake molds examined under Test HT. Like aluminum, molten brass does not contain carbon. And, also like aluminum, the lower pouring temperature (or decreased melt energy) was apparently the contributing factor. Emissions for both CO and CO_2 were found to be between iron and aluminum, as would be expected. However, because industrial brass greensand formulations contain different carbonaceous additives than were used for these tests, additional emissions tests need to be performed to develop brass emission factors.

2.3.1. Effect of Temperature

The CO and CO_2 results of the aluminum, brass, iron, and steel testing are plotted with pouring temperature in Figure 3. Aluminum results show non-detectible CO and CO_2 levels. As previously mentioned, this lack of CO and CO_2 emissions from aluminum could be due to the absence of carbon in the molten alloy, or the lower pouring temperature.

As the pour temperature of the metal increased, an increase was seen for both CO and CO_2 emissions for all metals tested except for steel. In this case, CO_2 continued to increase with temperature while CO emissions seemed to decrease. Assuming that the temperature was high enough to break down the chemical binder, the melt energy would predict the release of carbon from the binder systems. Brass is 9% denser than steel, but its melt energy (312 Btu/pound) is 54% that of steel (612 Btu/pound). The total carbon emissions of the brass pours were found to be 33% of the steel emissions.

Figure 3. Effect of Temperature on CO and CO_2 Emissions



2.3.2. Effect of Metal Carbon Content

By pouring iron and steel in seacoal-free greensand molds containing inorganic cores, the carbon content of the metal – along with any contribution from other mold and core material sources, such as carbonates – could be quantified. Although the pouring temperature of the steel greensand test was 2978°F, and that of the iron greensand test was 2632°F, the melt energies are similar between the two ferrous alloys.

A summary of results for iron and steel greensand tests are given in Table 6, together with theoretical zero metal carbon calculated emissions from iron and steel. The calculated emissions are the y-intercept values of the CO and CO_2 curves graphed in Figure 4.

Table 6. Effect of Metal Carbon Content in Greensand on CO and CO_2 Emissions

		lb/ton			
		C in Metal	**CO**	**CO_2**	**Total C Content in CO and CO_2**
Test GZ	Iron	3.31	1.40	4.06	1.71
Test HT	Steel	0.26	0.51	1.93	0.74
[1]Carbon from other sources (assumed zero C content in metal)		NA	0.43	1.75	0.66
[2] Estimated emissions from metal C		Iron	0.97	2.31	1.05
		Steel	0.08	0.18	0.08

