Foundry air contaminants from green sand molds

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The major gases evolved from foundry molds have been determined in the laboratory. The principal gases evolved during pouring and shakeout of castings include hydrogen, carbon monoxide, carbon dioxide, methane and other low molecular weight hydrocarbons with smaller amounts of ammonia, hydrogen cyanide, and sulfur dioxide.

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Conventional sand casting processes

Most ferrous castings are produced in green sand molds. The term "green sand" implies that the bonding agent in the sand is some form of clay, usually bentonite or fire clay. The clay is plasticized with about 3 to 5% water. Most green sand molds also contain some organic additives such as dextrine, cereal, oat hulls, wood flour, or pulverized coal dust.[1] These agents are present in amounts of up to about 6% of the weight of the sand and are added primarily to cushion the thermal expansion of the sand and to provide a reducing atmosphere inside the mold when metal is poured into the mold cavity. As the metal is poured, these materials in the mold partially decompose and some lighter, volatile hydrocarbon fractions are driven from the mold into the foundry atmosphere as smoke or gas. Heavier decomposition products are often driven from the vicinity of the casting and condensed in the cooler portions of the mold. As the entire mold heats up, these products may also be driven into the foundry atmosphere.

After the casting has solidified in the mold and cooled to an acceptably low temperature, it is removed from the mold, or "shaken-out," usually on some type of vibrating table or conveyor. During this action, the mold is broken away from the casting, exposing the hot sand mixture to the atmosphere. At this point, combustion or partial combustion of readily oxidizable organic materials in the sand may occur.

After the casting is removed from the mold, the sand is processed for reuse. This reconditioning consists of adding new sand to replace that lost during the previous cycle and adding appropriate amounts of wood flour,

coal dust, bentonite, and other additives to replace those burned out when the casting was made. The sand and additives are mechanically mixed in a muller. Water is then added to the sand mixture, and it is then transported back to the molding stations to be formed into new molds. As estimated 9 to 15 tons of sand must be processed for every ton of castings produced.

Experimental procedures

The gaseous emissions from green sand molds were studied by two experimental procedures. The first procedure consisted of pouring a casting into a mold cavity located in a flask that could be sealed immediately after the pouring was completed. This procedure allowed nearly all the gases to be collected with minimum air dilution. It also allowed the observation of small changes in gas composition that resulted from different sand mixtures and casting weights (expressed as a sand-to-metal ratio).

A sketch of this apparatus (Figure 1) shows an eight-inch diameter flask with a threaded cap for sealing. A mylar bag was attached to a vent to collect the gaseous effluent. An ice-water cold trap in the vent line prevented the condensation of vapors in the bag.

When this equipment was used, a green sand of known composition was prepared in a small muller and rammed into the flask. The mold was well vented to provide a path for the gas to leave the sand. The total volume of the gas produced was estimated by pumping out the sample bag at a known flow rate.
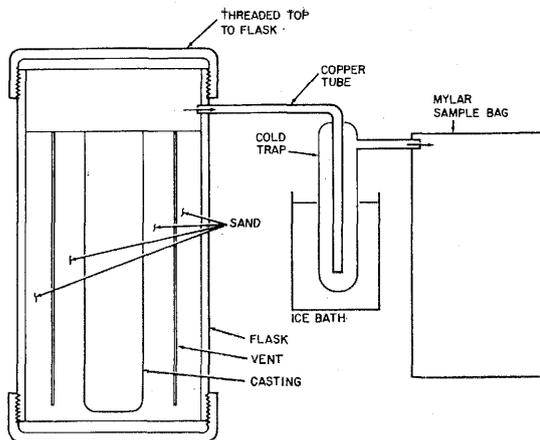
Figure 1—Cross section of a sealed flask mold that allows collection of all gaseous emissions in an evacuated mylar bag.

Figure 2—Schematic of portable gas sampling hood.

This test procedure permitted the effects of several normal foundry variables on the gaseous mold emissions to be determined. The important variables included sand-to-metal ratio, the amount and type of organic materials added to the sand, and the weight of the casting.

The second experimental procedure employed an exhaust hood and canopy over typical green sand molds. This hood is fitted with multiple sampling ports. This arrangement is shown schematically in Figure 2. An orifice plate and DC motor-driven exhaust fan in the stock were used to establish an known air flow through the hood. This arrangement drew air over the mold to simulate the draft conditions typically existing in a ventilated foundry oven.

The exhaust air volume was controlled with a reheostat on the DC motor to the fan and was set to maintain a constant pressure drop of ½-inch of water, as monitored with a manometer. This pressure drop corresponded to a volume flow of 35 cfm in the stack, or an air velocity of 50 ft/min over the mold surface. This velocity was chosen because it was high enough to prevent significant losses of effluent by diffusion under the hood.

