Casting Emission Reduction Program

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Core Manufacturing Process Variables Study
Part III – Core Storage

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Core Manufacturing Process Variables Study
Part III – Core Storage

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 as the process parameters were varied using the equipment installed at Technikon. You may not obtain the same results in your facility. Data was not collected to assess casting quality, cost, or producibility.

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Executive Summary

The objective of this testing was to determine the emission levels from the core storage process for the CERP standard phenolic urethane (PU) binder system. Cores selected for testing during storage were gleaned from the cores made during the part 2: Core Making (Blowing) experiment while it was operating under the various parameters explored in part 2. These cores carry the process consequences of the initial standard mixing as described in Part 1: Mixing and the core making process variables as described in Part 2: Core Making (Blowing) of this three-part report. The storage cores therefore do not enter the storage part of the experiment on an equal footing. They contain only the solvents that were not removed during mixing and core making. The measurements reported in this part 3 of the three-part report describe the airborne emissions from storing cores for 90 minutes under a single standard storage measurement condition.

The core storage experiment was originally conceived to test the impact on air borne emissions of the only two parameters available during storage, those being the storage area ambient air temperature and the air flow rate over the cured core surface. During the preliminary calibration of the storage setup it was observed that the storage emission rate from a core having gone through a make cycle was so small relative to the emission rate during making (about 1-3% of the make emission rate) and that these original parameter emission variations were minimal. As a result the storage study was expanded to evaluate a standard storage cycle on the results of cores having gone through various mixing and making parameters more typical of commercial foundries.

The Core Storage measurement was conducted within a glass-lined domed enclosure meeting the criteria for a temporary total enclosure (TTE) as specified in US EPA Method 204. Four cores from each parametric Core Making condition (sand temperature, binder content, blow time, blow pressure, purge air pressure, purge air temperature, purge duration, and sand particle size) were measured during the Core Storage test. Three of the four cores were sampled for Hydrocarbon Content (HC) as Hexane. The HC as Hexane was collected on sorbent tubes during each run for subsequent laboratory analysis in accordance with an approved Wisconsin DNR method. The results of these measurements are contained in this the third and final part of this three-part report. The fourth core of each set of four was monitored using US EPA Method 25A, Total Gaseous Organic Concentration (TGOC), but was not reported due to the predominance of the triethylamine catalyst. All sampling locations were consistent with US EPA Method 1.

The average amount of HC as Hexane emissions collected for each of the process parameter conditions during the 90 minute core storage process was approximately one percent of that collected during the 30-cycle long Core Making (30-minute test period/30 cores) process for those same process conditions.

The major emissions from the PU binders were caused by the evaporation of the solvents from the resin. The Core Storage process includes only two of the three physical parameters influencing evaporation: temperature and air movement over the surface of the coated sand grains.

The core entered the Storage process with a fixed geometry and cured binder. In the storage process the air passed only over the core surface not through the core as it additionally did in the Core Making process. The apparent evaporative surface is fixed. For emissions to occur solvents must diffuse out of the binder matrix to the interstitial space between the sand grains where they evaporate and then move along inter-granular voids to the core surface where the emission occurs.

The primary emission parameters during core storage were demonstrated to be the Mean Sand Particle Size (GFN) as used in the Core Making process, the Core Making purge air temperature, the binder content used in the Core Making process, and the Core Making purge pressure. These were apparent because of their higher relative sensitivity to the process parameter and their higher confidence values.

As was learned in the Core Making section, Part 2 of this report, all the Core Making parameters except the core sand sizing parameter led to increases in emissions with increasing parameter value. Even the emissions from the sand sizing parameter would have increased if the sand size measurement had been in terms of coarseness (grain size or inter-granular void size) instead of fineness (number of holes per inch in a sieving screen). Given that sand size measuring is done as coarseness, then increases in six of the eight Core Making parameters led to decreasing emission values in the Storage process. The binder content as measured during the original Mixing and the primary driver Sand Temperature are the notable exceptions.

The implication is that for cores having the same binder content at the start of the Core Making process the increased efficiency of solvent extraction associated with the parameter increases during the Core Making left a systemic deficiency of binder content that carried over to the Storage processing step.

The binder content experiment was no exception to this extraction bias; however, the programmed binder content range during the Core Making process was larger than the change in extraction efficiency resulting from the binder content. The net result was an increase in emissions during Storage with the increasing values of the binder content parameter as originally-measured during mixing.

Similarly, the primary emission driver Sand Temperature demonstrated a net emission increase with increasing sand temperature as measured during the core blowing. The core surface temperature upon removal from the core blower was observed to increase above the temperature of the sand charged to the core blower in response to the heated purge air.

Process Event	Core Storing Regression Equation, HC Emission as Hexane Lbs. x 1000	Correlation Coefficient R^2	Relative Store Ave. Emission Change Over the Parameter Range
Sand Mean Particle Size, GFN	$Y = -0.0012X^2 + 0.212X - 6.33$	0.85	13.6
Purge Temperature, F	Y = -0.012X + 3.34	0.63	-5.8
Binder Content, %	Y = 0.92X + 0.43	0.79	5.5
Purge Pressure, psi	Y = -0.013X + 1.84	0.41	-3.6
Sand Temperature, F	Y = 0.0061X + 0.75	0.22	1.8
Blow Pressure, psi	Y = 0.007X + 1.12	0.27	1.7
Purge Time, Seconds	Y = -0.095X + 1.36	0.37	-1.5
Blow Time, Seconds	Y = -0.021X + 1.30	0.12	-1.0

The table above illustrates the relative total emissions measured during Core Storage resulting from variation of the parameters during Core Making. The table is ranked by influence and correlation confidence. The negative sign in the relative emissions column indicates a reduction in emissions with an increase in parametric value.

It must be noted that the reference and product testing performed is not suitable for use as emission factors or for purposes other than evaluating the relative emission reductions 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, and 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

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 mobile 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). Its purpose is to evaluate alternative casting materials and processes that are designed to reduce air emissions and/or produce more efficient casting processes. Other technical partners directly supporting the project include: the American Foundry Society (AFS); the Casting Industry Suppliers Association (CISA); the US Environmental Protection Agency (US EPA); and the California Air Resources Board (CARB).

1.2 CERP Objectives

The primary objective of CERP is to evaluate the impact of new materials, equipment, and processes on airborne emissions from the production of metal castings. To accomplish this objective, the Technikon facility has been created to evaluate alternate materials and production processes designed to achieve significant airborne emission reductions, especially for organic Hazardous Air Pollutants (HAPs). HAP emissions reduction from the alternative materials, equipment and production processes is expressed as a comparison to similar emissions from a baseline or reference test. The facility has two principal testing arenas: a Pre-Production Foundry designed to measure airborne emissions from individually poured molds, and a Production Foundry designed to measure air emissions in a continuous, full-scale production process. Each of these testing arenas has been specifically designed to facilitate the collection and evaluation of airborne emissions, and associated process data. Candidate materials and/or processes are screened for emission reductions in the Pre-production Foundry and then further evaluated in the Production Foundry. The data collected during the various testing projects are evaluated to determine the impact of the alternate materials and/or processes on airborne emissions as well as on the quality and economics of casting and core manufacture. These alternate materials, equipment, and processes may need to be further adapted and defined so that they will integrate into current commercial green sand casting facilities smoothly and with minimal capital expenditure.

Pre-production testing is conducted in order to evaluate the impact on air emissions from a proposed alternative material, equipment or process. The Pre-Production Foundry is a simple, general-purpose manual foundry, which was adapted and instrumented to allow the collection of detailed emission measurements, using methods based on US EPA air testing protocols. Measurements are taken during pouring, casting cooling, and shakeout processes performed on discrete mold and core packages under tightly controlled conditions not feasible in a commercial foundry. The Pre-production foundry uses an eight-on, bottom-feed AFS step block as its test mold pattern. A report entitled Baseline Testing Emission Results – Pre-Production Foundry provides details of the baseline testing done in the Pre-Production Foundry. This report can be obtained from the Technikon web site at www.technikonllc.com.