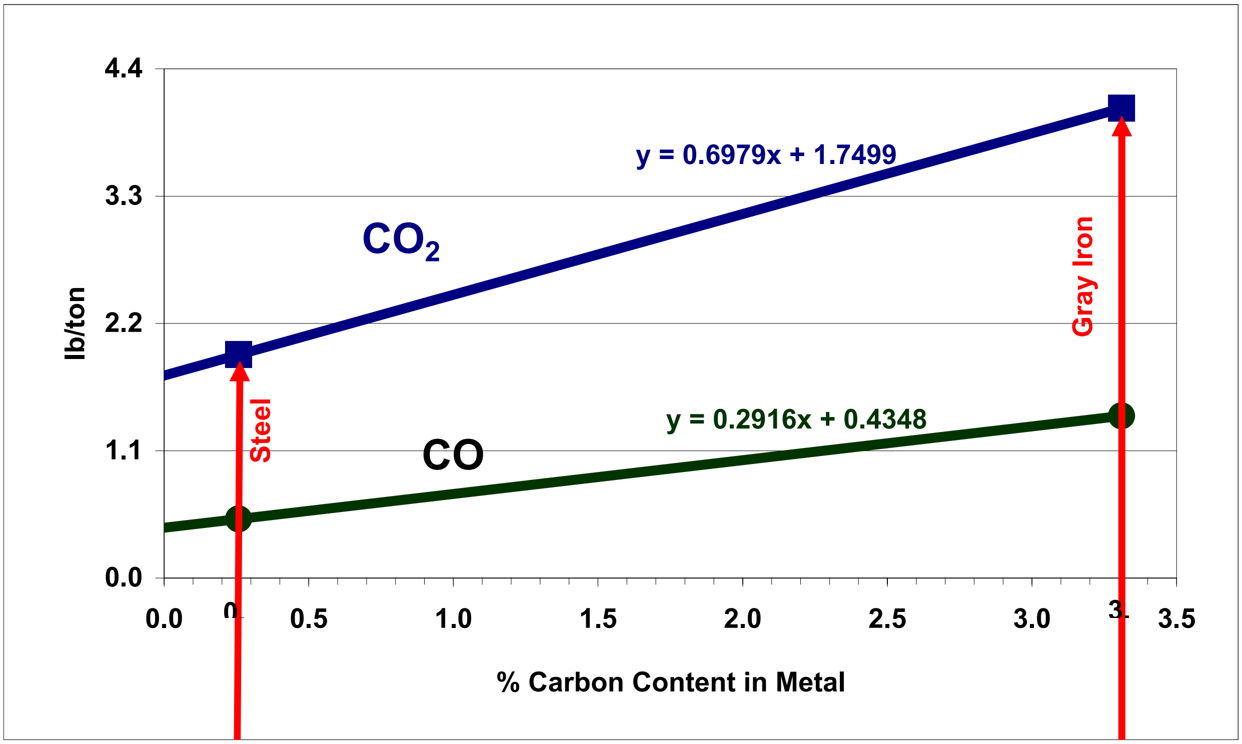
[1] From Figure 4

[2] Subtraction of zero carbon values from test results

Resultant emission levels from the steel test were significantly reduced when compared to the iron test, presumably due to the reduced carbon content in the metal. The steel carbon content was 0.26%. This is 8% of the cast iron carbon content of 3.31%, and equates to a 92% reduction in carbon content from iron to steel. If there were no additional carbon sources, this same reduction would be expected in the comparative emissions. Test results indicated that emissions from the steel test are actually higher than predicted, indicating that additional carbon sources must be present, even in seacoal-free greensand molds containing inorganic cores.

Figure 4 illustrates the data from Table 6 graphically. The lb/ton carbon values taken at the y-intercept (equivalent to a metal carbon content of zero) gives the minimum amount of carbon that must be contributed from other sources – such as inorganic core materials and sand additives, including carbonates. The intercept values are 0.43 pounds of CO per ton of metal and 1.75 pounds of CO_2 per ton of metal. The contributions of the carbon content from the molten metal itself on total CO and CO_2 emissions can be derived by subtracting these assumed zero metal carbon values from actual test results. From the iron itself, this computes to 0.97 pounds per ton of CO and 2.31 pounds per ton of CO_2, and 0.08 pounds per ton of CO and 0.18 pounds per ton of CO_2 from the steel.

Figure 4. CO and CO_2 as a Function of Carbon Content in Metal



2.3.3. Effect of Carbon Content from No-Bake Molds

A comparison was made between calculated and measured CO emissions from No-Bake molds for iron. This was accomplished by using the CO contributions from the metal carbon determined from Table 6, and the No-Bake mold CO contribution and summing them.

Subtracting the CO concentration attributed to the carbon contained in the steel from the CO results obtained from the steel No-Bake test determined under Test HT gave the CO contribution of the No-Bake mold: the carbon contribution from the steel pour in greensand was 0.08 pounds per ton, as given in Table 6. Subtracting this value from the No-Bake CO result of 2.31 pounds per ton (shown in Table 5) gives a No-Bake mold contribution to CO of 2.23 pounds per ton of metal.

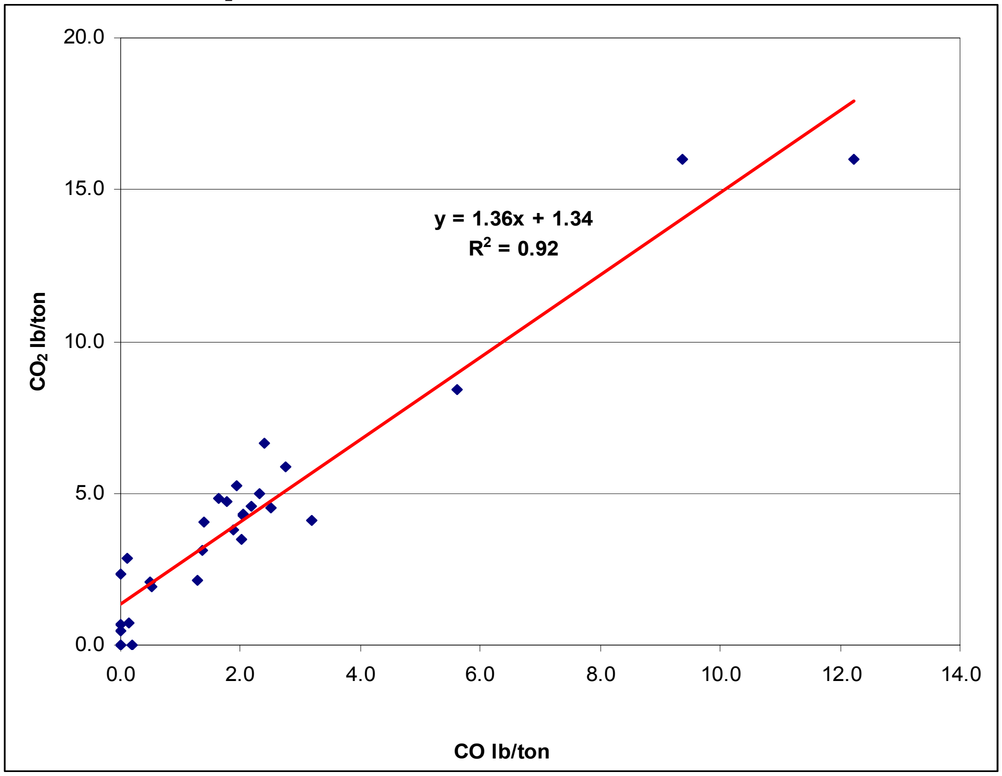
This value can be used to calculate theoretical CO emissions from iron in No-Bake assuming that it is constant. From Table 6, the estimated CO contribution from molten iron was determined from the greensand iron test to be 0.97 pounds per ton of metal poured. The addition of this value to the 2.23 pounds of CO per ton of metal attributed to the No-Bake mold should approximate the iron No-Bake emission level. This sum, 3.20 pounds per ton of CO, exactly matches the measured results of the iron No-Bake results from CERP Test HT (see Table 5). The following calculations summarize the above:

Measured No-Bake Test HT CO Results		2.31
Estimated Carbon Contribution to CO from Steel	–	0.08
Contribution of No-Bake Mold	=	2.23
Estimated Carbon Contribution to CO from Iron		0.97
Contribution of No-Bake Mold to CO	+	2.23
Total CO Concentration for iron No-Bake Mold	=	3.2
Measured No-Bake Test HT Results		3.2

2.4. Comparison of CO and CO_2 Emissions

A summary of the CO and CO_2 data from a majority of emissions tests conducted between 2002 and 2007 were graphed as a bivariate plot to determine whether these compounds are produced independently. Results are shown in Figure 5. The high correlation coefficient, R^2, of 0.92 shows the existence of a strong linear relationship between CO and CO_2. R^2 reflects the percent of variation in Y explained by the independent variable in the model. A value of near one indicates a perfect fit. This implies that the relationship between CO and CO_2 from metal foundry PCS operations is not independent or random, but governed by physicochemical processes in a predictable way that are currently not understood.

Figure 5. CO and CO_2 Bivariate Plot



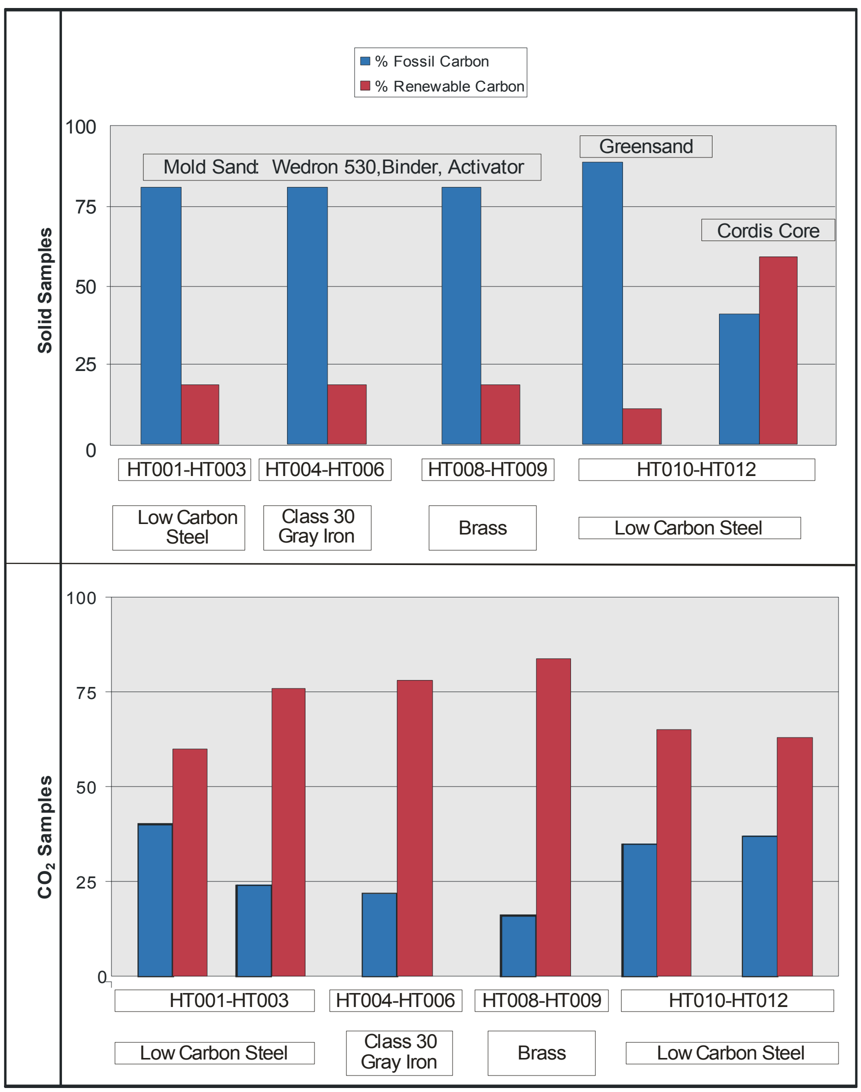
2.4.1. Determination of Carbon Sources through Isotopic Analysis