Gaseous emissions were collected periodically by drawing grab samples of the exhaust gases in the stack into 250 ml glass bulbs. Samples were taken at intervals starting immediately after the casting was poured, while the
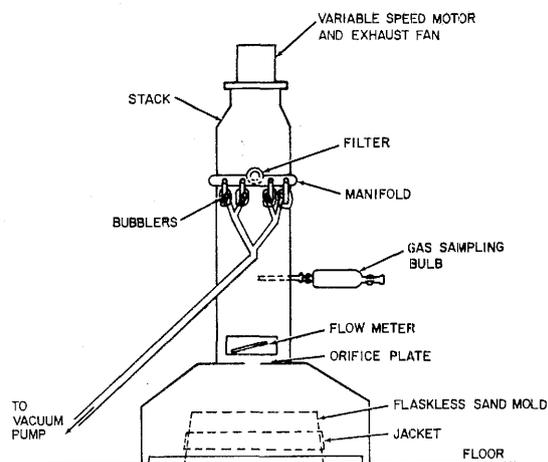
casting cooled in the mold, and as the casting was broken out of the mold.

Because of the low concentrations of hydrogen cyanide and ammonia in this exhaust gas, samples for determination of these compounds were taken by continuously pumping the stack effluent at a known rate through dimpled bubblers containing specific absorbing reagents.

Chemical analysis of gaseous effluents

Samples from the mylar bags used in the closed flask experiments were drawn from the bags with a gas tight syringe for gas chromatographic analysis. For compounds where a gas chromatography technique was not used, a measured volume of the effluent was pumped through dimpled bubblers containing specific absorbing reagents. The effluent from these experiments was analyzed for hydrogen, carbon monoxide, carbon dioxide, methane, C_2-hydrocarbons, total hydrocarbons, ammonia and cyanide. The gases were analyzed immediately after sampling to prevent errors caused by diffusion of hydrogen through the mylar bags.

Several of the above hydrocarbon compounds were present in such small quantities in the closed system that they were not analyzed for specifically in the diluted effluent of the hood experiments, but rather reported as total hydrocarbons. Green sand effluent from these experiments was analyzed only for carbon monoxide, carbon dioxide, ammonia, methane, cyanide and total hydrocarbons.

Apparatus and procedure

A Hewlett-Packard 5750 gas chromatograph equipped with flame ionization and thermal conductivity detectors and a linear temperature programmer was used. Carrier gas flow rates were adjusted to give optimum separation and sensitivity. The area of each component was measured using a disc integrator. The detector response was calibrated with standard gas mixtures analyzed under the same conditions used for sample analysis.

Hydrogen, carbon monoxide, methane and carbon dioxide were analyzed on a 2 ft by 0.25 inch O.D. activated 5A Molecular Sieve column with thermal conductivity detection. The column temperature was 25°C for hydrogen, 50°C for methane, 70°C for carbon monoxide and 260°C for carbon dioxide. Alternatively, the column was programmed from 25°C to 260°C for determining all the above gases in one analysis. Low concentrations of methane and the C_2-hydrocarbons (ethane, ethene and acetylene) were determined on the same column using flame ionization detection. The column temperature was programmed from 50°C to 260°C for these compounds.

Total hydrocarbons were determined by flame ionization detection. Gas samples were injected into the carrier gas stream and the increase in detector response was measured. The detector response was calibrated with standard samples of methane in air. Total hydrocarbons were reported as an equivalent concentration of methane that would give the same response as the total hydrocarbons in the sample.

Ammonia and cyanide were determined using specific ion electrodes. Ammonia was absorbed in 10 ml of 0.02N sulfuric acid in bubblers. The pH of the solution was adjusted to 11-13 with sodium hydroxide and the ammonia sample was bubbled through the condensed monia concentration determined using the ammonia specific ion electrode.

Cyanide was sampled in bubblers containing 10 ml of 0.01N sodium hydroxide. The sodium hydroxide solution containing the dissolved cyanide was treated with lead carbonate to remove any sulfides present. The clear solution containing the cyanide was then analyzed with a cyanide specific ion electrode.

Results and discussion

Gaseous emissions from sealed flasks

The first experiments were conducted by pouring molten iron into the green sand molds shown in Figure 1. These molds were rammed into flasks that could be sealed and then vented so that the volatile compounds evolved in the thermal decomposition of the mold materials could be collected and characterized as to quantity and composition. These tests were used to study the effect of such variables as casting weight, sand-to-metal ratio, and the amount and kind of organic materials present in the sand on the effluent composition. The effluent from these experiments was relatively undiluted, and would be expected to show greater sensitivity to changes in gas concentrations due to the above variables than could be observed in an unsealed mold under usual foundry conditions.