Alternative materials, equipment and processes that, during their testing in the Pre-Production Foundry, demonstrate significant air emission reduction potential and preserve casting quality parameters are further evaluated in the Production Foundry. The Production Foundry's design as a basic green sand foundry was deliberately chosen so that whatever is tested in this facility could be easily converted for use in existing mechanized commercial foundries. The Production Foundry emulates an automotive foundry in the type and size of equipment, materials, and processes used. A single cavity automotive I-4 engine block mold is used to further evaluate materials, equipment, and processes in a continuous real-world production-like environment. The Production Foundry provides simultaneous, detailed, individual emission measurements, according to methods based on US EPA air testing protocols, of the melting, pouring, sand preparation, mold making, and core making processes. The Production Foundry is instrumented so that process data on all activities of the metal casting process can be simultaneously and continuously collected in order to complete an economic impact evaluation of the prospective emission reducing strategy. Castings are randomly selected to evaluate the impact of the alternate material, equipment, or process on the quality of the casting.

Test results for a particular process or product may not be the same from both foundries due to differences in the testing process. The Pre-production Foundry is designed to screen new products, processes, or equipment, whereas the Production Foundry is designed to test the effect of the product, process, or equipment in a continuous production-like environment.

The results of the testing conducted at both the Production and Pre-production Foundries are not suitable for use as general emission factors. The specific materials used (gray iron from an electric melt furnace, greensand with seacoal, and a cold box core with a relatively old resin binding system); the specific castings produced (an eight-on step block in the Pre-production Foundry and an I-4 automotive block in the Production Foundry); the specific production processes employed (a stationary hand-poured mold in the Pre-production Foundry and an impact mold line in the Production Foundry); and the specific testing conditions (relatively low stack velocity, long sampling times, high capture rates, and combined emissions from pouring, cooling and shakeout processes at the Production Foundry) produce emission results unique to the materials, castings, casting processes and measurement conditions used. The data produced are intended to demonstrate the relative emission reductions from the use of alternative materials, equipment and processes, and not the absolute emission levels that would be experienced in commercial foundries. A number of process parameters such as casting surface area, sand to metal ratios, pouring temperatures, stack flow rates, LOI levels, seacoal and resin contents, and the type of foundry (Cope & Drag versus Disa for example) can have a significant impact on actual emission levels.

The Production Foundry provides simultaneous detailed individual emission measurements using methods based on US EPA protocols for the melting, pouring, sand preparation, mold making, and core making processes. The core making area of the Production foundry contains three core blowers, a Georg Fischer for the preparation of automotive block cores, a Redford that is used for the production of step cores, and a second smaller Redford to produce dogbone tensile test specimens.

1.3 Report Organization

This report has been designed to document the methodology and results of a specific test plan that was used to evaluate the variability of emissions from the core mixing, making and storage process. Separate reports will be issued to document the same information from the Core Making and Mixing processes. Section 2 of this report includes a summary of the methodologies used for data collection and analysis, emission calculations, QA/QC procedures, and data management and reduction methods. Section 3 presents the results of this experimentation. Section 4 of this report contains a discussion of the results.

The raw data for this test series are included in a data binder that is maintained at the Technikon facility.

1.4 Specific Test Plan and Objectives

This Part III report contains the results of testing performed to provide data on selected emissions from the core storage processes. Core sand mixing and core making results are reported in Parts I and II of this study. The table below provides a summary of the test plan for Test EU. The details of the approved test plan are included in Appendix A.

Test Plan Summary

	Test EU
Type of Process Tested	Core Sand: Part I - Mixing Part II - Core Making (Blowing) Part III - Core Storage
Test Plan Number	1409 – 131
Binder System	Phenolic Urethane Cold Box Ashland Isocure® 905/304
Number of Tests	13 at Core Mixing (Part I); 51 at Core Making (Part II); 51 at Core Storage (Part III)
Test Dates	11/13/02 through 1/22/03
Emissions Measured	TGOC as Propane (Part I), HC as Hexane (Parts II & III)
Process Parameters Measured	Process Sand Weight; Sand and Ambient Air Temperature; Binder Concentration; Mixer Cycle Time, Loading, Speed, & Ventilation; Core Blower Cycle Time and Blow & Purge Air Pressure, Air Temperature, & Duration.
Source Parameters Measured	Mixer, Core Blower Enclosure, & Storage Enclosure Exhaust Duct Temperature, Pressure and Volumetric Flow Rate

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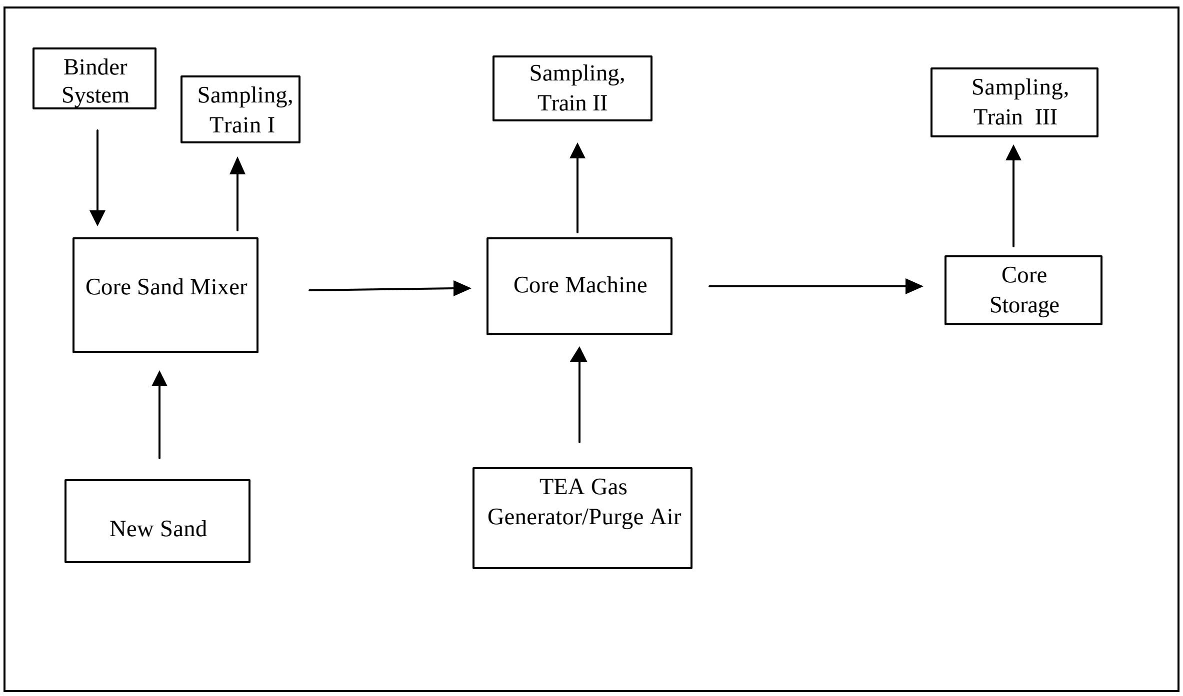
2.0 Test Methodology

2.1 Description of Process and Testing Equipment

Figure 2-1 is a diagram of the Phenolic Urethane Cold box core making process and testing equipment.

Figure 2-1 Core Making and Testing Process



2.2 Description of Testing Program

The specific steps used in this sampling program are summarized below:

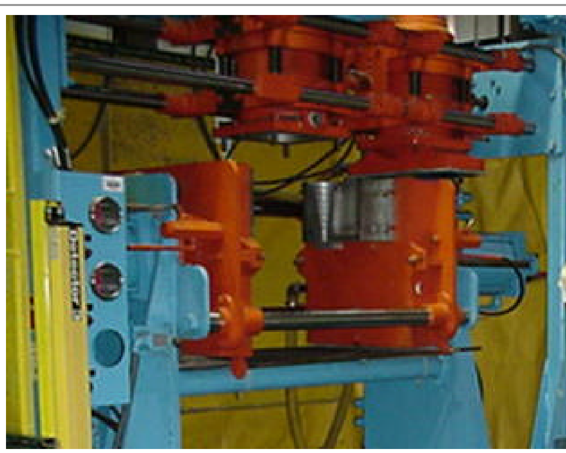
1. **<u>Test Plan Review and Approval:</u>** The proposed test plan was reviewed by the Technikon staff and the CERP Steering Committee, and approved.

2. **Sand Preparation:** Sands are mixed with quantities of designated binders in a covered 50-pound capacity paddle type cylindrical mixer qualifying as a temporary total enclosure, meeting US EPA Method 204 criteria. The sand is preheated or cooled as required to a standard temperature range. The mixer is continuously bathed in temperature-controlled air to maintain the process temperature. Weighted sand and binder components are introduced via an openable window in the cover and mixed for a designated period of time, then discharged. The cycle time is determined to maintain continuous mixing activity while providing a balanced supply of sand to the core making operation.


