# Final Report

# NON-INCINERATION TREATMENT TO REDUCE BENZENE AND VOC EMISSIONS FROM GREENSAND SYSTEMS

DE-FC0799ID13719

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# ABSTRACT

The role of advanced oxidation (AO) technologies in reducing emissions from foundry green sand systems and improving green sand system operating performance has been investigated. Studies have been conducted at the Penn State University laboratories, at pre-production scale foundry research facilities and at several production foundries across the U.S. In these AO systems, green sand process water is conditioned with small additions of ozone and hydrogen peroxide and is sonicated (irradiated by ultrasonic waves) to create opportunities for VOC destruction during foundry pouring, cooling and shakeout cycles. Tests at Penn State also explored an underwater plasma add-on to this AO system. AO processing simultaneously reduces air pollutants by 30%-70%, improves green sand system performance, and reduces clay and coal materials used by 10%-30% through improvement in clay activation and other phenomena. These effects are achieved for AO-clean water systems where AO-treated water is incorporated into green sand systems, as well as in AO-black water and AO-dry dust-to-black water systems where clays from wet recovery systems or baghouse dusts are returned to the sand system as part of AO-treated slurries.

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# ACKNOWLEDGMENTS

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The success of this Penn State University – Furness-Newburge Inc. research would not have been possible without the dedicated contributions of the Research Steering Committee and the Research Advisory Committee. Their generous donation of materials, time and expertise is gratefully acknowledged. Special thanks go to Neenah Foundry for their total support and commitment; to CERP/Technikon for the many AO trials that they performed; to Grede-Reedsburg Foundry, Wheland Foundry, and Navistar International for their valuable full-scale performance data; and to the other participating companies and individuals that supported the work in so many ways.

# 1. PROJECT INTRODUCTION

This final report summarizes the work done under U.S. Department of Energy (DOE) contract DE-FC0799ID13719 for the period 10/30/98 to 10/29/01. This work was conducted as part of the DOE Office of Industrial Technology's (OIT) Industries of the Future (IOF) program through the Cast Metals Coalition (CMC). In this study, the roles of advanced oxidation (AO) systems for reducing foundry green sand system emissions and improving green sand system performance have been investigated. Investigations have been conducted in laboratory scale, pre-production scale, and production scale facilities with the cooperative efforts of Furness-Newburge Inc. and industrial partners. Additional technical support was provided by the American Foundry Society (AFS) and Technikon LLC and their Casting Emission Reduction Program (CERP) facility. Table 1.1-1 lists the program participants on the Research Steering Committee and the Research Advisory Committee. Complete contact information for investigators and industry participants is contained in Appendix A.

High production green sand foundries in the U.S. are under increasing pressure to reduce hazardous air pollutants (HAPs) that are emitted during pouring, cooling, and casting shakeout. Although end-of-pipeline incineration systems could treat these stack gases, incineration systems are both energy intensive and expensive and therefore would inhibit foundry competitiveness. The need exists in the foundry industry to develop alternative pollution prevention strategies that economically comply with ever more demanding air quality requirements and materials conservation constraints. The recent development of advanced oxidation (AO) technologies for pollution prevention and waste remediation in other diverse industries clearly indicates that these technologies offer similar opportunities to the foundry industry. U.S. foundries have already started to exploit these technologies. At the beginning of this research program, first generation AO systems in various configurations had already been installed at three high-production green sand iron foundries. At present more than six AO systems have been installed in foundries, and some of these foundries have been direct participants in this research program.

In the foundry AO systems, green sand process water is conditioned with small additions of ozone and hydrogen peroxide and is sonicated to create scavengers in the green sand mold that reduce VOC emissions during subsequent pouring, cooling, and shakeout. These effects have been observed for AO-clean water (AO-CW) systems where only AO treated water is incorporated into green sand systems, as well as in AO-black water (AO-BW) and AO-dry dust-to-black water (AO-DBW) systems where clays from wet recovery systems or baghouse dusts are returned to the sand system as part of

AO treated slurries. An underwater plasma add-on to this system has also been explored at Penn State.