Most ferrous foundries use a molding sand containing 4-6% clay, 1-2% cereal binder, 3-5% seacoal or other organic additives, and 3-4% water. Sands within these composition ranges were used in the sealed flask experiments. Table I lists the average composition of the emission gases, as well as typical ranges for a common green sand mixture. The effluent has been passed through an ice-water trap to remove steam and other condensables. The major gaseous constituents were found to be hydrogen and carbon monoxide, with concentrations of about 50% and 22%, respectively. Total hydrocarbons constituted approximately 9% of the effluent, with methane accounting for nearly half that amount. It should be noted that the actual percentage of gaseous organic compounds is probably less than 9%. The 9% value is relative to a methane standard.

Cyanide was found present at 125 ppm and ammonia at 3 ppm. These concentrations may be greater than these measured, since the gas
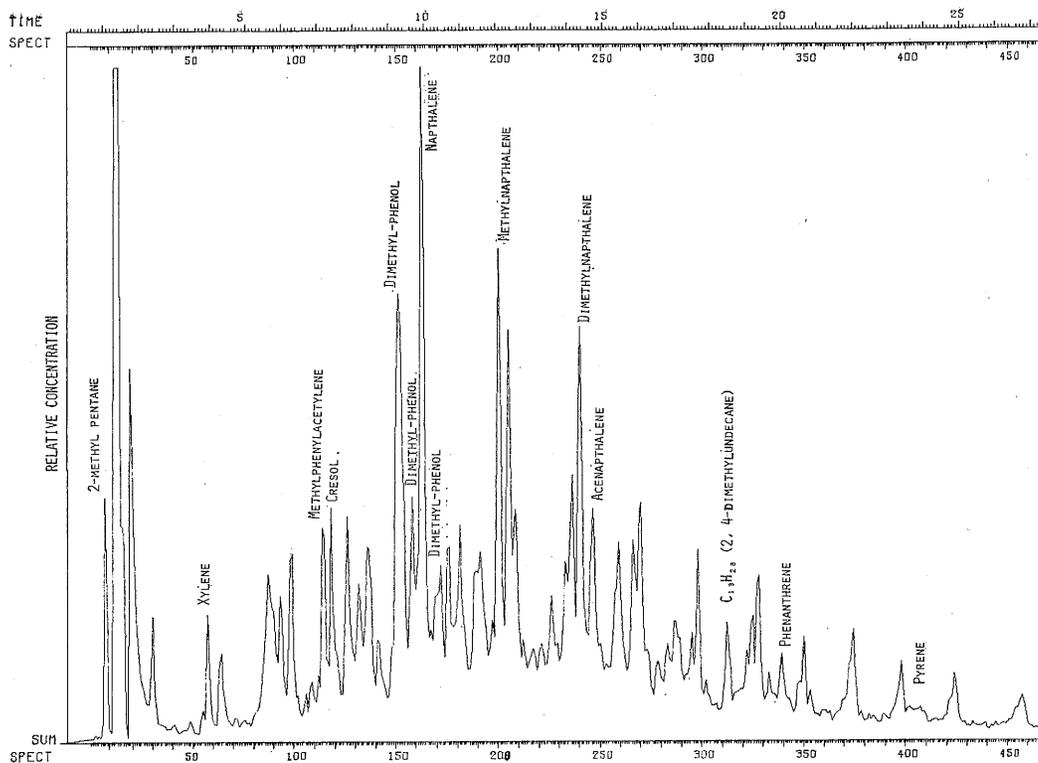
Figure 3—Gas chromatograph-mass spectrograph scan of heavy organic fraction condensed in closed flask cold trap.

water in the cold trap and the vent lines were made of copper, which is known to absorb ammonia. Steam is a major constituent of the effluent, as is evidenced by the condensate in the cold traps. The remainder of the gas present is expected to consist primarily of oxygen and nitrogen, which were present in the mold and sampling lines at the start of the experiment.

Studies have been conducted on the effect of mold atmosphere on the quality of a casting and the prevention of certain defects, especially in steel.[2-4] For example, Locke and Ashbrook[2] analyzed the effluent inside the mold cavity as it filled up with steel at 2900°F. The sand mixture they used contained an alkyd oil and kerosene rather than seacoal. Their results showed carbon monoxide to be 30.4% of the gases, hydrogen to be 25.6%, and a concentration of paraffins of 2.2% Our results are in general agreement, but the concentration of hydrogen was greater than observed by Locke and Ashbrook.