Sand Mixing
Enclosure not shown

3. **Core Preparation:** Step cores were prepared for this test in the Production foundry core room area. The sand and binder were mixed and then introduced (blown) into the core tooling of the Redford-Carver core machine. The core-making machine was contained in a permanent total enclosure meeting US EPA Method 204 criteria. An aliquot of the catalyst triethylamine (TEA) gas was heated to 84^{o}F and allowed to expand into the piping leading to the core box. Finally, purge air, heated to 80^{o}F, pushed the catalyst into the sand in the core box to cure the core, and then flushed the catalyst from the core. All these gases were exhausted to a wet gas scrubber charged with sulfuric acid at pH 2 or less. Step cores were fabricated in a single cavity core box. One blow produces a single step core.

4. **Individual Sampling Events:** During the production of step cores, air samples were collected to determine the amount of solvent vented off of the core process. The samples were collected after the background had stabilized during each of the thirty (30) core runs that comprised this portion of the test.


Core Making
Enclosure not shown


Core Storage

The storage segment of the test consisted of placing four (4) cores in the individual storage flow-through sampling enclosures as soon as they were removed from the core machine. Replacement air was allowed to enter under the lower edge of the enclosure through a regulated annular gap to replace the sample air extracted from the top. A ninety (90) minute integrated sample was collected. All of the enclosures used during this test meet or exceed US-EPA Method 204 criteria for Temporary Total Enclosures.

5. **Parameter Measurements:** Table 2-1 lists the process parameters that are monitored during each test. The analytical equipment and methods used are also listed.

Table 2-1 Process Parameters Measured

Parameter	Analytical Equipment and Methods
Binder Weight (mixing)	Mettler PJ8000 Digital Scale (Gravimetric)
Core Sand Weight (mixing)	Simpson IQ-800-3A Digital Scale
Sand Temperature (mixing)	Stem type dial thermometer & thermocouple
Sand Temperature (blowing)	Thermocouple
Cycle Time	Digital elapsed time clocks
Purge & Blow Air Temperature	Thermocouple
Purge & Blow Air Pressure	Digital & analog pressure gauges
Enclosure Air Temperature	Thermocouple
TEA Weight	Mettler PB302 Scale (310 gm)
Step Core Weight	OHAUS 110# digital platform scale

6. **Air Emissions Analysis:** The specific sampling and analytical methods used in the core sand mixing, making, and core storage tests are based on the US EPA reference methods shown in Table 2-2. The details of the specific testing procedures and their variance from the reference methods, if any, are included in the Technikon Standard Operating Procedures.

Table 2-2 Sampling and Analytical Methods

Measurement Parameter	Test Method*
Port location	EPA Method 1
Number of traverse points	EPA Method 1
Gas velocity and temperature	EPA Method 2
HC as Hexane	NIOSH 1500
TGOC (THC) as Propane	EPA Method 25A

* These methods were specifically modified to meet the testing objectives of the CERP Program.

7. **Data Reduction, Tabulation and Preliminary Report Preparation:** The analytical results of the emissions tests provide the mass of each analyte in the sample. For the core-storage segment of the test, the total mass of the analyte emitted is calculated by multiplying the mass of analyte in the sample times the ratio of the sample volume to the total stack gas volume during the test. The total stack gas volume was calculated from measured stack gas velocity and duct diameter. The total mass of analyte was then related to the varied process parameters.

   In the case of the core storage segment of this test, the stack parameters are replaced by the total volume of gas flowing through the storage enclosure during each sampling period. The total flow rate through the enclosure was controlled with critical orifices. The total mass of the analyte emitted is then calculated by multiplying the measured mass of analyte in the sample times the ratio of sample volume to total gas volume over the same time period as measured by a BIOS Dry Cal Model DC – d1B (DC – HC – 1) flow meter. Again the total mass of analyte was related to the varied process parameter.

8. **Report Preparation and Review:** The Preliminary Draft Report is reviewed by the Manager, Process Engineering, and the Emissions Team to ensure its completeness, consistency with the test plan, and adherence to the prescribed QA/QC procedures. Appropriate observations, conclusions and recommendations are added to the report to produce a Draft Report. The Draft Report is reviewed by the Vice President-Measurement Technologies, the Vice President-Operations. Comments are incorporated into a Final Report prior to final signature approval and distribution.

2.3 Quality Assurance and Quality Control (QA/QC) Procedures

Detailed QA/QC and data validation procedures for the process parameters, stack measurements, and laboratory analytical procedures are included in the Technikon Standard Operating Procedures. In order to ensure the timely review of critical quality control parameters, the following procedures are followed:

- Immediately following the individual sampling events performed for each test, specific process parameters are reviewed by the Manager - Process Engineering to ensure that the parameters are maintained within the prescribed control ranges. Where data are not within the prescribed ranges, the Manager - Process Engineering and the Vice President-Operations determine whether the individual test samples should be invalidated or flagged for further analysis following review of the laboratory data.

- The source (stack) and sampling parameters, analytical results and corresponding laboratory QA/QC data are reviewed by the Emissions Measurement Team to confirm the validity of the data. The VP-Measurement Technologies reviews and approves the recommendation, if any, that individual sample data should be invalidated. Invalidated data are not used in subsequent calculations.

3.0 Test Results

Table 3-1: Weight of emissions as Hexane recovered from 90 minute core storage process.

Figure3-1 shows the variation in emissions as Hexane derived from silica sands that have mean particle sizes (GFN) of 50, 70, & 90 equivalent US sieve sizes.

Figure 3-2 shows the variation in emissions as Hexane derived from Lake sand cores blown at 2, 5, & 8 seconds.

Figure 3-3 shows the variation in emissions as Hexane derived from Lakesand cores made with sands at 63, 82 & 100 degrees Fahrenheit.

Figure 3-4 shows the variation in emissions as Hexane derived from Lakesand cores containing 1.00 & 1.75 % Phenolic Urethane binder.

Figure 3-5 shows the variation in emissions as Hexane derived from Lakesand cores made with the purge temperature varied from 171 to 232 degrees Fahrenheit.

Figure 3-6 shows the variation in emissions as Hexane derived from Lakesand cores made as the purge pressure was varied from 22 to 57 psi.

Figure 3-7 shows the variation in emissions as Hexane derived from Lakesand core made as the purge time was varied from10 to 30 seconds.

Figure 3-8 shows the variation in emissions as Hexane derived from Lakesand cores made as the blow pressure was varied from 15 to 45 psi.

Table 3-2 Process Regression Equations and Relative Impact on Emissions

Table 3-1 Weight of Emissions as Hexane Recovered from 90 Minute Cycle Core Storage Process

Core Making Parameter	Parameter Value	Emission Weight Recovered as Hexane, pounds
Sand Mean Particle Size, GFN	50	0.0012
	70	0.0025
	95	0.0028
Blow Time, Sec	2	0.0012
	5	0.0012
	8	0.0011
Sand Temperature, F	63	0.0012
	82	0.0012
	100	0.0014
Binder Content, %(BOS)	1.00	0.0014
	1.75	0.0023
Purge Temperature, F	171	0.0015
	181	0.0012
	201	0.0006
	232	0.0009
Purge Pressure, Psi	22	0.0017
	32	0.0012
	57	0.0012
Purge Time, Sec	10	0.0018
	20	0.0012
	30	0.0011
Blow Pressure	15	0.0013
	32	0.0012
	45	0.0015

Note: Parameter values are those of the core make process that produced cores for the core storage.

