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> US Army Contract DAAE30-02-C-1095 FY 2003 Tasks WBS # 3.1.17

# **Characterization of Fine Particulate Emissions from Casting Processes**

Technikon # 1410- 3117

April 2005 Revised for public distribution.







UNITED STATES COUNCIL FOR AUTOMOTIVE RESEARCH

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# **Characterization of Fine Particulate Emissions from Casting Processes**

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Submitted to Journal of Aerosol Science February 2, 2005

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#### Abstract

Fine particulate  $(PM_{2,5})$  emissions from gray iron metal casting processes were characterized from No-Bake molds poured at the Research Foundry located at Technikon, LLC (McClellan, CA). For each mold, PM<sub>2.5</sub> was collected for chemical analysis, and particle size distributions were measured by an Electrical Low Pressure Impactor (ELPI) to understand PM emissions in the casting process. Molds prepared with phenolic urethane binders were poured with Class 30 gray cast iron at 1,427–1,480°C. PM<sub>2.5</sub> was collected from the pouring, cooling, and shakeout processes for each mold. The majority of  $PM_{2.5}$  mass emitted from these processes was found to be composed of carbonaceous compounds, including 37–67% organic carbon (OC) and 17–30% soot (elemental carbon [EC]). Oxides of aluminum [Al], silicon [Si], calcium [Ca], and iron [Fe] comprise 8–20% of PM<sub>2.5</sub> mass, and trace elements (e.g., K, Ti, Mn, Cu, Zn, Pb) comprise 3– 6%. Chemical abundances in PM were different between pouring and shakeout for each discrete mold. PM<sub>2.5</sub> mass emissions from pouring are only 15–25% of the total from each discrete mold. Ultra fine particles (<0.1 µm) comprise less than 1% of PM<sub>2.5</sub> mass. Different mechanisms between pouring and shakeout result in variations in chemical abundances and particle size distributions. The highest  $PM_{2.5}$  mass and number concentrations were observed when shakeout started. Distribution of PM<sub>2.5</sub> mass concentration in shakeout contains particles in the tail of coarse particles (1.6-2.5 µm) and growth of condensable species onto solid particles (0.65-1.6 µm). Flame conditions, vaporization, thermal decomposition of organic materials, and the variability of mold breakup during shakeout affect the source paths of PM formation. The observations in this study suggest that a detailed chemical speciation for size-segregated PM samples at different process points needs to be investigated for a better understanding of PM emission mechanisms. This will also improve emission control strategies and quality assurance of molds in the casting process.

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#### Introduction

U.S. foundry operations face many environmental challenges with implications for their competitiveness in the world market. The passage of the U.S. Clean Air Act Amendments led to Air Toxics Regulations that included Maximum Achievable Control Technologies (MACT) regulations. MACT regulations require foundries to meet hazardous air pollutant (HAP) emission levels equal to the average of the top 12% of the industry. The final version of the iron and steel foundry MACT (40 CFR Part 63), promulgated on April 22, 2004, requires that metal casting plants begin controlling and monitoring their source emissions by April 23, 2007.

Although stationary source testing methods have not yet been specified for  $PM_{2.5}$  (particles with aerodynamic diameter less than 2.5 µm), MACT requires each foundry to demonstrate initial compliance by conducting performance tests for metal HAPs as well as organic HAPs. A dilution tunnel method (i.e., EPA Method 5G), is used for EPA certification of particulate

A dilution tullier method (i.e., EFA Method 3G), is used for EFA certification of particulate emissions from residential wood combustion (Houke et al., 2000; McCane and Williamson, 1984; Merill and Harris, 1987). In addition, the procedure developed to determine PM emissions from mobile sources employs a dilution tube to dilute tailpipe emissions with ambient air maintained at a specified range of relative humidity (RH) and temperatures (ISO 8178). In this case, mobile source emissions are sampled isokinetically from a dilution sampling system at a temperature of less than 52°C and are collected on various sampling substrates. The PM mass is then determined gravimetrically from the filter.

A dilution sampling system is used to simulate the natural processes of PM formation in the atmosphere. Comparisons between dilution sampling methods and the EPA hot-filter/impinger train method for collecting PM from a stationary source suggest that heated filter methods underestimate condensable species that are not collected at hot temperatures (Hildemann et al., 1989), and that the impinger method (in which the impinger is surrounded by ice at a temperature ~0–  $4^{\circ}$ C) overestimates condensable species due to the formation of aerosols at ice cold temperatures and the adsorption of gases to water (Wien et al., 2001; Watson, 2002). The sampling bias is more pronounced for sources containing low levels of solid particles and high condensable species in the stack. The discrepancy of source profiles developed from different source sampling methods may result in difficulties for emission inventory development, air quality modeling, and environmental credit trading. An ongoing effort of the American Society of Testing Methods (ASTM, D22.03) and the U.S. EPA is to define performance-based dilution sampling methodologies for stationary emission sources.