AO processing has also been observed to improve green sand system performance due to improvements in clay activation during mulling. This enhanced clay activation leads to improved mold strength, which results in an AO-driven green sand system optimization that lowers sand system bond (clay and coal) consumption. In addition, the presence of AO in blackwater clarifiers as part of AO-BW or AO-DBW systems appears to improve bond recovery significantly, further improving green sand system performance and lowering operating costs.

This report describes an initial investigation to further understand the complex role of advanced oxidants in the green sand mold environment, in particular the effects on emissions and green sand system performance. The results of Penn State laboratory studies, concurrent pre-production-scale AO trials at CERP/Technikon, and production foundry trials are reported. The Penn State laboratories investigated the AO reactions taking place in green sand systems to further understand the mechanisms by which AO can be expected to reduce foundry emissions and bond use. In informal collaboration, concurrent pre-production-scale and full-scale AO casting trials at CERP/Technikon have focused on the quantification of emissions for AO-CW systems that operated under various green sand system conditions, including baseline conditions (without AO) and AO-driven sand system operating conditions. Production foundry trials at Neenah, Wheland, Grede-Reedsburg and Navistar foundries were conducted using AO-CW, AO-BW and/or AO-DBW systems. They include careful study of historical data as well as careful monitoring of baseline and AO emission and sand system performance properties under controlled production conditions.

This report begins with a summary of the available literature on AO reactions, green sand emissions, and the performance of green sand systems. Sections describing the procedures, results and discussions for the various phases of this research effort follow. Finally, the key findings of this research are summarized and directions for future critical research are presented.

**Table 1.1-1: Company affiliates.**

**Steering Committee**

American Foundry Society
Ford Motor Company
Furness-Newburge, Inc.
GM Powertrain
Iron Casting Research Institute
Keramida Environmental, Inc.
Neenah Foundry Company
Technikon (CERP)

**Other Participants**

Advanced Cast Products, Inc.
American Colloid Company
Argonne National Laboratory
Carpenter Brothers, Inc.
General Motors Corp.
Grede-Reedsburg Foundry
Hill and Griffith Company
Kohler Company
Navistar International Transportation Corp.
Simpson Technologies Corp.
U.S. Pipe and Foundry Company
Victaulic Company of America
Waupaca Foundry

# 2. BACKGROUND

The fundamentals of sonoperoxone-based (AO) reactions from the technical literature will be discussed. This will be followed by a summary of emissions and sand system performance for green sand systems.

## 2.1 ADVANCED OXIDATION PROCESSES

Due to the new restrictions and permitting requirements placed on the foundries by the Clean Air Act Amendments (CAAA) of 1990, innovative techniques of controlling air pollution in foundries are being investigated. Advanced oxidation (AO) treatment represents a novel approach to diminishing foundry green sand emissions. The advanced oxidation processes described in this report either employ one or a combination of ozone, hydrogen peroxide, sonication, and (as a new addition) underwater plasma energy.

### 2.1.1 AO Fundamentals

Advanced oxidation processes (AOPs) are near-ambient temperature reactions that generate highly reactive intermediates, including the hydroxyl radical (OH•), aqueous electrons, H•, and $HO_2$• (Glaze, *et al.*, 1992). The mechanism of advanced oxidation is the decomposition of ozone and/or hydrogen peroxide by sonication and UV light to form highly oxidizing or reducing radicals, in particular the hydroxyl radical, OH• (Forbes and McManus, 1996). The radicals formed by advanced oxidation processes attack the organic contaminants in, i.e. groundwater and wastewater, as well as volatile organic compounds generated during the casting process. These radicals also alter the coals and clays in a green sand system. Although these processes are called "advanced oxidation," they often involve both radical oxidation and radical reduction processes, in that they can generate the oxidants OH• and $O_3$, as well as the reductive species H•, $HO_2$•, a soluble electron ($e^-$), and others. However, advanced oxidation is a term that is commonly used in the science and industry community and we will, therefore, use "advanced oxidation" herein.