In the sealed flask experiments, vapors were condensed out of the effluent in the ice bath cold traps. Preliminary analysis shows this liquid to be approximately 98% water. The rest was a complex mixture of organic compounds that may be of significant hygienic importance, since in a foundry operation these condensable compounds might be vented to the atmosphere.

Several samples of the condensed liquid were examined by gas chromatography, and one sample of the condensate from the cold trap of a sealed flask was analyzed using a gas chromatography-mass spectrometry technique. The sample was analyzed on a 14 ft. by 0.125 inch 3% OV-101 column programmed from 50°C to 220°C at 8°/min. The reconstructed chromatogram in Figure 3 illustrates the complex nature of the condensed material. Several compounds in this mixture were identified, including 2-methyl-pentane, xylene, methylphenylacetylene, cresol, dimethylphenol, napthalene, methylnapthalene, dimethylnapthalene, acenapthalene, 2,4-dimethyllundecane, phenanthrene, and pyrene. No attempt was made to determine all of the organic compounds present in this mixture, or their actual
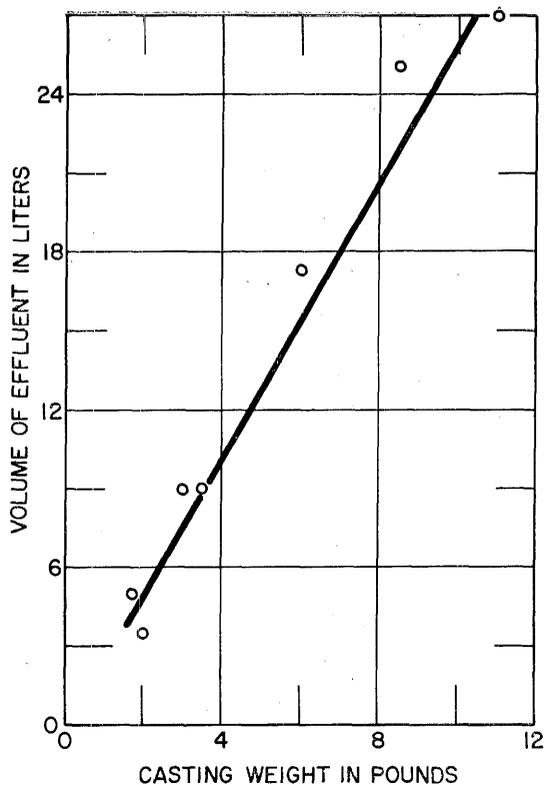
Figure 4–Effect of casting weight on the volume of effluent from sand containing 3% seacoal, 1% cereal and 4% water.

concentrations. It is estimated from the quantity of condensate other than water that these organic compounds amount to about 1% of the total effluent in the sealed flask experiments, but their presence may have important hygienic significance.

The variations in the composition of gaseous effluent as functions of green sand composition and size of casting were studied in the sealed flask experiments. All these experiments were conducted using the same flask size, so as the weight and size of the casting increased, the ratio of the sand weight to metal weight decreased.

The effect of casting weight on the total volume of gaseous effluent is illustrated in Figure 4. The volume of the gas produced increased linearly with increased casting weight (decreased sand-to-metal rub). The increase in gaseous effluent volume is a result of the fact that heavier castings evolve proportionately more heat, which must be absorbed by decreasing weights of sand. The result is that the sand
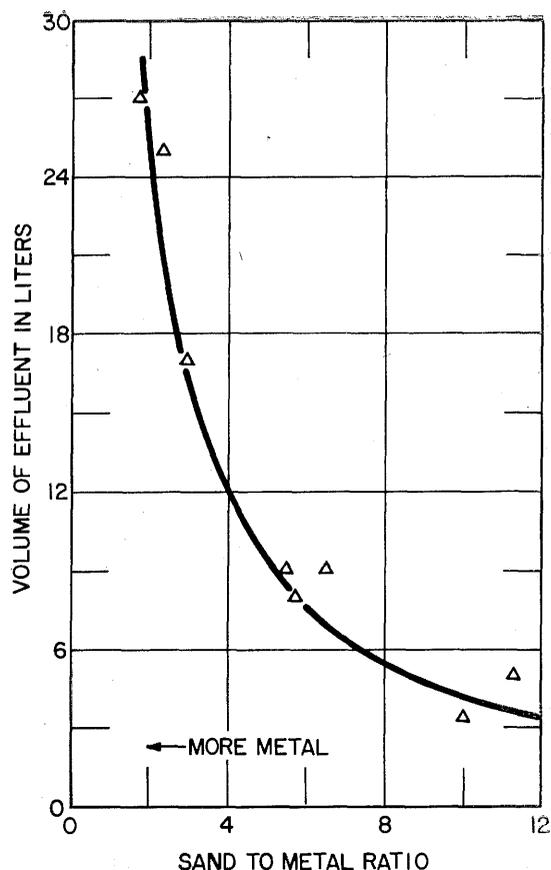