A lack of understanding about emission characteristics makes it difficult for the foundry industry to develop control and management strategies to comply with MACT. An objective of the Casting Emission Reduction Program (CERP) is to obtain representative PM emission data from different parts of the casting process. This study is the first of its kind to: 1) develop relationships among emissions of total hydrocarbon (THC),  $PM_{2.5}$ , and stack parameters; 2) characterize the physical properties (distributions of particle number and mass concentrations) of  $PM_{2.5}$  emissions in single-pour molds; 3) establish the baseline of speciated  $PM_{2.5}$  emissions in single-pour molds; and 4) validate the applicability and optimize the operation of the dilution sampling method for foundry emissions.

#### EXPERIMENTAL TEST METHOD AND FACILITY

#### **Test Facility**

Samples from casting processes were collected from the Research Foundry at Technikon, LLC (McClellan, CA), under CERP. The Research Foundry is designed to measure emissions from individual poured molds and is used to evaluate the impact on emissions from proposed alternative materials, equipment, or processes, prior to further validation at a full-scale foundry. Measurements at the Research Foundry were taken during the pouring, cooling, and shakeout processes for discreet molds under tightly controlled conditions. The flue gas exhaust was withdrawn from approximately the center of a 10 cm diameter stack at a port 1 m above ground level. The extracted sample was

split into two streams: One was connected to the Desert Research Institute (DRI) Source Dilution Sampling System (Hildemann et al., 1989; Chow et al., 2004), and the other connected to an EPA Method 201A/202 sampling train (Figure 1).





The Technikon CERP testing team prepared the molds to a standard composition and recorded the following data: the weight of the metal, mold binder composition and weight, the number of cavities poured; the percent lost on ignition (LOI), the pouring temperature, and alloy weights. The mold pattern was a 4-on gear, made with Wexford W450 Lakesand. The HA International (Illinois)Techniset® No-Bake® Phenolic-Urethane mold binder was 1.8% total binder (BOS) composed of number 6000 Part I resin (55%), 6433 Part II co-reactant (45%), and 17-727 Part III activator at 7% of Part I. Molds were poured with Class 30 gray cast iron at 1,427–1,482°C. The stack conditions—such as concentrations of THC, gas velocity, temperature, and moisture, gas density and molecular weight, and absolute pressure in the stack—were monitored throughout the test. The initial sand temperature into the hood was maintained at 26.5– 32.2°C with a minimum system process air temperature of 43.3°C. No particulate removal equipment was installed in the stack before the flue gas exhaust was extracted.

#### **Dilution Sampling System**

The DRI Source Dilution Sampling System (Figure 2) draws 20–25 L/min of combustion exhaust through a venturi flowmeter. The sample line is heated at a temperature slightly higher than that of the exhaust temperature to reduce particle thermophoresis losses and gas condensation on

the wall. Ambient air passes through a high-efficiency particle arresting (HEPA) filter to remove PM, followed by a granulated activated carbon (GAC) bed to remove gaseous species and volatilized PM. The clean, cool ambient air dilutes and mixes with the exhaust gas in the U-shaped mixing zone. At the end of the mixing zone, 113 L/min of diluted sample is drawn into a residence time chamber for 90 seconds of aging time, which permits the particles to cool, nucleate, co-





agulate, and grow by condensation. The excess flow is removed by a high-volume pump. The  $PM_{2.5}$  cyclone is used to remove larger particles (Bendix 240; Chan and Lippman, 1977). Sample flow then enters the Teflon-coated source sampling cone, where two filter pads collect the PM sample that then undergoes physicochemical characterization in the laboratory. An additional port is connected to an Electrical Low Pressure Impactor (ELPI, Dekati, Finland) in the cone to measure particulate size distribution. The filter pack configurations include: 1) polyolefin-ringed Teflon membranes (Gelman [Ann Arbor, MI], 2.0 µm pore size, 47-mm diameter [#R2PJ047], for mass and elemental analysis) used to remove larger particles (Bendix 240; Chan and Lippman, 1977). Sample flow then enters the Teflon-coated source sampling cone, where two filter pads collect the PM sample that then undergoes physicochemical characterization in the laboratory. An additional port is connected to an Electrical Low Pressure Impactor (ELPI, Dekati, Finland) in the cone to measure particulate size distribution. The filter pack configurations include: 1) polyolefin-ringed Teflon membranes (Gelman [Ann Arbor, MI], 2.0 µm pore size, 47-mm diameter [#R2PJ047], for mass and elemental analysis) followed by a pre-fired quartz-fiber filter (Pallflex [#2500QAOT-UP]) to quantify volatized carbon; and 2) a pre-fired quartz-fiber filter for soluble ion and carbon analyses followed by a cellulose-fiber filter (Whatman 31ET) impregnated with citric acid to collect gaseous ammonia (NH3). The flow rate, monitored by calibrated mass flowmeters (Model 3063, TSI Shoreview, MN), was 51 L/min through each Teflon/quartz and quartz/citric acid impregnated cellulose filter pack, and was 10 L/min for ELPI. The filter packs were equipped with quick-release connectors to minimize contamination. A data acquisition system monitored and recorded the flow rates of the venturi flowmeter and sample ports, as well as the temperature and RH of the ambient air and the diluted exhaust.