Table 2.1-1 displays the first-order rate constants for reactions of radical intermediates with benzene, toluene, and xylene-type (BTX) compounds which represent the more common volatile organic compounds (VOCs) in green sand foundry systems. The hydroxyl radical is the most reactive radical with the BTX compounds, and therefore, has been the focus of the majority of current research on advanced oxidation processes. The hydroxyl radical is a highly reactive oxidant, with a rate constant as high as $1x10^9$ $M^{-1}s^{-1}$ (Glaze, *et al.*, 1992, Brant and Cannon, 1996). OH• adds oxygen-containing functional groups to organic matter (Zhang and Cannon, 1999) to oxidize them to less volatile compounds and minerals.

**Table 2.1-1: First order rate constants ($M^{-1}sec^{-1}$) for ambient-temperature reactions between radical intermediates and benzene-toluene-xylene (BTX) compounds.**

| Compound | $e^-_{aq}$ | H• | OH• |
|---|---|---|---|
| Benzene | $9.0 x10^6$ | $9.1 x10^8$ | $7.8 x10^9$ |
| Toluene | $1.4 x10^7$ | $2.6 x10^9$ | $3.0 x10^9$ |
| m-Xylene | not found | $2.6 x10^9$ | $7.5 x10^9$ |
| p-Xylene | not found | $2.0 x10^9$ | $6.7 x10^9$ |

Advanced oxidation processes have been used in a variety of applications. One such application is treating contaminated groundwater. Ozone and hydrogen peroxide have treated groundwater that contains volatile organic compounds (Forbes and McManus, 1996). Hydrogen peroxide effectively oxidizes BTX compounds and halogenated organic compounds (Ravikumar and Gurol, 1994). Ozone destroys organic nitrogen compounds such as glycine in groundwater (Berger, *et al.*, 1999). A study by Forbes and McManus (1996) showed that the combination of ozone or peroxide and sonication and ultraviolet (UV) radiation can increase the rates at which organic contaminants are degraded by several orders of magnitude over UV light or peroxide/ozone treatments alone.

AOPs can effectively treat a wide variety of organic compounds. AOPs can oxidize hydrocarbons, and if enough advanced oxidants are added to carry this process to completion, the AOPs can degrade the hydrocarbons to carbon dioxide and water (Peyton, 1992; Boncz, *et al.*, 1997; Glaze, *et al.*, 1992; Forbes and McManus, 1996). For the most part, the AO reactions in the foundry setting are not expected to proceed to that extent of degradation, except at the molten metal interface. AOPs are even more favorable considering that the chemicals used in AOPs, namely hydrogen peroxide and ozone, decompose to harmless or beneficial by-products (Peyton, 1992).

AOPs break down organic contaminants in several different ways. These include direct photolysis by UV radiation, direct oxidation by molecular ozone and hydrogen peroxide, and indirect oxidation by means of radical intermediates, including the hydroxyl radical, that are produced from ozone or hydrogen peroxide decomposition (Boncz, *et al.*, 1997).

Ozone ($O_3$) is a major component of most advanced oxidation processes. Ozone directly reacts with an aromatic compound (i.e., benzene, toluene, or xylene) by adding a hydroxyl (OH) group to the ring (Boncz, *et al.*, 1997). However, under sonication ozone decomposes to radical intermediates, becoming even more reactive (Weavers and Hoffmann, 1998).