Figure 3-1 Total Emissions from Storage vs. Sand Particle Size

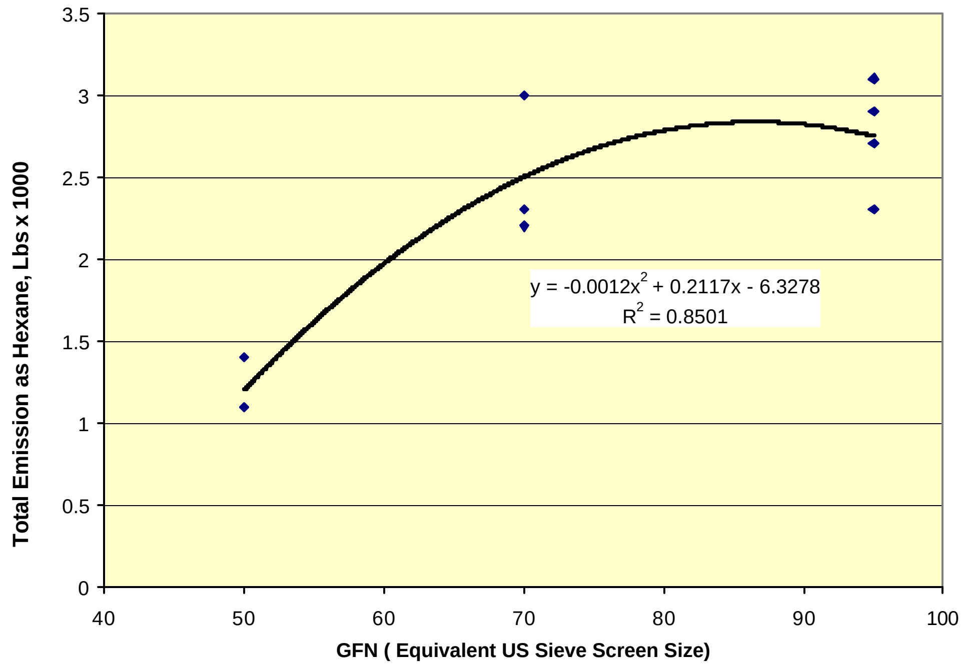


Figure 3-2 Total Emissions from Storage vs. Blow Time during Core Making

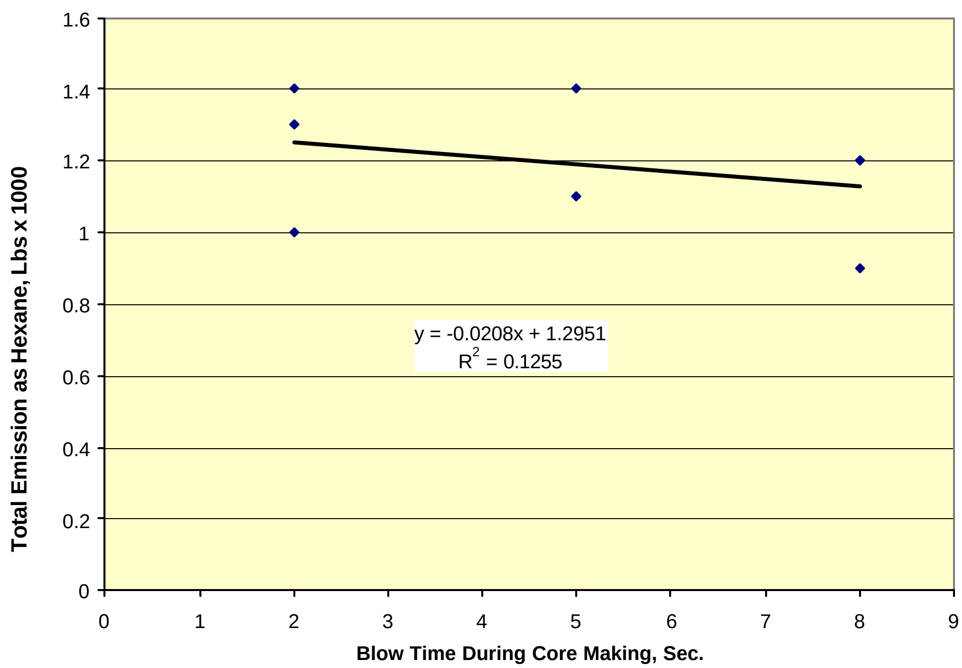


Figure 3-3 Total Emission from Storage vs. Sand Temperature during Core Making

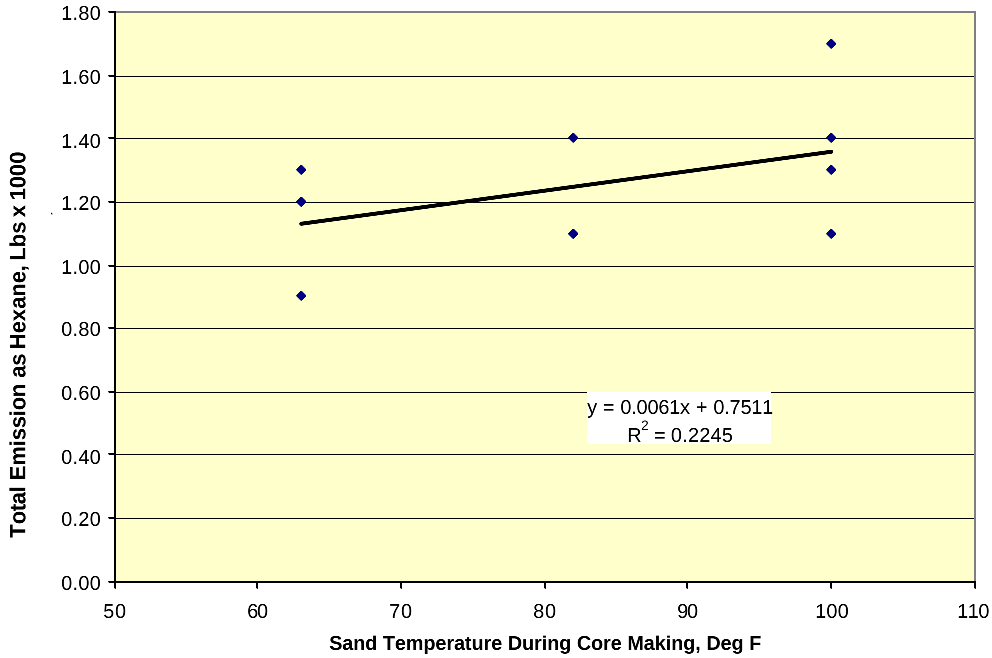


Figure 3-4 Total Emission from Storage vs. Binder Content

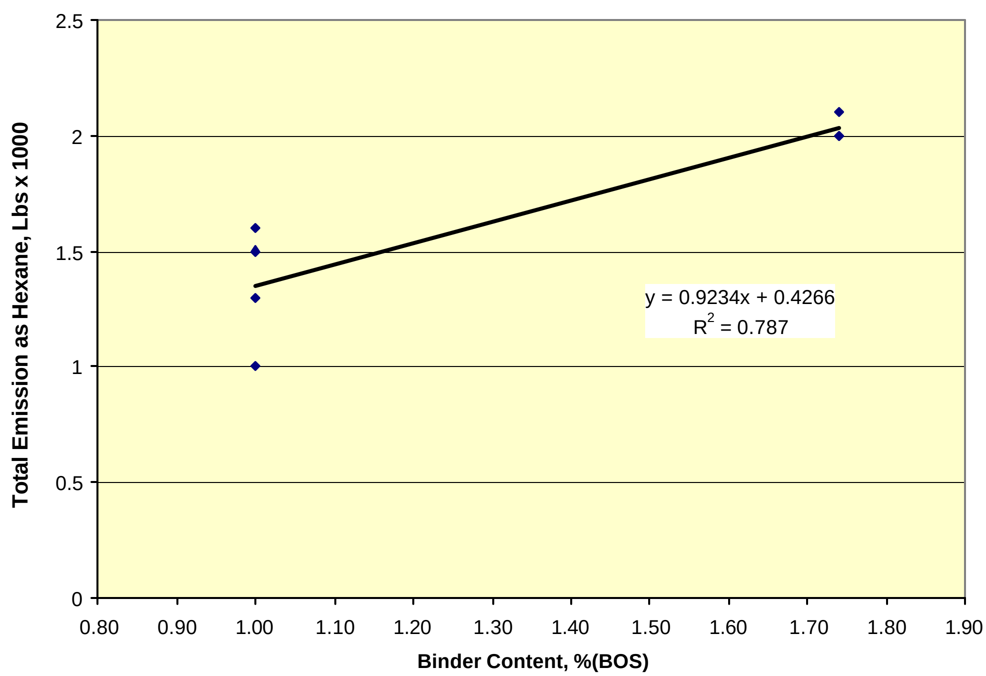


Figure 3-5 Total Emissions from Storage vs. Purge Air Temperature during Core Making