Figure 5–Volume of effluent from green sand molds containing 3% seacoal, 1% cereal and 4% water as a function of sand-to-metal ratio.

is heated to higher temperatures, which causes greater thermal decomposition of the hydrocarbons present in the mold. The volume of gas evolved was approximately 2.5 liters per pound of casting for casting sizes ranging from two to ten pounds.

Essentially the same phenomenon is shown in Figure 5, where the gas emission volume is plotted as a function of the sand-to-metal ratio in the mold. Again, relatively little gas is produced per pound of metal when a great deal of sand is in the mold. It is expected that there will be a maximum value of gas that can be driven off, but that this will be achieved for sand-to-metal ratio less than one and will correspond to a casting physically large enough to hold enough heat to vaporize all the water in the sand and raise the sand temperature above 600°F, where essentially all the organic additives will be converted to gaseous decomposition products. In normal foundry practice
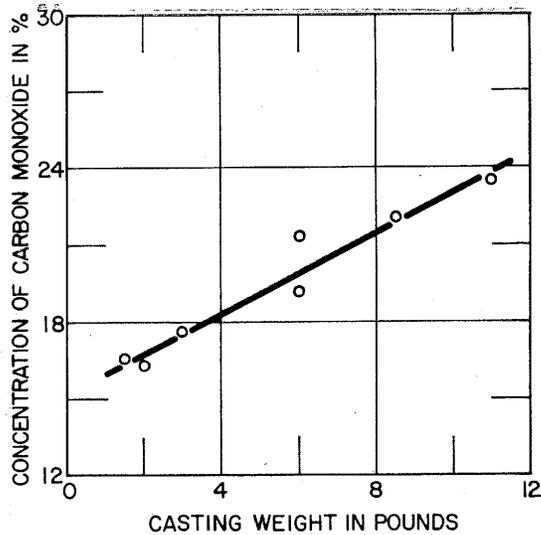
Figure 6—Concentration of carbon monoxide as a function of casting weight from a green sand containing 3% seacoal, 1% cereal and 4% water.
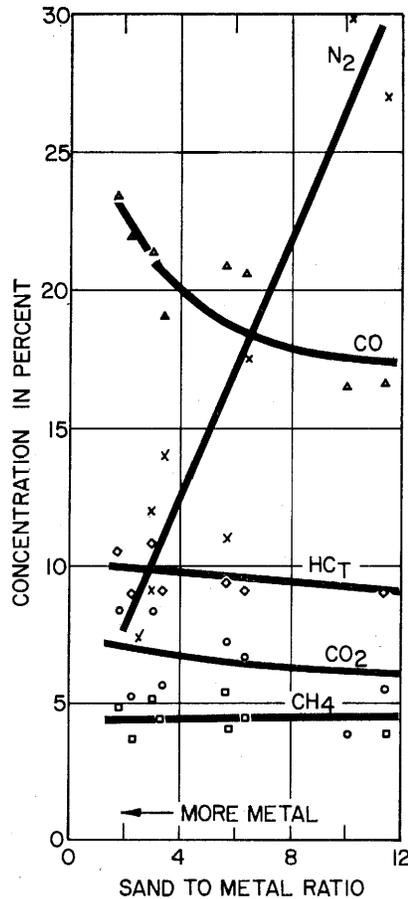

Figure 7—Variations in effluent composition as a function of sand-to-metal ratio for a green sand containing 3% seacoal, 1% cereal and 4% water.

the sand-to-metal ratio is between 5 and 10 to 1.

The increased extent of pyrolysis of organic materials caused by larger castings is reflected by the carbon monoxide concentration in the gaseous effluent. The concentration of CO increased from a minimum of about 16.5% with a 2 lb casting to as high as 23% with 11-pound castings, as shown in Figure 6. These values reflect the composition of the gases formed inside the mold cavity by distillation, thermal decomposition, and partial oxidation of the organic material present. The actual breathing zone concentrations of carbon monoxide at typical foundry operations would be substantially lower than these values because the CO would be substantially diluted and would be free to burn to CO_2.