"Sonication" is the process of the irradiation of a material with ultrasonic sound waves. The ultrasonic agitation induces cavitation using sound waves to reduce the pressure in the liquid to a level that is below the liquid's vapor pressure. This typically happens during the rarefaction cycle. As multiple cycles occur, micro bubbles form in the low-pressure regions and begin to expand. Once the micro bubbles reach a critical size they collapse, releasing a large amount of energy. Temperatures on the order of 5000 to 120,000 K and pressures from 500 to 1400 atm have been calculated and/or observed at the collapsing interface in micro bubble implosions while the bulk solution stays near ambient conditions (Suslick, *et al.*, 1983; Weavers and Hoffmann, 1998; Glanz, 1996; Suslick, *et al*., 1997). To put this into perspective, this is the temperature of the sun and the pressure of deep ocean trenches. The intense energy can disassociate water molecules into OH• and H•, the latter of which can enter into redox reactions. This extreme environment can directly destroy contaminants by breaking carbon-carbon bonds in organic compounds.

The collapse of the cavitation bubbles also assists in the decomposition of ozone to form radical intermediates, including the hydroxyl radical, OH•. The ozone undergoes pyrolysis (thermal decomposition) inside the cavitation bubble or at the bubble surface (Weavers and Hoffman, 1998; Olson and Barbier, 1994). The equations describing this process are as follows, where ozone decomposes into atomic oxygen before reacting with water to form the hydroxyl radical:

$$O_3 \rightarrow 3O$$
$$3O + 3H_2O \rightarrow 6OH\bullet$$

Note that sonicative destruction of one ozone molecule produces six hydroxyl radicals. According to another study conducted by Weavers, *et al*. (1998), atomic oxygen can react with water vapor within the cavitation bubbles, producing a gas phase hydroxyl radical. With the creation of the hydroxyl radical in the cavitation bubble, Weavers, *et al*., concluded that organic compounds were destroyed in the cavitation bubble itself.

Along with sonication, UV radiation of wavelength shorter than 185 nm also decomposes ozone to form the hydroxyl radical. Photons of UV light are generated during sonication, a phenomenon called sonoluminescence. Brief photons of UV and visible light are produced when pockets of water vapor inside the cavitation bubbles are rapidly expanded and contracted by the pressure of sound waves, which builds up energy inside the bubble. Characteristics of sonoluminescence are that smaller cavitation bubbles emit light more readily than larger bubbles, and more light is released as the water approaches the freezing point (Glanz, 1996). The center of the cavitation bubble is extremely hot and contains water vapor, gas, and contaminants (Weavers, *et al*., 1998). The slightly cooler halo around the center of the bubble emits the photon of light. The cavitation bubble walls snap back at near supersonic speeds as the bubble collapses. The collapsing bubble generates a sound wave that implodes, creating hot, glowing plasma (Glanz, 1996).

Hydrogen peroxide ($H_2O_2$) is another chemical commonly used in AOPs. Hydrogen peroxide reacts directly with organic compounds via hydrogen abstraction.

Hydrogen peroxide removes two hydrogen atoms from a contaminant to produce two molecules of water. In the presence of naturally occurring iron salts in sand, including green sand used in the foundry for molds, hydrogen peroxide readily decomposes into hydroxyl radicals. This mix of hydrogen peroxide and iron salts is known as Fenton's Reagent (Ravikumar and Gurol, 1994; Brant and Cannon, 1996; Zhang and Cannon, 1999; Zhang, 1999). UV light causes photolysis of hydrogen peroxide (Glaze, *et al.*, 1992; Hoigné, 1997; Boncz, *et al.*, 1997) into two hydroxyl radicals (Forbes and McManus, 1996):

$$H_2O_2 \rightarrow 2OH\bullet$$

In addition, $H_2O_2$ is broken down into hydroxyl radicals by ozone. The use of ozone and ozone plus hydrogen peroxide to form the highly reactive hydroxyl radicals has become well established as a water and wastewater treatment operation called "Peroxone" (Prendiville, 1986; Edwards and Benjamin, 1992; Chandrakanth and Amy, 1996; Chandrakanth, *et al.*, 1996; Camel and Bermond, 1998; Jekel, 1998). This method is an advanced oxidation process which "promotes the generation of high energy, short-lived hydroxyl radicals (OH•) through the decomposition of ozone with hydrogen peroxide (Wolfe *et al.*, 1998). The generation of the aqueous OH• allows it to enter into "non-selective reactions with most organic and many inorganic solutes with very high rate constants that approach diffusion controlled limits (Hoigne, 1997). The hydroxyl radical is highly reactive with many species as shown in Table 2.1-2. The rate of primary oxidation of the compound M is given by the expression (Wolfe, *et al.*, 1998):