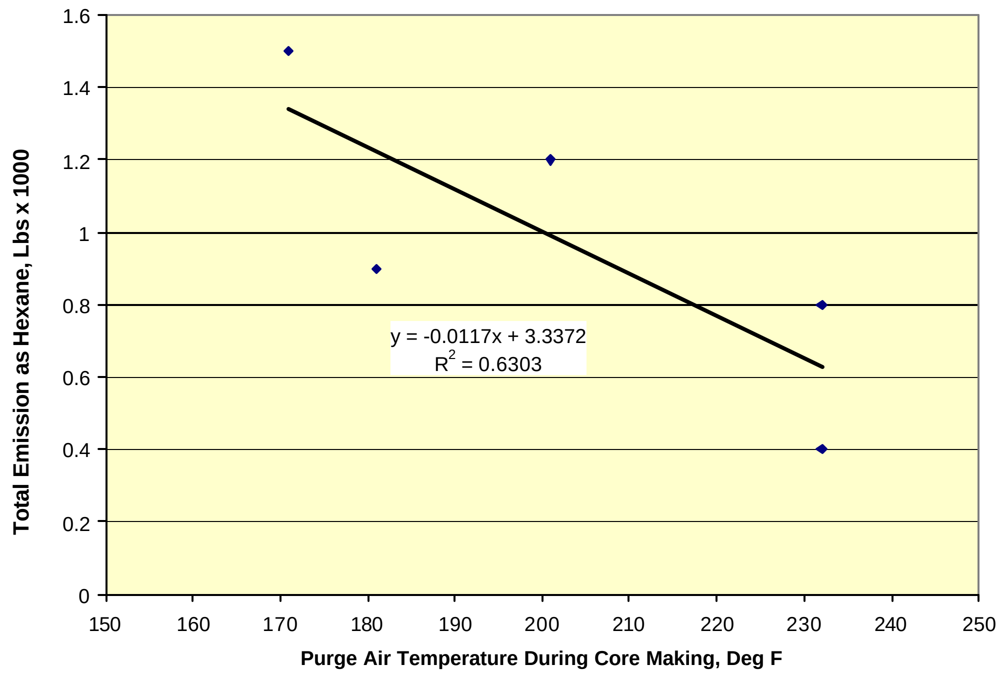


Figure 3-6 Total Emission from Storage vs. Purge Pressure during Core Making

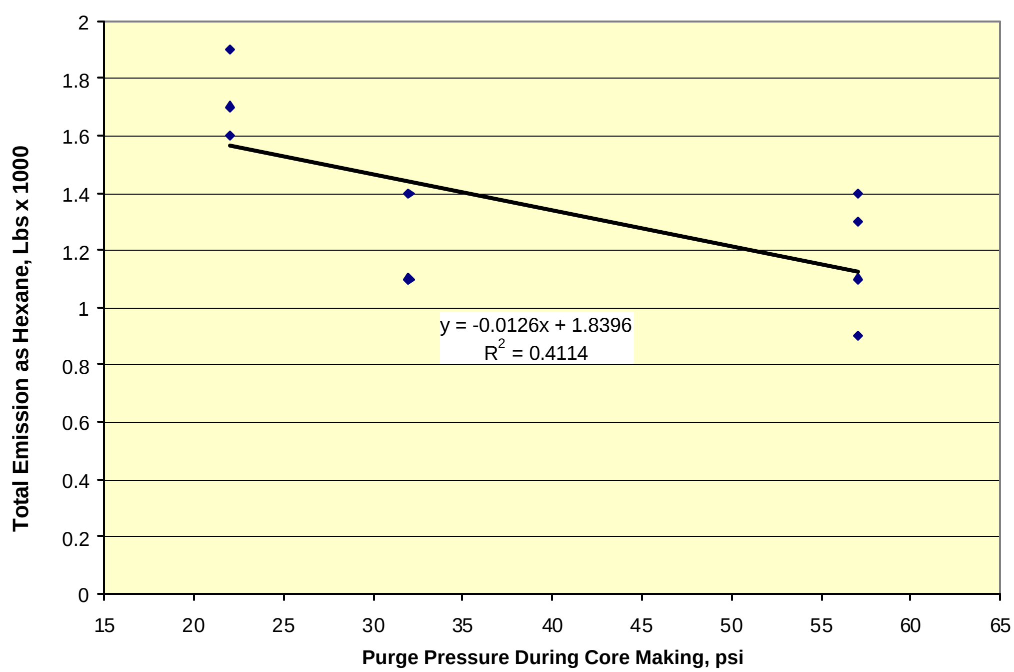


Figure 3-7 Total Emissions from Storage vs. Purge Duration during Core Making

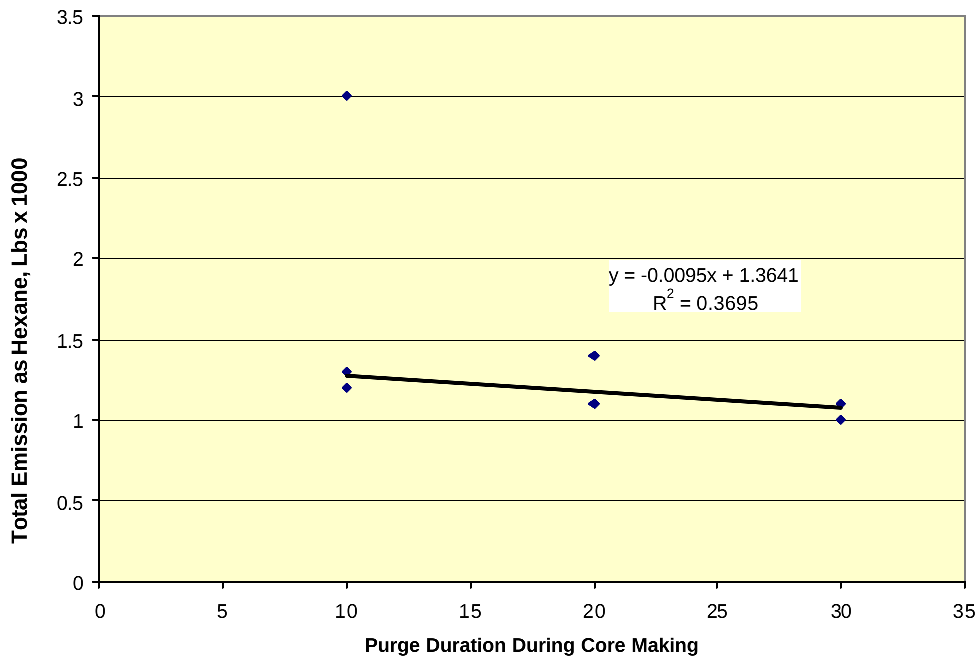


Figure 3-8 Total Emissions from Storage vs. Blow Pressure During Core Making

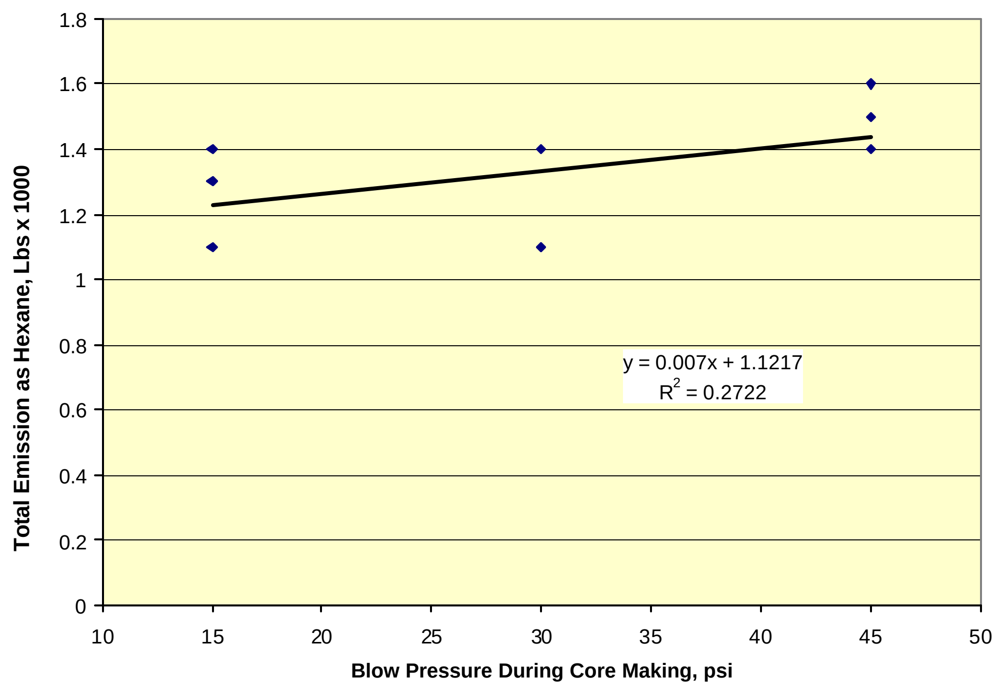


Table 3-2 Process Regression Equations and Relative Impact on Emissions

Process Event	Core Storing Regression Equation, HC Emission as Hexane Lbs. x 1000	Correlation Coefficient R^2	Parameter Range		Calculated Emission Lbs x 1000		Emission Range for Parameter Range Lbs. x 1000	Relative Emission Change Over the Parameter Range
			Low	High	Low	High		
Sand Mean Particle Size, GFN	$Y = -0.0012X^2 + 0.212X - 6.33$	0.85	50	95	1.27	2.98	1.71	13.6
Purge Temperature, F	Y = -0.012X + 3.34	0.63	171	232	1.29	0.56	-0.73	-5.8
Binder Content, %	Y = 0.92X + 0.43	0.79	1.00	1.75	1.35	2.04	0.69	5.5
Purge Pressure, psi	Y = -0.013X + 1.84	0.41	22	57	1.55	1.10	-0.46	-3.6
Sand Temperature, F	Y = 0.0061X + 0.75	0.22	63	100	1.13	1.36	0.23	1.8
Blow Pressure, psi	Y = 0.007X + 1.12	0.27	15	45	1.23	1.44	0.21	1.7
Purge Time, Seconds	Y = -0.095X + 1.36	0.37	10	30	1.27	1.08	-0.19	-1.5
Blow Time, Seconds	Y = -0.021X + 1.30	0.12	2	8	1.26	1.13	-0.13	-1.0

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4.0 Discussion of Results

The objective of this testing was to determine the emission levels from the core storage process for the CERP standard phenolic urethane (PU) binder system.

Hydrocarbon emissions as hexane based on an approved Wisconsin method were measured during core storage activities associated with the use of a phenolic urethane binder system in the Technikon research and development core production facility. All of the core-storage measurements were conducted within enclosures meeting the criteria for a temporary total enclosure according to US EPA Method 204. Results in this report are expressed in pounds.

The HC as Hexane represents the sum of all compounds that elute from a gas chromatograph between the retention times of hexane and hexadecane. The emission mechanism is principally sand surface evaporation from the core surface

Cores selected for testing during storage were gleaned from the cores made during the part 2: Core Making (Blowing) experiment while it was operating under the various parameters explored in part 2. Test cores were made in a Redford/Carver Model CB22 vertical core machine. The test piece was a standard 1-on, 7.25 pound, AFS step core. The standard process was as follows with each parameter varied one at a time from this standard method.

Sand Type:	50 GFN 4 screen Lakesand
Binder content:	1.0% (BOS) of Ashland Isocure® 905/304 binder mixed in a 55/45 ratio of part I/ part II
Mixing Time:	7 minutes
Sand Temperature:	80^{o}F
Blow Time:	5 seconds
Blow Pressure:	30 psi
Purge Time:	20 seconds
Purge Pressure:	45 psi
Purge Temperature:	176^{o}F

The core-make tests and the core-storage tests were run at the same time. Each core for the core-storage test was selected from those cores being tested for core-making. Storage test cores were selected from each core-make test parameter. The transfer time from the core-make test to the core storage test was less than 5 seconds. These cores carry the process consequences of the initial seven (7) minute mixing as described in Part 1: Mixing and the core making process variables as described in Part 2: Core Making (Blowing) of this three part report. They contain only the solvents that were not removed during mixing and core making. The measurements reported in this part 3 of the three part report describe the airborne emissions from storing cores having been produced under various core make conditions for 90 minutes under a single standard condition.

The core storage was conducted within a glass lined domed enclosure meeting the criteria for a temporary total enclosure (TTE) as specified in US EPA Method 204. Four cores from each parametric Core Making condition (sand temperature, binder content, blow time, blow pressure, purge air pressure, purge air temperature, purge duration, and sand particle size) were measured during the Core Storage test. Three of the four cores were sampled for Hydrocarbon Content (HC) as Hexane. The HC as Hexane was collected on sorbent tubes during each run for subsequent laboratory analysis in accordance with an approved Wisconsin DNR method. The results of these measurements are contained in this the third and final part of this three part report. The fourth core of each set of four was monitored using US EPA Method 25A, Total Gaseous Organic Concentration (TGOC), but was not reported due to the predominance of the triethylamine catalyst. All sampling locations were consistent with US EPA Method 1.