Figure 7 represents the variation of several gaseous constituents with changes in sand-to-metal ratio for a typical green sand of 3% seacoal, 1% cereal, 5% western bentonite and 4% water. There appears to be no significant change in concentrations for methane, total hydrocarbons or carbon dioxide. However, Figure 8 indicates that the hydrogen concentration drops significantly as the sand-to-metal
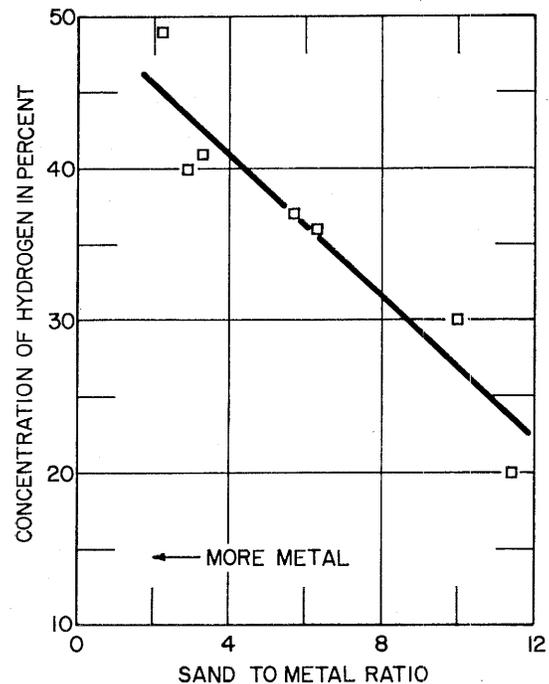

Figure 8—Variation in hydrogen concentration as a function of sand-to-metal ratio for green sand containing 3% seacoal, 1% cereal and 4% water.

ratio is increased. The same general behavior is noted for other green sand mixtures.

The content of cereal binder in the sand was varied over the range of common foundry practice, from zero to two percent, but this had no apparent effect on the relative concentrations of the gases in the effluent. When the sand-to-metal ratio was fixed at two to one, the cereal binder level maintained at one percent and the amount of seacoal varied, the concentrations of methane, hydrogen, carbon monoxide and total hydrocarbons increased with an increase in the amount of seacoal in the sand mix. This is shown in Figure 9. Increasing the amount of seacoal makes the mold atmosphere more reducing, which is why the foundryman adds it to the sand.

Neither a variation in the sand-to-metal ratio nor in the composition of the green sand had a significant effect on the concentrations of cyanide and ammonia present in the effluent.

The above analyses were on samples drawn from mylar bags. Since the volumes of the effluent differed (Figure 5), while the amount of residual air trapped in the sampling system was approximately the same, the relative concentrations of several species may decrease without apparent increase in other spe-
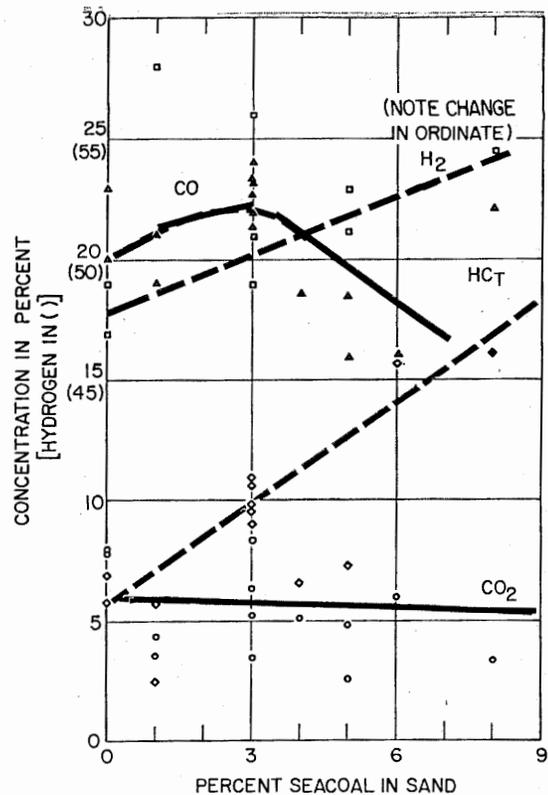