Five tests were conducted under the same duct-supplied air temperature (29°C– 35°C) and duct velocity. The sample collection schedule, duct flow rate, cast weights, and binder weights are shown in Table 1. Each dilution sampling test consisted of a complete casting process of 75-minutes (45 minutes of pouring and cooling, 15 minutes of shakeout, and 15 minutes of after-cooling), except for Run 2, which sampled only 36 minutes of pouring and cooling due to a regional power failure. For filter media sampling and ELPI measurements, 2–3 minutes of sampling time was added to adjust the target dilution air ratio at the beginning of every test and to include the 90-second aging time in the residence temperature chamber.

							Cast	Binder
	Start	End	DRI Run	Technikon Mold	Sample Time	Duct Flowrate	Wt.	Wt.
Date	Time	Time	Number	Number	(min)	(scfm)	(lb)	(lb)
2/25/2004	9:50	10:35	Run 2	GA-2A	36	253.0	122.0	5.930
2/26/2004	9:00	10:20	Run 3	GA-3A & 3 B	75	236.0	120.6	5.680
2/26/2004	15:05	16:24	Run 4	GA-3C	75	239.0	95.6	5.910
2/27/2004	11:30	12:50	Run 5	GA-4A & 4B	75	233.0	120.9	5.710
2/27/2004	13:52	15:08	Run 6	GA-4A & 4B	75	237.0	122.0	5.940

 Table 1
 Daily Test Condition Schedule For Comparisons of the Dilution Sampling Method

and EPA Method PRE4/202 Sampling Train at the Technikon Pre-Production Foundry from February 25–27, 2004.

PM<sub>2.5</sub> mass was determined as the difference between pre- and post-sampling masses measured on Teflon-membrane filters with an MT 5 microbalance (Mettler, Placerville, CA; Chow et al., 2004). After gravimetric analysis, Teflon-membrane samples collected were analyzed by energy dispersive X-ray fluorescence (ED-XRF, Kevex0700, Kevex Corp., Foster City, CA) (Watson et al., 1999). Inorganic ions and carbon were determined from deposits on quartz-fiber filters. Chloride (Cl-), nitrate (NO3-), and sulfate (SO4=) were measured by ion chromatograph (IC) (Chow et al., 1999) with a Dionex 500x (Dionex, Sunnyvale, CA). Ammonia (NH4+) was measured by the indolphenol method using an automated colorimetric (AC) system (Astoria-Pacific, Clackamas, OR). Eight organic and elemental carbon (OC and EC) fractions were determined following the Interagency Monitoring of Protected Visual Environmental (IMPROVE) protocol (Chow et al., 1993) using a DRI Model 2001 thermal/optical carbon analyzer. PM<sub>2.5</sub> particle size distributions of diluted samples were measured by ELPI, which uses a unipolar corona charger to impart a positive charge on the measured aerosol and separates particles by impaction at size ranges of 0.03, 0.06, 0.108, 0.17, 0.26, 0.40, 0.65, 1.0, 1.6, 2.5, 6.5, 8.4, and 10 µm. The impaction substrates are electrically isolated with Teflon supports, and the accumulating charge on each substrate is measured by an array of electrometers. The measured current is proportional to the number of particles depositing on the stage, which can be converted to mass. The 1-second response time of ELPI allows characterization of rapid changes of particle-size distribution in the casting cycle.

#### RESULTS

Dilution Sampling Run	Total Sampling Volume (m3) at STP*	Average Dilution Air Ratio	Filter PM <sub>2.5</sub> Mass Conc (µg/m3)	Average ELPI PM <sub>2.5</sub> mass conc (ug/m3) for Pouring and Cooling	Average ELPI PM <sub>2.5</sub> Mass Conc (ug/m3) For a single mold	PM <sub>2.5</sub> ELPI/ Filter Mass Ratio	Fraction of P from Pouring, Cooling**
2	1.47	26.25	991.14		723.00	0.73	NA
3	3.26	31.81	2050.98	4.9E+02	1837.00	0.90	0.267
4	3.32	44.00	809.46	1.5E+02	771.00	0.95	0.200
5	3.07	42.10	2404.12	2.8E+02	1841.00	0.77	0.153
6	3.04	60.30	1114.34	1.6E+02	871.00	0.78	0.179

Table 2 PM<sub>2.5</sub> Mass Concentrations Determined by Filter Sampler and ELPI. Average EPLI PM<sub>2.5</sub>

#### **Emission Rate**

Table 2 compares  $PM_{2.5}$  mass, as determined by filter samplers and ELPI, and  $PM_{2.5}$  mass emission rates for each mold. The pouring and cooling portions of the casting process are regarded as a single step; the time for that step is then divided by the total time of the casting process. Chang et al. (2004) found that a minimum dilution air ratio of 20 is sufficient to achieve stable particle size distributions in a dilution method for stationary source emission. This was applied to Run 2 initially; however, the dilution air ratio was increased two- to three-fold, based on average  $PM_{2.5}$  mass concentration estimated by ELPI from a previous run. Optimizing the operating dilution air ratio applied to these tests ranged from 26 to 60. The emission rate was determined as:

$$In - StackPM_{2.5}MassConcentration = \frac{MassCollectedOnFilter}{FlowRate * SamplingTime} * averageDilutionAirRationAirR$$

and

$$DilutionAirRatio = \frac{(\sum Q_{filters} + Q_{ELPI} + Q_{byPassFlow})atSTP}{Q_{venture}} * (293.13K / stackTemp @ K)$$