Sand, core and gas emission samples from Test HT were subjected to isotopic analysis for the determination of the abundance of carbon 14. The amount of carbon 14 in a sample can provide information about the origination of the carbon in CO_2 emissions. Isotopic analyses can show that if an organic molecule contains carbon 14 at atmospheric levels, the carbon in it most likely originated from a biomass based source. If it contains no carbon 14, the sample is from a fossil source. And, if a sample contains some intermediate level of carbon 14, then its carbon is from a mixture of both biomass and fossil sources.

Preliminary results shown in Figure 6 indicate that although the No-Bake molds (runs HT001 - HT009) contained 81% fossil carbon, CO_2 emissions had a higher percentage of biomass carbon for all metals tested, ranging from an average of 68% for low carbon steel to 84% for brass. This indicates that a mixture of carbon sources that are dominated by petroleum or fossil origins are in the mold materials. In contrast, the primary carbon sources contributing to CO and CO_2 emissions are from renewable carbon. Greensand had the highest percent of fossil carbon (89%), and Cordis had the lowest (41%). Cordis was the only material dominated by bio-based carbon.

The percent of renewable carbon seemed to increase slightly in the gas emissions going from steel and iron to brass in No-Bake molds. Emissions from both greensand and Cordis cores poured with steel were similar in the proportion of renewable and fossil carbon to the No-Bake steel emissions at about 40% fossil and 60% renewable carbon.

Figure 6 Carbon 14 Analysis of Solid and Gas Samples from Test HT



3.0 CONCLUSIONS

Observations from CO and CO_2 emissions testing at CERP described in this paper include the following:

1. Cast iron PCS operations resulted in the highest CO and CO_2 emission levels of the metals tested, most likely due to the comparatively high carbon level in the molten iron.

2. Both steel and cast iron PCS operations produced CO and CO_2. Steel emissions were lower, presumably due to the much lower carbon levels in the molten steel, 0.26% vs. 3.31%.

3. Carbon in molten iron accounts for an estimated 0.97 pounds of CO and 2.31 pounds of CO_2 per ton of iron poured.

4. Seacoal used as a carbonaceous additive in molding sand is the major contributor to CO and CO_2 emissions in greensand molds containing seacoal.

5. The addition of high carbon containing additives to greensand, such as seacoal, for industrial PCS processes can be expected to produce higher CO and CO_2 emissions than those from low carbon containing additives.

6. Cores contribute to the formation of CO and CO_2 in cored greensand molds, with a range of emissions between 0.54 to 0.77 pounds of CO per ton of metal.

7. Additional sources of carbon include carbonates in bentonite clays as well as unidentified sources. These additional sources can contribute 0.43 pounds of CO per ton of metal and 1.75 pounds of CO_2 per ton of metal.

8. Pouring temperature and the energy released during metal cooling and solidifying, can affect emissions of CO and CO_2.

9. Aluminum appears to generate no detectable levels of CO and CO_2 when emission results are corrected for background levels. The lack of carbon in the molten metal and the alloy's low melting temperature are the likely reasons for the lack of CO and CO_2 emissions.

10. Although copper does not contain a carbon source in the molten metal, the pour temperature and melt energy seem sufficient to form CO and CO_2 from No-Bake molds. Emissions were intermediate between aluminum and steel.

11. Copper emission factor estimates cannot be determined from the testing performed, since typical industrial copper greensand mold packages were not used.

12. CO_2 emissions contain mostly renewable carbon although the mold and core materials contain mostly fossil carbon.

APPENDIX A ACRONYMS AND ABBREVIATIONS

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ACRONYMS AND ABBREVIATIONS

AFS	American Foundry Society
CERP	Casting Emission Reduction Program
CISA	Casting Industry Suppliers Association
CO	Carbon Monoxide
CO_2	Carbon dioxide
CRADA	Cooperative Research and Development Agreement
DOD	Department of Defense
DOE	Department of Energy
EPA	Environmental Protection Agency
Lb/Tn	Pound per ton of metal poured
PCS	Pouring, Cooling, Shakeout
ppm	Parts per Million
PTE	Potential to Emit
US EPA	United States Environmental Protection Agency
USCAR	United States Council for Automotive Research
WBS	Work Breakdown Structure