$$R_{M,OH} \;=\; -d[M]/dt \;=\; k_{M,OH}[M][OH]_{ss}$$

The very high reaction rate constants of the hydroxyl radical with compounds shown in Table 2.1-2 indicate that advanced oxidation processes which form the

**Table 2.1-2: Reaction rate constants of OH• with contaminants that can be found in water or air.**

| **Compound "M"** | **$k_{M,OH}$ x $10^9$ $M^{-1}s^{-1}$** |
|---|---|
| Benzene | 7.80 |
| Toluene | 2.00 |
| 1-Butanol | 4.20 |
| Vinyl Chloride | 7.10 |
| Trichloroethylene | 4.00 |
| Tetrachloroethylene | 2.30 |
| Pyridine | 3.80 |
| Chlorobenzene | 4.50 |
| Nitrobenzene | 3.90 |
| Dichloromethane | 0.058 |
| Chloroform | 0.005 |
| Bicarbonate Ion | 0.0085 |
| Carbonate Ion | 0.39 |

hydroxyl radical can be employed to oxidize otherwise tough-to-remove contaminants. Within the Peroxone process, the decomposition of ozone to OH• is accelerated by the addition of $H_2O_2$ (Wolfe *et al.*, 1998). The proposed mechanism for the generation and reactions of OH• in water absent of contaminants and scavengers using the Peroxone process is as follows:

Ozone dissolution: $O_3 + OH^- \Rightarrow HO_2^- + O_2$

Hydrogen peroxide disassociation:

$H_2O_2 + H_2O \Rightarrow HO_2^- + H_3O^+$

$O_3 + HO_2^- \Rightarrow OH\bullet + O_2^- + O_2$

Hydroxyl radical reactions: $O_3 + OH\bullet \Rightarrow HO_2\bullet + O_2$

$O_3 + O_2^- \Rightarrow O_3^- + O_2$

$O_3^- + H_2O \Rightarrow OH\bullet + OH^- + O_2$

$OH\bullet + HO_2\bullet \Rightarrow H_2O + O_2$

In the presence of organics (R), the above reactions will not be terminated as shown, but may cascade down through reactions with intermediate products (Q) (Kuo and Chen, 1996):

$$R + OH\bullet \Rightarrow Q$$

In addition, radical scavengers such as the carbonate ion, the bicarbonate ion, natural organic matter, and even excess hydrogen peroxide and ozone, can decompose the OH• before it can react with the contaminants (Glaze *et al.*, 1992; Liao and Gurol, 1995; Weavers and Hoffman, 1998; Ku and Wang, 1999).

A number of researchers have appraised one or a combination of several of the advanced oxidation processes relative to their ability to oxidize, mineralize, or alter organic compounds. A number of these studies have also characterized advanced oxidation radical reaction mechanisms (Atkinson, 1986; Glaze and Kang, 1989; Strukul, 1992; Sun and Pignatello, 1993; Glaze, *et al.*, 1995; Chen and Pignatello, 1997; Choi and Hoffman, 1997; Gurol, *et al.*, 1997; Hua and Hoffman, 1997; Mak, *et al.*, 1997; Waite, *et al.*, 1997; Bolton, *et al.*, 1998; Lin and Gurol, 1998; Valentine and Wang, 1998).