The average ELPI  $PM_{2.5}$  mass concentrations show reasonable agreement with filter media.  $PM_{2.5}$  mass concentrations measured by ELPI are approximately 77–95% of those determined by filter samplers, and a ratio of 0.73 was observed for Run 2 (pouring and cooling). This result shows that ELPI can be used to project  $PM_{2.5}$  mass concentrations by applying an effective density of 1.175 for molds with the binder and other materials used in these tests. The average  $PM_{2.5}$ 

mass concentration during different processes (i.e., pouring and cooling to shakeout and aftercooling), is compared by integrating the PM<sub>2.5</sub> mass concentrations measured by ELPI during each process. The results show that PM<sub>2.5</sub> emitted from the pouring and cooling is approximately 15–26% of that from each complete mold, as shown in Table 2. The average PM<sub>2.5</sub> mass concentration for each mold ranges from 35 to 101 mg/m3. The variations of pouring and cooling emissions in the mold and the wide range of PM<sub>2.5</sub> mass emissions will be discussed later. An average PM<sub>2.5</sub> mass concentration of 1,114  $\mu$ g/m3 was observed in diluted air samples for Run 6. The high PM<sub>2.5</sub> mass concentration in the diluted sample resulted in high mass loading of 2.7–4.7 mg on filter media for each 75-minute test. ISO 7187 recommends a gas face velocity of 35–80 cm/s and 0.576  $\mu$ g/mm2 (i.e., 1mg/47mm filter); thus, a dilution air ratio of 60 or higher should be used in the dilution method for PM sampling from a gray iron foundry under these conditions.

The emission rate of  $PM_{2.5}$  chemical species is shown in Table 3 in both lb species/lb binder and lb species/ton metal. For a complete mold, the most abundant species are carbonaceous compounds with an emission rate of 3.03\*10-1 to 6.26\*10-1 lb OC/ton metal (2.45\*10-3-6.42\*10-3 lb OC/lb binder) and 1.59\*10-1 to 5.47\*10-1 lb EC/ton metal (1.28\*10-3-5.80\*10-3 lb EC/lb binder). Other major species (>1.00\*10-4 lb/ton metal [i.e., 1.00\*10-2 lb/lb binder]) include silicon (Si), manganese (Mn), and iron (Fe). This study does not intend to develop a PM<sub>2.5</sub> emission inventory. The emission rate and source profiles are applicable only to the core and binder materials used in this study.

#### Table 3 Emission Factors of PM<sub>2.5</sub> Chemical Species from the Foundry Process

(4-on irregular gear No Bake® molds). No weighing factors for metal oxides and organic carbon were applied.