Figure 9—Effect of seacoal additions on green sand decomposition products (1% cereal level). Sand-to-metal ratio = 2:1.
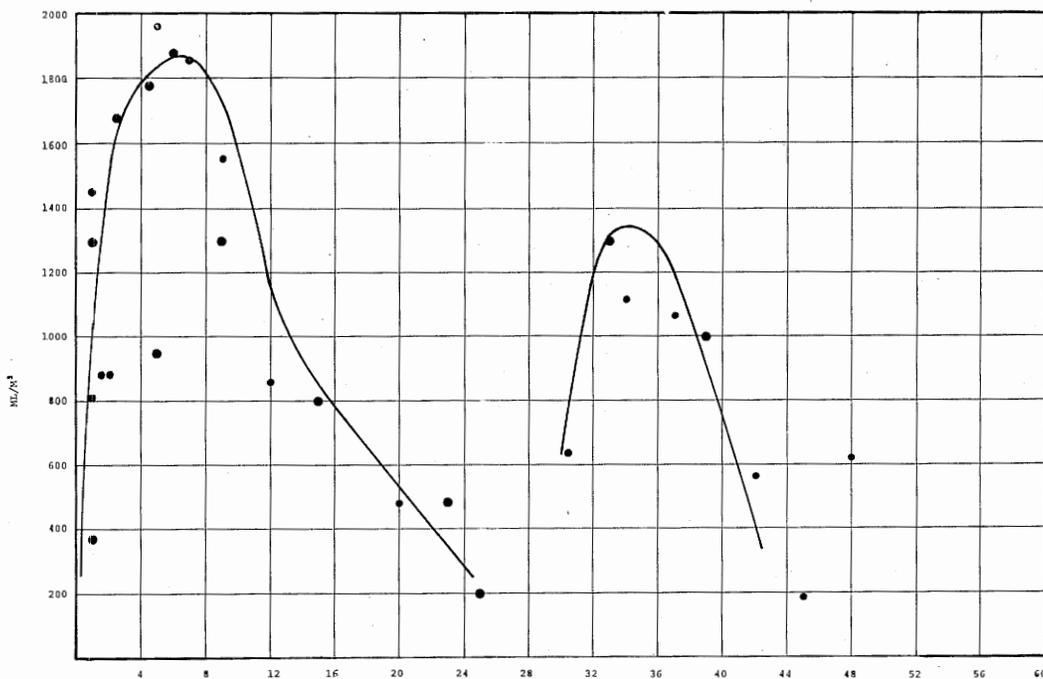

Figure 10—Variation of carbon monoxide concentration with time for green sand mold under the hood.
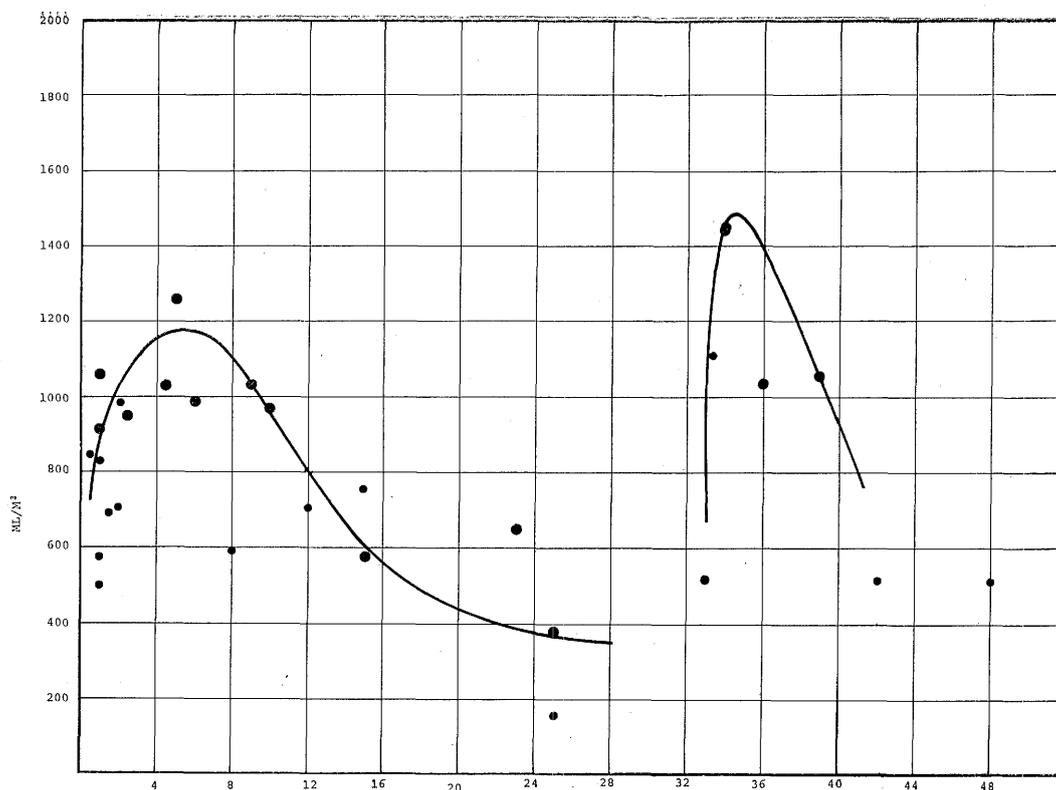
Figure 11—Variation of total hydrocarbons concentrated with time for green sand under mold.

cies, as shown in Figure 7. In fact, there will be a corresponding increase in the relative percentages of oxygen and nitrogen in the effluent.