In most applications, AO technology has been primarily limited to treatment at ambient or slightly elevated temperatures. In experiments at moderately elevated temperatures, a Penn State team found that 3% hydrogen peroxide, when heated to 70°C or when combined with iron salts to promote Fenton's reaction, completely removes asphalt from glass or steel surfaces within 5-60 minutes (Brant and Cannon, 1996; Cannon and Brant, 1998; Zhang and Cannon, 1999; Zhang, 1999). In contrast, when control experiments were conducted with tap water at 70°C, the asphalt could not be completely removed (Brant and Cannon, 1996). The Penn State team also observed that UV-developed advanced oxidants could improve the reactivation of activated carbons that had been used to adsorb organic compounds from the air phase (Dusenbury and Cannon, 1996, 2002; Cannon *et al.*, 1996).

Advanced oxidation methods have been observed to destroy and/or oxygenate phenol (Joshi *et al.*, 1995; Sato *et al.*, 1999), halogenated organics (Al-Arainy *et al.*, 1996; Willberg *et al.*, 1996; Bystritskii *et al.*, 1997) and volatile organics including benzene and toluene (Lubicki *et al.*, 1996).

### 2.1.2 Foundry AO Systems

A novel advanced oxidation system (Sonoperoxone$^{TM}$) has been devised and developed for the foundry industry by Furness-Newburge, Inc. This AO system includes the use of hydrogen peroxide, ozone, sonication, and (in pilot testing) underwater plasma. This system (currently without underwater plasma) has been installed in several full-scale foundries, and these systems have achieved encouraging results. Following AO installation, foundries have been experiencing emission reductions of 20-70%. Not only has this AO technology reduced foundry emissions, but it also has decreased the amount of green sand materials used and waste generation at foundries. By reactivating clay and coal for reuse in the green sand system, AO has reduced material use and waste by 10-30%.

While AO technology appears to work in the foundry setting, we have sought herein to understand the science behind these improvements. With knowledge of the fundamental science of AO, we may further improve its application in the full-scale foundry green sand system.

Figure 2.1-1 shows a schematic of the casting process in the full-scale foundry. Following mold preparation, the molten metal is poured into the green sand mold. After a time of cooling, shakeout segregates the casting from the green sand material. The castings then proceed to machining and finishing, while the green sand is recycled through the system to be used again. Emissions and dust are exhausted from the pouring, cooling, and shakeout areas and collected in either bag house collectors or wet scrubbers. The useful clay and coal can be separated from the silica fines in a clarifier; and the clay and coal can then be used again in the green sand system.

There are several ways that this AO system can be implemented in the full-scale green sand system. The first is a clean water AO (AO-CW) system, as shown in Figure 2.1-2. Tap water enters the system and is treated by ozone and hydrogen peroxide before exposure to sonication. This AO-treated water is then sent to the muller and the coolers to treat the green sand. The Neenah Plant 3 DISA system has been utilizing the AO-CW system.

The second method of AO installation is the AO blackwater (AO-BW) intercept system. Figure 2.1-3 shows the application of this blackwater method in the green sand foundry. In this method, the ventilation-collected fines of clay, coal, and silica are collected in wet scrubbers and the resulting “blackwater” is treated with hydrogen peroxide, ozone, and sonication. A clarifier then separates the useful clay and coal from the waste silica fines. The clay and coal proceed as a 10-17% slurry to the mullers and sand coolers for reuse.