Run Number	Emission F Run 2	Rate (Ib/ton Run 3	metal) Run 4	Run 5	Runő	Emission I Run 2	Rate (Ib/Ib I Run 3	nder)] Run 4	Run 5	Run 6
Maee	2 4 15 -0 1	1205+00	8 365-01	1835+00	1 22 5 +0.0	2.485-03	1.285.02	6 765-03	1.935-02	1.255-02
Ammonia Gas (AC)	3.44E-03	2 735 -02	2.64E-0.2	2.515-02	3.865-02	3.545-05	2 905-04	2 145-04	2.655-04	3.965-04
Carbon in Backup Eilter		Protocol	2.042-02	2.012-02	5.00E-02	0.04E-00	2.902-04	2.14E-04	2.00 2-04	0.90E-04
Carbon in Backup Filler	by IMP ROVE	11010601								
OC1 backup OC2 backup	2.45E-03 2.42E-03	6.82E-03 7.37E-03	9.41E-03 9.87E-03	6.45E-03 9.55E-03	1.31E-02 1.32E-02	2.52E-05 2.49E-05	7.24E-05 7.83E-05	7.61E-05 7.98E-05	6.83E-05 1.01E-04	1.34E-04 1.36E-04
OC3 backup	2.40E-03	4.27E-03	5.89E-03	6.51E-03	8.90E-03	2.47E-05	4.63E-05	4.76E-05	6.89E-05	9.14E-05
OC4 backup OPC backup	4.94E-04	2.03E-03	2.58E-03	3.62E-03	5.52E-03	5.08E-06	2.15E-05	2.09E-05	3.83E-05	5.67E-05
OC backup	7.76E-03	2.09E-02	2.84E-02	2.86E-02	4.46E-02	7.98E-05	2.22E-04	2.30E-04	3.02E-04	4.58E-04
EC1 backup	3.21E-04	2.34E-03	3.01E-03	4.69E-03	6.88E-03	3.30E-06	2.48E-06	2.44E-05	4.86E-05	7.07E-06
EC2 backup EC3 backup	2.47E-04 0.00F+00	1.13E-03 0.00E+00	2.06E-03	1.03E-03	3.00E-03 4 42E-04	2.64E-06 0.00F+00	0.00F+00	1.60E-06	1.94E-06 0.00E+00	3.90E-06 4.54E-06
EC backup	5.68E-04	3.03E-03	4.46E-03	4.05E-03	7.29E-03	5.84E-06	3.22E-05	3.60E-05	4.29E-05	7.49E-06
TC backup	8.33E-03	2.40E-02	3.28E-02	3.26E-02	5.19E-02	8.57E-05	2.54E-04	2.66E-04	3.45E-04	5.33E-04
Inorganic lons by IC/AC										
CI-	3.49E-04	6.97E-03	6.44E-03	1.94E-02	1.45E-02	3.59E-06	7.40E-05	4.40E-05	2.05E-04	1.49E-04
NO3 <sup>-</sup>	1.03E-04	3.36E-04	3.97E-04	6.06E-04	9.07E-04	1.06E-06	3.56E-06	3.21E-06	6.41E-06	9.32E-06
NH4*	2.74E-04	1.20E-03	6.62E-04	7.14E-03	4.16E-03	2.82E-06	1.27E-06	5.28E-06	7.66E-06	4.27E-06
Carbon in front filter by IM	IPROVE Prot	locol								
001	4 725 03	0.265.02	4 145 0.2	5 46E 02	5 86E 0.2	4865.05	0.825.04	3 365 04	5 78E 04	6 015 04
0C2	7.60E-03	8.64E-02	4.54E-02	6.32E-02	5.46E-02	7.82E-05	9.17E-04	3.67E-04	6.69E-04	5.61E-04
003	7.86E-03	6.05E-02	3.02E-02	3.90E-02	3.63E-02	8.08E-05	6.43E-04	2.44E-04	4.13E-04	3.73E-04
004	4.30E-03 0.00E+00	0.00E+00	0.00E+00	4.42E-02 0.00E+00	4.66E-02 0.00E+00	4.50E-05 0.00E+00	0.00E+00	2.01E-04 0.00E+00	4.00E-04 0.00E+00	4.70E-04 0.00E+00
oc	2.83E-02	5.24E-01	3.03E-01	5.20E-01	6.26E-01	2.91E-04	5.67E-03	2.45E-03	5.50E-03	6.42E-03
EC1	5.14E-02	4.22E-01	2.79E-01	6.77E-01	4.56E-01	5.29E-04	4.48E-03	2.25E-03	7.16E-03	4.68E-03
EC3	1.08E-03	1.43E-03	1.60E-03	4.44E-03	2.42E-03	1.11E-05	1.62E-06	1.29E-05	4.70E-06	2.49E-06
EC4	5.80E-02	1.99E-01	1.59E-01	5.47E-01	2.78E-01	5.97E-04	2.11E-03	1.28E-03	5.80E-03	2.86E-03
	0.002-02	1.202-01	4.022-01	1.072.00	0.046-01	0.002-04	1.002-00	0.702-00	1.102-02	0.202-00
Elements By XRF										
Al	0.00E+00	3.88E-03	2.92E-03	1.64E-03	2.86E-03	0.00E+00	4.11E-05	2.36E-05	1./4E-05	2.94E-05
P	0.00E+00	0.00E+00	9.46E-05	4.00E+02 0.00E+00	4.47E-02 6.12E-04	0.00E+00	0.00E+00	4.00E-04 7.65E-07	4.32E-04 0.00E+00	4.59E-04 6.28E-06
S	6.60E-04	1.11E-03	7.52E-04	3.86E-04	6.07E-04	5.66E-06	1.18E-06	6.08E-06	4.09E-06	6.23E-06
CI	4./0E-04	1.04E-02	7.02E-03	1.67E-02	1.08E-02	4.83E-06	1.10E-04	6.68E-06	1.6/E-04	1.11E-04
K Ca	1.29E-04 294E-04	6.33E-03 2.30E-03	5.64E-03 2.05E-03	6.30E-03 2.42E-03	6.29E-03 2 19E-03	1.32E-06	6.72E-05 2.44E-05	4.56E-05	6.66E-05 2.57E-05	6.46E-05 2.25E-05
TI	0.00E+00	1.59E-04	1.48E-04	5.61E-05	0.00E+00	0.00E+00	1.69E-06	1.20E-06	5.93E-07	0.00E+00
Va	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
CI Ma	0.765.00	2.092-04	1.042-04	7.045.00	0.322-00	0.045.04	2.222-00	1.24E-00	1.90E-00	0.04E-07
Fe	3.02E-02	4.66E-02	4.02E-02 2.54E-02	4.56E-02	2.79E-02	3.11E-04	4.95E-04	2.05E-04	4.83E-04	2.21E-04 2.86E-04
Co	6.12E-06	9.29E-06	6.64E-06	6.67E-06	6.24E-06	6.27E-07	9.86E-07	6.29E-07	6.00E-07	6.38E-07
Cu	9.63E-06 2.62E-03	9.26E-06 2.46E-03	4.68E-05 1.99E-03	8.18E-05 4.05E-03	5.70E-05 1.47E-03	9.81E-07 2.59E-05	9.82E-07 2.61E-05	3.78E-07 1.61E-05	8.66E-07 4.29E-05	5.86E-07 1.51E-05
Zn	2.41E-03	3.20E-03	1.74E-03	5.15E-03	1.30E-03	2.48E-05	3.39E-05	1.40E-05	5.45E-05	1.33E-05
Ga	0.00E+00	0.00E+00	0.00E+00	3.16E-05	0.00E+00	0.00E+00	0.00E+00	0.00E+00	3.35E-07	0.00E+00
AS	1.99E-05 0.00E+00	2.10E-05 0.00E+00	0.00E+00	0.00E+00 3.09E-06	5.46E-06 0.00E+00	2.05E-07 0.00E+00	2.23E-07 0.00E+00	0.00E+00	3.27E-08	0.00E+00
Br	0.00E+00	3.12E-05	2.66E-06	2.13E-06	1.23E-05	0.00E+00	3.31E-07	2.06E-07	2.26E-08	1.26E-07
Rb	1.33E-06	2.30E-05	2.40E-06	1.67E-06	1.66E-06	1.36E-08	2.44E-07	1.94E-07	1.66E-07	1.59E-07
Sr Yt	3.15E-06 5.79E-07	3.32E-05	2.50E-05 1.02E-05	1.37E-05 1.02E-05	1.46E-05	3.24E-08 5.96E-09	3.53E-07 1.22E-07	2.02E-07 8.27E-08	1.45E-07 1.08E-07	1.50E-07
Zr	1.47E-06	1.14E-05	1.36E-05	9.87E-06	1.60E-05	1.52E-08	1.21E-07	1.10E-07	1.04E-07	1.65E-07
Мо	3.05E-05	3.13E-05	0.00E+00	3.75E-05	0.00E+00	3.14E-07	3.32E-07	0.00E+00	3.97E-07	0.00E+00
Pd	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.46E-05	0.00E+00	0.00E+00	0.00E+00	0.00E+00	1.50E-07
Cd	2.60E-06	2.31E-06	2.16E-06	0.00E+00	6.43E-06	2.57E-08	2.46E-08	1.76E-07	0.00E+00	6.67E-08
In	0.00E+00	1.16E-06	6.62E-06	0.00E+00	0.00E+00	0.00E+00	1.23E-07	4.66E-08	0.00E+00	0.00E+00
Sn	2.29E-04	2.27E-04	1.78E-04	2.10E-04	1.20E-04	2.36E-06	2.41E-06	1.44E-06	2.23E-06	1.24E-06
Sb P.a	8.06E-05	2.42E-05	1.38E-04	0.00E+00 2 16E-04	1.87E-04	8.29E-07	2.57E-07 1.37E-06	1.12E-06	0.00E+00 2.29E-06	1.92E-06
La	0.00E+00	0.00E+00	1.84E-04	2.15E-04	2.91E-04	0.00E+00	0.00E+00	1.49E-06	2.28E-06	2.99E-06
Au	0.00E+00	0.00E+00	0.00E+00	7.30E-06	0.00E+00	0.00E+00	0.00E+00	0.00E+00	7.73E-08	0.00E+00
нg	1.04E-05	1.00E-U5	0.00E+00	1.17E-05	4.04E-06	1.00E-V/	1./0E-0/	0.00E+00	1.24E-0/	4./0E-V0
TI	2.43E-06	3.86E-06	0.00E+00	0.00E+00	0.00E+00	2.50E-08	4.10E-08	0.00E+00	0.00E+00	0.00E+00
PD Ur	0.00E+00	0.00E+00	4.00E-06	2.00E-04 8.46E-06	6.80E-06	0.00E+00	2.93E-06	8.90E-08	2.70E-06 8.96E-08	6.98E-08