Gaseous emissions from green sand foundry molds

Gaseous emissions from typical green sand molds have also been studied by placing molds without cores under an exhaust hood and collecting emissions as a function of time after pouring and during shakeout. The draft air effectively dilutes the effluent and permits oxidation of some combustible gases present in the effluent. This simulates normal foundry practice where ventilation is present and the burning of mold gases is observed.

Concentration-time plots of the carbon monoxide from duplicate green sand molds containing about 5% seacoal are shown in Figure 10. The castings were 4-inch cubes with appropriate ingates and pouring basin which gave a total weight of approximately 30 lb. The castings were poured at a sand-to-metal ratio of approximately 3 to 1. The first peak in the concentration-time curve represents the

carbon monoxide in the effluent after pouring. The second peak represents the CO concentration when the mold was broken open.

The carbon monoxide concentration increased from a low value just after pouring to over 1800 ppm about five minutes after pouring, and then began to gradually decrease. The casting was held in the mold for approximately 25 minutes to permit it to cool to an acceptably low temperature, as is done in normal foundry practice. The casting was then moved to a shakeout area, where it was manually removed from the mold under the exhaust sampling system. During the simulated shakeout operation, the CO content of the effluent increased as the mold was broken open and the hot sand exposed to the atmosphere. The CO concentration reached a level of about 1350 ppm during this operation and then began to decrease as the sand cooled.

Similar data is shown in Figure 11 for the concentration of total hydrocarbons evolved after pouring and during shakeout of green sand molds. The hydrocarbon concentration

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TABLE II
Open Mold Green Sand Emissions

COMPOUND (PPM)	BAR MOLD SAND: METAL RATIO = 7:1		CUBE MOLD SAND: METAL RATIO = 3:1	
	POUR	SHAKEOUT	POUR	SHAKEOUT
Carbon monoxide	1350	230	1510	650
Carbon dioxide	4920	2360	—	—
Total Hydrocarbons*	1780	640	1400	470
Methane	630	80	520	250
Cyanide	0.6	0.4	1.3	3.3
Ammonia	1.4	1.1	1.1	3.4

*Relative to methane standard.

progressively increased after the mold was poured, to a value of about 1200 ppm at six minutes, and then began to decrease. The casting was broken out of the mold about 30 minutes after pouring and hydrocarbon concentrations of about 1500 ppm were observed.

The average concentrations of the major gaseous constituents from the green sand effluent appear in Table II. This sand was of the same mixture as that reported in Table I for the closed system, which allows a direct comparison of how ventilation will change the characteristics of the effluent. Two different castings were made: the 4-inch cube discussed above and a set of bars on an ingate that weighed about 15 lb. (with a corresponding sand-to-metal ratio of 7:1). The values listed in Table II represent the average maximum concentrations observed during the pouring and breaking out of the castings. The size of the casting does not appear to be of major importance when the mold is well ventilated, and the values for the concentrations are not significantly different.

Hydrogen concentration was below the 1% level of detection for our procedure and was not determined in these trials; it probably burns in the mold. Combustion can also account for some of the variations in values for carbon monoxide and carbon dioxide.

Hygienic Importance

The results of these experiments indicate foundry workers may be exposed to considerable amounts of carbon monoxide evolved from green sand molds containing carbonous materials. Adequate ventilation and fresh make-up air may be necessary in the pouring area, the run-out lines where the casting cool in the sand, and in the shakeout area. Carbon monoxide alarms and other warning devices might be advisable in these areas to insure proper functioning of the ventilation system.

A reducing atmosphere is generally accepted as being necessary to produce good castings in a sand mold. Recently several products have been marketed that reportedly reduce toxic emissions, while producing acceptable castings.[5] It may also be possible to produce certain castings in molds that do not require organic additives. Cast iron water pipe is procuded in reuseable steel molds. Other permanent mold techniques are being developed and appear to offer a much cleaner environment as well as some metallurgical and economic advantages.[6-7] Not only are gaseous emissions reduced, but the potential for silicosis is significantly reduced with the elimination of most of the sand in the foundry process. Additional development work must be done in the area of permanent mold casting to prove its commercial and economic potential.

Acknowledgements

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