The average HC as Hexane emissions collected for each the process parameter variations during the 90 minute storage was approximately one percent of that collected during the 30-cycle core make process for those same process parameter variations.

The major emissions from the PU binders were caused by the evaporation of the solvents from the resin. The Core Storage process includes only two of the three physical parameters influencing evaporation: temperature and air movement over the surface of the coated sand grains.

The core entered the Storage process with a fixed geometry and cured binder. In the storage process the air passed only over the core surface not through the core as it additionally did in the Core Making process. The apparent evaporative surface is fixed. For emissions to evaporate the solvents must diffuse out of the binder matrix where they evaporate, and then move along intergranular voids to the core surface where the emission occurs.

The primary emission parameters during core storage were demonstrated to be the Mean Sand Particle Size (GFN) as used in the Core Making process, the Core Making purge air temperature, the binder content used in the Core Making process, and possibly the Core Making purge pressure. These stuck out because of their higher relative sensitivity to the process parameter and their higher confidence values.

As was learned in the Core Making section, Part 2 of this report, all the Core Making parameters except the core sand sizing parameter led to increases in emissions with increasing parameter value. Even the emissions from the sand sizing parameter would increase if the sand size measurement were in terms of coarseness (grain size or inter-granular void size) instead of fineness (number of holes per inch in a sieving screen). Given that sand size measuring is done as coarseness, then increases in six of the eight Core Making parameters led to decreasing emission values in the Storage process. The Binder Content as measured during the original Mixing and the primary driver Sand Temperature are the notable exceptions.

The implication is that for cores having the same binder content at the start of the Core Making process the increased efficiency of solvent extraction associated with the parameter increases during the Core Making left a systemic deficiency of binder content that carried over to the Storage processing step.

The binder content experiment was no exception to this extraction bias; however, the programmed binder content range during the Core Making process was larger than the change in extraction efficiency resulting from the binder content. The net result was an increase in emissions during Storage with the increasing values of the binder content parameter as originally measured during mixing.

Similarly the primary emission driver temperature demonstrated a net emission increase with increasing sand temperature as measured during the core blowing. The core surface temperature upon removal from the core blower was observed to increase above the temperature of the sand charged to the core blower in response to the heated purge air.

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APPENDIX A APPROVED TEST PLAN FOR TEST EU

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TECHNIKON TEST PLAN

- > **CONTRACT NUMBER:** 1409 **TASK NUMBER:** 1.3.1
- > **WORK ORDER NUMBER:** 1169 **Series:** EU
- > **SAMPLE EVENTS:** 8 TGOC preliminary,9 mix, 51 make , 17 store TGOC & tubes
- > **SITE: ___PRE-PRODUCTION (243) _X__ FOUNDRY (238)**
- > **TEST TYPE:** Core mixing, core making, core storage. Process variables study.
- > **METAL TYPE:** None
- > **MOLD TYPE:** None
- > **NUMBER OF TESTS:** 5 Preliminary, 9 core sand mixing, 17 core-making with scratch hardness, 17 core storage, all in triplicate.
- > **CORE TYPE:** AFS Step Core, Ashland ISOCURE® 305/904 phenolic urethane binder at 1.0% and 1.4% and 1.75% total resin, 55% Part I, 45% part II, TEA gas catalyzed.
- > **TEST DATE:** **START:** 4 Nov 2002
  FINISHED: 12 Dec 2002

TEST OBJECTIVES:

1. Measure VOCs and HAPs from Core Mixing, Core Making & Core Storage by the methods established in the **Core Mix, Make, & Store Baseline 2002** from a regiment of tests in each venue which explore the range of process variation normally encountered in commercial foundry practice.

VARIABLES:

1. **Preliminary Tests**: The first tests will include a battery to outline the process sensitivity to the operating environment and define a stable region of testing. This series will include heat gain from gear and sand friction, emission sampling rate, environmental temperature, and mixer fullness for each condition.