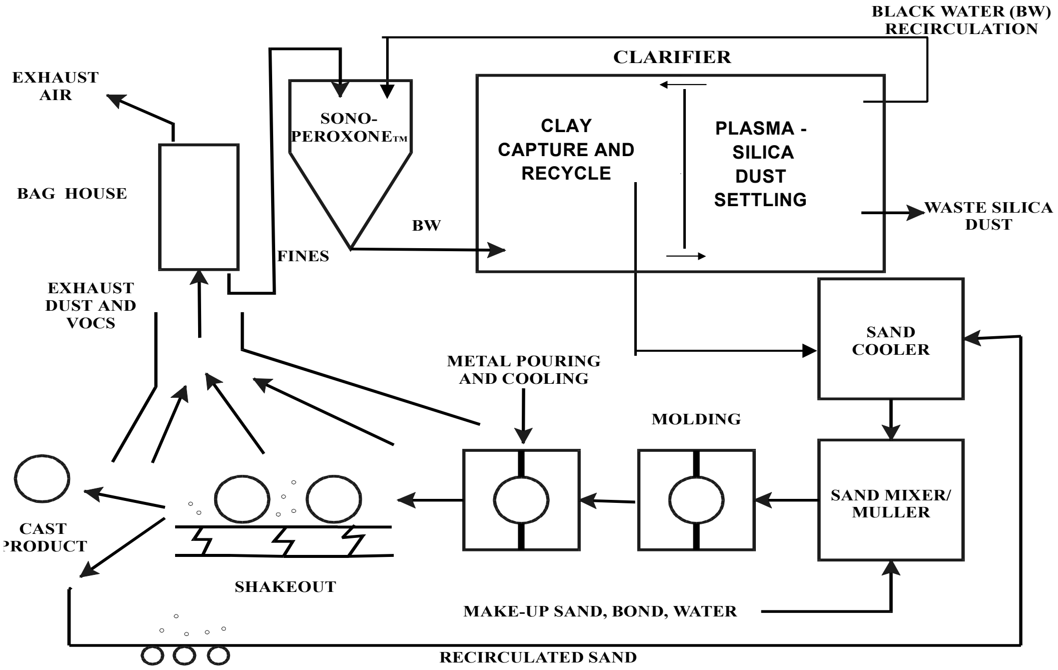


**Figure 2.1-1 Schematic of the casting process in a green sand foundry.**

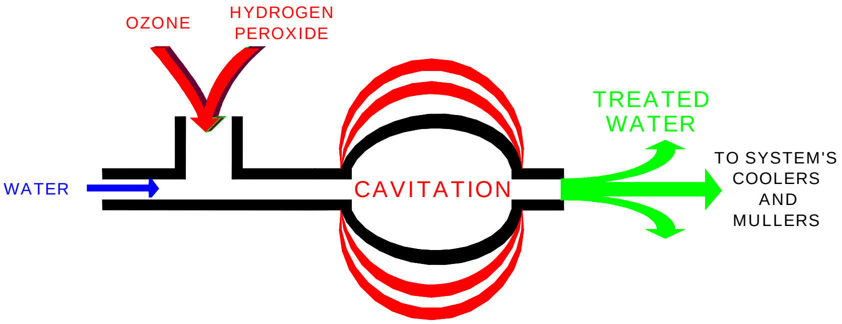


**Figure 2.1-2: Schematic of the clean water AO system in a green sand foundry (Sonoperoxone$^{TM}$, adapted from Furness-Newburge, Inc. brochures).**

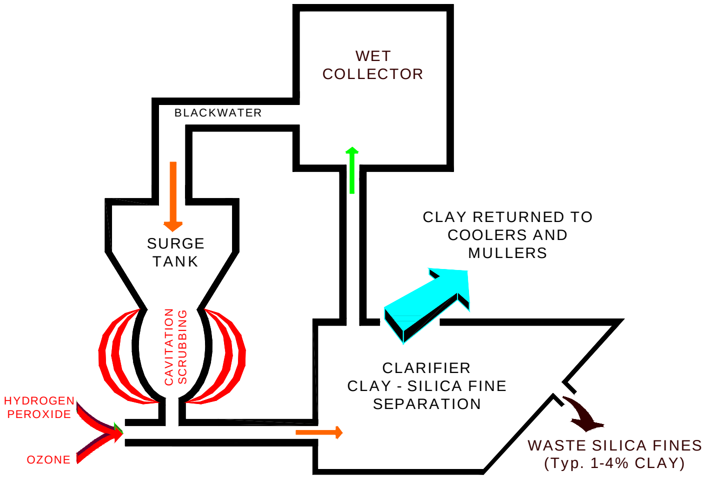


**Figure 2.1-3: Schematic of the AO blackwater intercept system in a green sand foundry (Sonoperoxone$^{TM}$, adapted from Furness-Newburge, Inc. brochures).**