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#### Process Variation of PM<sub>2.5</sub> Emissions

The process variations of stack conditions (stack temperature, carbon monoxide [CO], and THC concentrations), and  $PM_{2.5}$  mass and number concentrations for Runs 3–6 are shown in Figures 3 and 4. Consistent patterns were observed in the casting process, with maximum emissions occurring as shakeout started. In general,  $PM_{2.5}$  mass and number concentrations, stack temperature, and CO concentration increased rapidly as the pouring started and decreased after the cooling period. THC concentration was elevated by two-to four-fold and stabilized in cooling after the cast iron was poured.

High variations were observed among the runs, especially during shakeout. In Runs 3 and 4, the highest stack temperatures in the shakeout period were around 200°C, much less than those in Runs 5 and 6 (more than 300°C). Peak PM<sub>2.5</sub> mass concentrations (when shakeout started) in Runs 5 and 6 were twice of those in Runs 3 and 4. Since measurements of stack conditions (i.e., stack temperature, THC, and CO concentrations) were not affected by the dilution method used, the variation of the PM<sub>2.5</sub> mass emission rate is probably due to casting variations, not the dilution air ratio. Dual peaks of THC and PM<sub>2.5</sub> number concentrations in shakeout were observed in Runs 3, 4, and 6 (Panels a, b, and d of Figures 3 and 4). Between the two peaks, lower THC concentrations at 2,720– 2,760 seconds (immediately after shakeout starts) correspond to increasing PM<sub>2.5</sub> number concentrations. When the THC concentration in the second peak was relatively close to the first peak, the second peak of PM<sub>2.5</sub> number concentration was less observable. In Run 4, a small increase in PM<sub>2.5</sub> number concentration was observed.