2. **Core Sand Mixing:** The Mixing parameters will include sand GFN, sand temperature, binder concentration, and mixing speed. The reference uncoated sand shall be Wexford W450 Lakesand. It shall be preheated or cooled to a reference temperature of 80 +/-2 degrees Fahrenheit. The reference binder concentration shall be 1.4 +/-0.014% Ashland ISOCURE® 305/904 mixed Part I/Part II in the ratio of 55/45. The sand will be coated in a Redford/Carver 50 pound core sand mixer for 7 minutes. One minute shall be used to

dispense the sand and the two binder components and one additional minute shall be used strictly for discharging the mixer. Each core sand-mixing test shall be three (3) seven (7)-minute 50 pound cycles, monitored continuously by TGOC and adsorption tubes. Prior to the first mixing test five (5) batches shall be run to normalize the background within the muller. Sampling media will be changed after each three-cycle test during which time mixing will continue in order to maintain the background concentration. A total of three (3) mixing cycles shall be run at each of 3 parameter levels for each variable.

3. **Core Making:** The Make tests will each include effects of sand temperature, binder content, blow time, blow pressure, purge pressure, purge air temperature, purge duration, & sand GFN with sand mixed to a standard duration, sand temperature, binder content, and/or ambient (enclosure) air temperature as called out in the attached test plan tables. Make tests will include scratch hardness testing at 2 hours age The Redford/Carver core machine will operate on a nominal one (1) minute door-to-door cycle. The environmental enclosure shall be supplied with air controlled to 82 +/- 5 degrees Fahrenheit. TEA will be fed to the core machine at a nominal 5 grams per cycle. The reference purge pressure shall be 45+/-2 psi for 20 seconds. Reference blow pressure shall be 30 psi. The core-make test will begin after the core machine has run sufficient time, at rate, to have the background emission concentration stabilize. Each core-make test will be 30 core cycles, about one half hour long, with continuous TGOC and adsorption tube sampling. Sample media will be changed after each 30 cycle test. The core machine will run continuously during media change and testing to maintain the background concentration. The gas & purge and fugitive emissions will be collected to a common sampling stack. Each core will be weighed.

4. **Core Storage**: The storage test will consist of weighed cores sequentially sampled, four (4) in a group, from the core machine during the make test and placed in individual sampling domes. The domes are in a temperature controlled room at 82+/-5 degrees Fahrenheit and sampled continuously with TGOC and adsorption tubes for 1.5 hours.

BRIEF OVERVIEW:

Core making is not a single process but rather a series of steps each with its own process collectable and fugitive emissions. This test will look at selected HAP & VOC emissions from combined process collectable and fugitive emission streams during each of the core sand mixing, core making, and core storage steps. Each step will have a series of parameters varied per the attached test plan tables while all other controllable parameters are held in reference value ranges.

SPECIAL CONDITIONS:

The sand mixer will have a removable lid that allows air to infiltrate radially from the perimeter. Materials will be charged though a closeable door in the lid. Samples will be extracted from the center of the headspace below the lid. The mixer shall be surrounded on 4 sides with an insulating wall that extends 3 inches above the mixer to reduce room ambient influences. The enclosure shall be flooded with air controlled to the reference temperature range. The emission samples shall be extracted at a reference rate.

The core machine with step core tooling shall be housed in a double walled emission enclosure. The area between the walls shall be flushed with temperature controlled air at 82+/-5 degrees Fahrenheit. This air shall be the ambient make up air for the core process within the enclosure. The core box and core machine shall be tightly plumbed to extract gasses passed through the core box into a common sampling stack with the fugitive gasses. The sampling environment will be maintained at 75-85^{o}F. Core storage will be individual cores tested under individual glass domes in groups of four (4) cores for a period of 1.5 hours. The environment will be totally captured. One dome will be monitored by TGOC.

Process Engineering Manager (Technikon)	Date
V.P. Measurement Technology (Technikon)	Date
V.P. Operations (Technikon)	Date
Test Design Committee Representative	Date
Emission Committee Representative	Date

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APPENDIX B SUMMARY TABLES FOR CHART DATA

EU Core Make & Store Process Variables Summary (page 1)

Test No.	Test Date	Test Purpose	Make Sample No.	Make Emission Weight Lbs x 10	Store Sample No.	Store Emission Weight Lbs. x 1000	Sand Type	Sand Weight Lbs	Sand Temp F	Binder Content % (BOS)	Ambient Fdry Air Temp F	Probe Air Temp F	Blow Time Sec.	Blow Press psi	Purge Air Press psi	Purge Air Temp F	Purge Air Duration Sec.
Mk2a1	11/26/02	Emission vs low sand temp	EU201	2.721	EU301	1.3	W450	50	63	0.98	66	80	5	30	45	176	20
Mk2a2	11/26/02	Emission vs low sand temp	EU202	2.620	EU302	1.2	W450	50	63	0.98	66	80	5	30	45	176	20
Mk2a3	11/26/02	Emission vs low sand temp	NA	NA	Dup	0.9	W450	50	63	0.98	66	80	5	30	45	176	20
Mk2a3	11/26/02	Emission vs low sand temp	EU203	2.685	EU303	1.2	W450	50	63	0.98	66	80	5	30	45	176	20
MK2b1	11/26/02	Emission vs mid sand temp	EU204	2.877	EU304	1.4	W450	50	82	0.98	68	83	5	30	45	176	20
MK2b1	11/26/02	Emission vs mid sand temp	EU205	2.809	EU305	1.1	W450	50	82	0.98	69	83	5	30	45	176	20
MK2b2	11/26/02	Emission vs mid sand temp	Dup	2.724	NA	NA	W450	50	82	0.98	69	83	5	30	45	176	20
MK2b3	11/26/02	Emission vs mid sand temp	EU206	2.921	EU306	1.1	W450	50	82	0.98	69	83	5	30	45	176	20
MK2c1	11/26/02	Emission vs high Sand temp	EU207	2.821	EU307	1.3	W450	50	100	0.98	69	80	5	30	45	176	20
MK2c2	11/26/02	Emission vs high Sand temp	NA	NA	Dup	1.1	W450	50	100	0.98	69	80	5	30	45	176	20
MK2c2	11/26/02	Emission vs high Sand temp	EU208	2.877	EU308	1.4	W450	50	100	0.98	69	80	5	30	45	176	20
MK2c3	11/26/02	Emission vs high Sand temp	EU209	3.050	EU309	1.7	W450	50	100	0.98	70	80	5	30	45	176	20
MK1a1	12/02/02	Emission vs Lo% binder	EU210	2.615	EU310	1.6	W450	50	82	1.00	64	84	5	30	45	176	20
MK1a2	12/02/02	Emission vs Lo% binder	EU211	2.659	EU311	1.5	W450	50	80	1.00	64	84	5	30	45	176	20
MK1a2	12/02/02	Emission vs Lo% binder	NA	NA	Dup	1.0	W450	50	80	1.00	64	84	5	30	45	176	20
MK1a3	12/02/02	Emission vs Lo% binder	EU212	2.627	EU312	1.3	W450	50	83	1.00	65	84	5	30	45	176	20
MK1b1	12/02/02	Emission vs Hi% binder	EU213	2.643	EU313	2.0	W450	50	82	1.74	65	84	5	30	45	176	20
MK1b2	12/02/02	Emission vs Hi% binder	EU214	2.695	EU314	2.1	W450	50	83	1.74	66	84	5	30	45	176	20
MK1b3	12/02/02	Emission vs Hi% binder	EU215	2.870	EU315	2.0	W450	50	83	1.74	67	84	5	30	45	176	20
MK3a1	12/03/02	Emission vs Mid Blow time	EU216	2.413	EU316	1.4	W450	50	80	0.98	70	84	2	32	45	176	20
MK3a1	12/03/02	Emission vs Mid Blow time	NA	NA	Dup	1.0	W450	50	80	0.98	70	84	2	32	45	176	20
MK3a2	12/03/02	Emission vs Mid Blow time	EU217	2.552	EU317	1.3	W450	50	79	0.98	70	84	2	32	45	1.76	20
MK3a3	12/03/02	Emission vs Mid Blow time	EU218	2.619	EU318	1.3	W450	50	82	0.98	71	84	2	32	45	1.76	20
MK3b1	12/6/02	Emission vs hi Blow time	EU219	2.595	EU319	1.2	W450	50	83	0.98	62	82	8	32	45	176	20
MK3b2	12/6/02	Emission vs hi Blow time	EU220	2.495	EU320	1.2	W450	50	80	0.98	63	82	8	32	45	176	20
Mk3b2	12/6/02	Emission vs hi Blow time	Dup	2.797	Dup	0.9	W450	50	80	0.98	63	82	8	32	45	176	20
MK3b3	12/6/02	Emission vs hi Blow time	EU221	3.003	EU321	1.2	W450	50	82	0.98	64	82	8	32	45	176	20
MK4a1	12/3/02	Emission vs mid blow pres	EU222	2.687	EU322	1.4	W450	50	80	0.98	63	81	5	15	45	176	20
MK4a2	12/3/02	Emission vs mid blow pres	EU223	2.584	EU323	1.3	W450	50	79	0.98	64	81	5	15	45	176	20
MK4a3	12/3/02	Emission vs mid blow pres	EU224	2.861	EU324	1.3	W450	50	83	0.98	65	81	5	15	45	176	20
MK4a3	12/3/02	Emission vs mid blow pres	NA	NA	Dup	1.1	W450	50	83	0.98	65	81	5	15	45	176	20
MK4b1	12/3/02	Emission vs hi blow pres	EU225	2.714	EU325	1.6	W450	50	80	0.98	66	82	5	45	45	176	20
MK4b1	12/3/02	Emission vs hi blow pres	Dup	2.822	NA	NA	W450	50	80	0.98	66	82	5	45	45	176	20
MK4b2	12/3/02	Emission vs hi blow pres	EU226	2.897	EU326	1.4	W450	50	83	0.98	67	82	5	45	45	176	20
MK4b3	12/3/02	Emission vs hi blow pres	EU227	2.472	EU327	1.5	W450	50	83	0.98	68	82	5	45	45	176	20

EU Core Make & Store Process Variables Summary (page 2)

Test No.	Test Date	Test Purpose	Make Sample No.	Make Emission Weight Lbs x 10	Store Sample No.	Store Emission Weight Lbs. x 1000	Sand Type	Sand Weight Lbs	Sand Temp F	Binder Content % (BOS)	Ambient Fdry Air Temp F	Probe Air Temp F	Blow Time Sec.	Blow Press psi	Purge Air Press psi	Purge Air Temp F	Purge Air Duration Sec.
Mk5a1	12/4/02	Emission vs Lo Purge pres	EU228	2.087	EU328	1.9	W450	50	83	0.98	61	84	5	32	22	176	20
MK5a2	12/4/02	Emission vs Lo Purge pres	EU229	1.732	EU329	1.7	W450	50	80	0.98	62	84	5	32	22	176	20
MK5a3	12/4/02	Emission vs Lo Purge pres	EU230A	2.761	EU330a	1.6	W450	50	81	0.98	69	84	5	32	22	176	20
MK5a3	12/4/02	Emission vs Lo Purge pres	Dup	3.067	NA	NA	W450	50	81	0.98	65	84	5	32	22	176	20
MK5b1	12/4/02	Emission vs Mid Purge pres	EU231	2.845	EU331	1.4	W450	50	80	0.98	65	85	5	32	57	176	20
MK5b2	12/4/02	Emission vs Mid Purge pres	EU232	2.781	EU332	1.3	W450	50	79	0.98	66	85	5	32	57	176	20
MK5b2	12/4/02	Emission vs Mid Purge pres	NA	NA	EU332	0.9	W450	50	79	0.98	67	85	5	32	57	176	20
MK5b3	12/4/02	Emission vs Mid Purge pres	EU233	2.669	EU333	1.1	W450	50	82	0.98	67	85	5	32	57	176	20
MK6a1	12/17/02	Emission vs Purge temp	EU234A	2.174	EU334A	1.5	W450	50	81	0.98	63	82	5	32	45	171	20
MK6a2	12/17/02	Emission vs Purge temp	EU235	2.508	EU335a	1.2	W450	50	78	0.98	64	82	5	32	45	201	20
MK6a3	12/17/02	Emission vs Purge temp	EU236	2.186	EU336a	0.8	W450	50	80	0.98	65	82	5	32	45	232	20
MK6a3	12/17/02	Emission vs Purge temp	NA	NA	Dup	0.4	W450	50	80	0.98	65	82	5	32	45	232	20
Mk6b3	12/17/02	Emission vs Purge temp	EU237	1.382	EU337	0.9	W450	50	79	0.98	66	79	5	32	45	181	20
	12/17/02	Emission vs Purge temp	NA	NA	EU338	0.9	W450	50	82	0.98	66	79	5	32	45	----	20
	12/17/02	Emission vs Purge temp	NA	NA	EU339	0.8	W450	50	80	0.98	66	79	5	32	45	----	20
	12/17/02	Emission vs Purge temp	NA	NA	Dup	0.7	W450	50	80	0.98	66	79	5	32	45	----	20
MK7a1	12/9/02	Emission vs short Purge dur	EU240	2.241	EU340	1.2	W450	50	80	0.98	62	82	5	32	45	176	10
MK7a2	12/9/02	Emission vs short Purge dur	EU241	2.409	EU341	1.3	W450	50	82	0.98	63	82	5	32	45	176	10
MK7a2	12/9/02	Emission vs short Purge dur	Dup	2.531	EU341	NA	W450	50	82	0.98	63	82	5	32	45	176	10
MK7a3	12/9/02	Emission vs short Purge dur	EU242	2.486	EU342	3.0	W450	50	80	0.98	64	82	5	32	45	176	10
Mk7b1	12/9/02	Emission vs long Purge dur	EU243	2.658	EU343	1.1	W450	50	80	0.98	64	82	5	32	45	176	30
Mk7b2	12/9/02	Emission vs long Purge dur	EU244	2.618	EU344	1.0	W450	50	81	0.98	64	82	5	32	45	176	30
Mk7b3	12/9/02	Emission vs long Purge dur	EU245	2.550	EU345	1.1	W450	50	80	0.98	65	82	5	32	45	176	30
Mk7b3	12/9/02	Emission vs long Purge dur	Dup	2.634	NA	NA	W450	50	80	0.98	65	82	5	32	45	176	30
MK8a1	12/18/02	Emission vs lo GFN	EU246A	2.175	EU346	3.0	A70	50	77	1.75	60	82	5	30	45	176	20
MK8a2	12/18/02	Emission vs lo GFN	EU247	2.135	EU347	2.3	A70	50	77	1.75	60	82	5	30	45	176	20
MK8a3	12/18/02	Emission vs lo GFN	EU248	1.327	EU348	2.2	A70	50	77	1.75	60	82	5	30	45	176	20
Mk8b1	12/18/02	Emisisn vs hi GFN	EU249	1.486	EU349	2.7	F-95	50	75	1.75	63	83	5	30	45	176	20
Mk8b1	12/18/02	Emisisn vs hi GFN	NA	NA	Dup	2.3	F-95	50	75	1.75	63	83	5	30	45	176	20
MK8b2	12/18/02	Emisisn vs hi GFN	EU250	1.347	EU350-	2.9	F-95	50	75	1.75	64	83	5	30	45	176	20
MK8b2	12/18/02	Emisisn vs hi GFN	Dup	1.775	NA	NA	F-95	50	75	1.75	64	83	5	30	45	176	20
MK8b3	12/18/02	Emisisn vs hi GFN	EU251	1.709	EU351	3.1	F-95	50	75	1.75	64	83	5	30	45	176	20

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APPENDIX C GLOSSARY

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Glossary

ACFM	Actual Cubic Feet Per Minute
BO	Based on ( ).
BOS	Based on Sand.
HAP	Hazardous Air Pollutant defined by the 1990 Clean Air Act Amendment
HC as Hexane	Calculated by the summation of all area between elution of Hexane through the elution of Hexadecane. The quantity of HC is performed against a five-point calibration curve of Hexane by dividing the total area count from C6 through C16 to the area of Hexane from the initial calibration curve.
I	Invalid, Data rejected based on data validation considerations
NA	Not Applicable
ND	Non-Detect
NT	Not-Done, Lab testing was not done
POM	Polycyclic Organic Matter (POM) including Naphthalene and other compounds that contain more than one benzene ring and have a boiling point greater than or equal to 100 degrees Celsius.
PPMV	Parts Per Million by Volume
TGOC	Total Gaseous Organic Carbon
TGOC as Propane	Weighted to the detection of more volatile hydrocarbon species, beginning at C1 (methane), with results calibrated against a three-carbon alkane (propane).
VOC	Volatile Organic Compound