#### Figure 3 Process Variations of Stack Temperature

Process variations of stack temperature (°C), carbon monoxide (CO) concentration (ppm), and total hydrocarbon concentration (THC) (ppm), measured in: a) Run 3, b) Run 4, c) Run 5, and d) Run 6. (Note that peak stack temperature [°C] in Runs 5 and 6 during shakeout period exceeds 300°C; in Runs 3 and 4 it is ~200°C.)

#### a) a) 3.E+03 250 TH 3.E+02 - 00 200 (udd) 2.E+03 Stack Temp 100 to 100 E 2.E+02 Concentrati 1.E+03 1 E+00 50 Gas Mass 0.E+0 0.E+0 -1000 0 1000 2000 3000 4000 5000 1000 Process Time (s) b) b) 5.E+03 250 5.E+0 -THC 4.E+03 CO 200 100 100 100 100 100 00 00 200 3.E+03 2.E+0 5 1.E+03 9 0.E+00 -1000 0 1000 2000 3000 Process Time (s) 4000 5000 6000 0.E+0 -1000 0 c) 2.0E+03 c) 400 THO 8.0E+02 co mdo 1.5E+03 Stack Ter 300 m'g'm (c) 6.0E+0 ature 1.0E+03 200 4.0E+0 ame 5.0E+02 100 100 2.0E+02 0.0E+00 -1000 2000 3000 4000 5000 0 1000 6000 0.0E+00 Process Time (s) -1000 0 d) d) 4.E+03 600 5.E+02 THC Gas concentration (ppm) - CO 3.E+0 entration (mg/m 4 E+ (0°) 3 E+0 erature 2.E+03 200 2 E+( 1.E+03 1.E+02 Aass 0.E+0 0.E+00 -1000 0 1000 2000 3000 4000 5000 -1000 0 Process Time (s)

#### Figure 4 Process Variations of PM<sub>2.5</sub> Concentration

Process variations of  $PM_{2.5}$  concentrations ( $\mu g/m3$ ) and number concentrations (particles/cc) measured by ELPI for: a) Run 3, b) Run 4, c) Run 5, and d) Run 6. (Note that PM2.5 mass concentrations in Runs 5 and 6 are approximately twice those of Runs 3 and 4, whereas PM2.5 number concentrations are similar.)



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#### PM<sub>2.5</sub> Particle Size Distribution Measured by EPLI

The average mass fractions of nine size ranges of  $PM_{2.5}$  are shown in Table 4. More than 90% of  $PM_{2.5}$  mass is in the range of 0.3–2.5 µm, and ultra fine particles (particles less than 0.1 µm in diameter) from the last 3 impactor stages comprise less than 1%. The mass fraction of ultra fine particles in  $PM_{2.5}$  is usually small when primary particles from emission sources—such as a foundry, coal power plant, or steel mill—are dominated by solid particles. However,  $PM_{2.5}$  particle number concentrations are usually higher in ultra fine particles due to their formation through nucleation of condensable species, condensational growth, and rapid coagulation. Therefore, emitted particle number concentrations are more sensitive to the process and should be examined.

Dilution Sampling	PM size range (um)								
D	0.03-	0.06-	1.08-	0.17-	0.26-	0.4-	0.65-	1.0-	1.6-
Kun	0.06	1.08	0.17	0.26	0.4	0.65	1.0	1.6	2.6
Run 3	0.0%	0.0%	0.1%	1.0%	7.9%	21.0%	28.7%	22.2%	19.3%
Run 4	0.0%	0.0%	0.2%	1.7%	9.2%	24.8%	24.8%	19.9%	19.6%
Run 5	0.0%	0.0%	0.0%	0.5%	4.9%	15.9%	26.0%	26.3%	26.3%
Run 6	0.0%	0.0%	0.1%	1.1%	7.5%	21.5%	24.0%	22.2%	23.6%

 Table 4
 Average PM<sub>2.5</sub> Mass Fraction Determined by ELPI.15

Particle size distributions in mass and number concentrations during the casting process are shown in Figures 5 and 6 for Runs 3–6. Particle size distributions are shown as:

$$ParticleConcentration = \frac{dW}{d\log(dp)}$$

Where dp is particle size, dlog (dp) is the size difference between impactor stages, and dW is the concentration (in mass or number) measured in the particle size dlog (dp). The unit in dW is particles/cm3 for number concentration and  $\mu$ g/m3 for mass concentration. All the concentrations are corrected by applying the dilution air ratio at each measurement. No effective density for particles is corrected for ELPI measurements. A 300–400 second lagging of the measurement results is adjusted for the time needed for pouring (120 seconds) and the 90-second particle aging time in the dilution sampling system.



As shown in Figures 5 and 6, the mode of  $PM_{2.5}$  mass distributions for pouring is approximately 0.6–0.7µm. When the shakeout process starts, particle mass concentrations (Figure 5) show a

bimodal distribution between 2,700 and 2,760 seconds. One of the two modes (>1.6  $\mu$ m) is likely the end of a tail of coarse particles that penetrate through the cyclone (2.5  $\mu$ m cut point) in the dilution sampling system; the other mass mode contains particles in the size range of 0.65–1.6  $\mu$ m formed by condensational growth of condensable species onto pre-existing solid particles, and coagulation. Three peaks of PM<sub>2.5</sub> particle number concentrations appear in Figures 6: 20–50 nm during pouring (0– 500 seconds), 0.2–0.6  $\mu$ m in the first peak of shakeout (2,700–2,760 seconds), and 20– 200 nm in the second peak (after 3,000 seconds) of the shakeout. The high PM<sub>2.5</sub> number concentration observed in the size range of 0.1–0.26  $\mu$ m was mostly due to the nucleation of vapor species and coagulation of which. The size of the number mode depends on the concentration of vapor species available for nucleation and coagulation.

#### PM<sub>2.5</sub> Emission Mechanisms in the Casting Process

PM emission depends on thermal processes and on the materials used in the casting process. Different PM emission characteristics observed in the pouring and shakeout processes were examined. It is hypothesized that as cast iron is poured into the mold, the heat transfers from the hot core material (~1,500°C) to the cold mold (ambient temperature 21°C), resulting in chemical reactions, vaporization, thermal decomposition, and the combustion of some organic compounds in the binder. The thermal decomposition and combustion occur where the metal and mold are in contact. Only limited organic and metal vapors are released as PM sources.

During cooling, the heat transfer process slowly reaches a balance among the metal, the mold, and the air velocity around the mold. The vaporization and thermal decomposition of the binder continue steadily, which is measured as THC, yet the majority of organic fumes are trapped within the mold. Some flame combustion might occur on the surface of the mold.

As shakeout starts, the mold physically breaks down, releasing heat and trapped organic fumes. Larger particles are re-suspended and/or particles in condensation mode are formed from 2,700–2,730 seconds through chemical reactions, and vapor species grow on the pre-existing solid particles by condensation. Therefore, two modes of  $PM_{2.5}$  mass concentration are observed: 1) the end of coarse particles, and 2) the accumulation mode of ~0.65–1.6 µm.

Concurrently, the released heat raises the stack temperature and the organic material is available for combustion. Depending on the flame condition, the organic material is consumed or combusted to carbon dioxide (CO2), CO, and some secondary organic compounds. Depending on the

vapor pressure, part of the secondary organic compounds form particles through nucleation in the dilution sampling system, so that a mode (less than  $0.3 \ \mu m$ ) of PM<sub>2.5</sub> particle number concentration is observed; part is measured as THC, along with residual organic fumes. It is noted that the decreases as the THC concentration increases as PM<sub>2.5</sub> number concentration decreases and decreases as the PM<sub>2.5</sub> number concentration increases.

#### Conclusion

Particulate emissions from casting processes were characterized in a Research Foundry at Technikon, LLC (McClellan, CA). The goal was to characterize air pollutant emissions and optimize the operating parameters of the DRI Source Dilution Sampling System for foundry gray iron casting processes. Five tests were conducted from February 26–28, 2004, including one test for pouring only and four tests for individual molds which consisted of pouring, cooling and shakeout. A dilution air ratio of 60 or higher is recommended so that PM<sub>2.5</sub> mass is not overloaded on filter sampling media. The most abundant PM<sub>2.5</sub> chemical species are total carbonaceous compounds, iron (Fe), and manganese (Mn). PM<sub>2.5</sub> emission rates and speciation profiles obtained in these tests were intended to establish a baseline for emission measurements with the particular binder and casting materials studied and should not be used for PM<sub>2.5</sub> inventory development. High variability of air pollutant emissions was observed for each mold. PM<sub>2.5</sub> mass emissions in the pouring process alone comprise 15–26% of the complete molding process. The mass fraction of ultra fine particles in PM<sub>2.5</sub> is negligible. Concentrations of PM<sub>2.5</sub> mass, CO, THC, and stack temperature increase when the pouring and shakeout processes start. For the PM<sub>2.5</sub> number concentration, a second peak was observed during the shakeout process.

The two mass modes observed in the shakeout result from the pre-existing solid particles which represent the larger size fraction, and particles ranging in size from  $0.65-1.6\mu$ m which were likely formed through chemical reactions, nucleation, and condensational growth of vapor species. A second peak of PM<sub>2.5</sub> number concentrations was found in shakeout. The PM<sub>2.5</sub> emission mechanism in the foundry process depends on flame conditions, vaporization, and thermodecomposition of organic materials, and the variability of mold breakup during shakeout can greatly affect the source paths of PM formation.

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### Acknowledgement:

This work is supported by the Casting Emission Reduction Program (CERP), the American Foundry Society (AFS), the Casting Industry Supplier Association (CISA), the U.S. Environmental Protection Agency (EPA), the California Air Resources Board (ARB), and the U.S. Army (contract DAAE30-02-C-1095).

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