The third method of AO installation differs from the previous two only in how the clay, coal, and silica fines are collected and introduced to AO treatment. Figure 2.1-4 shows how the AO dry dust-to-blackwater (AO-DBW) system is implemented in the casting process. This method begins with the collection of dry silica fines, coal, and clay from the ventilation into bag house collectors. The captured fines are then mixed with water, and this slurry is treated with hydrogen peroxide, ozone, and sonication. Next, a clarifier removes the waste silica fines from the clay and coal so that the clay and coal can be reused in the mullers and coolers. The Neenah Plant 2 foundry has been employing this process.

With full-scale emissions reductions seen in stack tests following the installation of AO, more research of this technology in the foundry setting was warranted. This project report discusses the various tests that have been conducted at Penn State that aim at more fully understanding the science of AO and its effect on the foundry green sand system. Pilot-scale and bench-scale tests have explored the effects of AO on emissions and characterized the green sands that have been treated with various AO treatments.

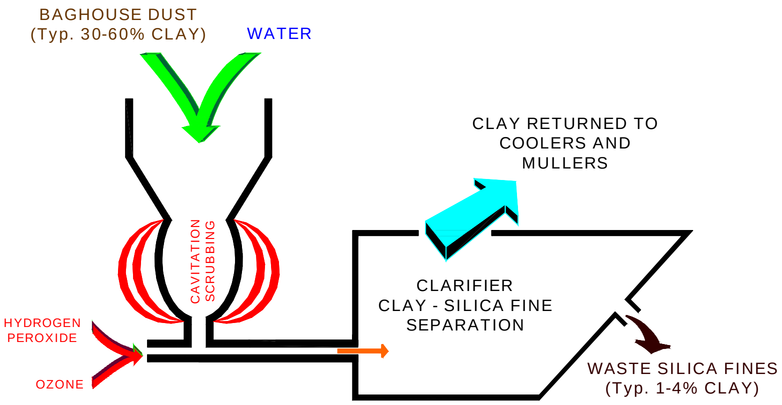


**Figure 2.1-4: Schematic of the AO dry dust to blackwater system in a green sand foundry (Sonoperoxone$^{TM}$, adapted from Furness-Newburge, Inc. brochures).**

## 2.2 EMISSIONS FROM GREEN SAND MOLDS

Some of the more prominent compounds generated during the casting process that are classified as hazardous air pollutants (HAPs) are listed in Table 2.2-1 (Technikon, 2001). The major compounds of interest that are generated at higher concentrations are benzene, toluene, xylenes, and hexane, as well as phenol if phenolic urethane cores are used. Several studies have shown that coal and binder systems contribute to the majority of emissions during the casting process that are listed as HAPs in the CAAA of 1990 (Landis, 1996; McKinley, *et al.*, 1993; Volkmar, *et al.*, 1997). There are two primary sources of emissions during the casting process. Coal is a major source of emissions in the green sand. Emissions generated by coal pyrolysis during the casting process are hydrocarbons including HAPs such as benzene, toluene, xylenes, napthalenes, and similar derivatives of these. Cores are also major sources of emissions in the foundry. HAPs are produced as un-reacted core binder pyrolyzes during the casting process (McKinley, *et al.*, 1993). Core binder emissions are primarily phenol and formaldehyde, accompanied by smaller amounts of benzene, toluene, and xylenes.

Not all the emissions that are initially generated by the coal and core binders during the casting process reach the exhaust. During the casting process, the carbonaceous materials (coal) that are closest to the mold-metal interface are destroyed, while those farthest away remain unaffected (LaFay, *et al.*, 1998a). The cooler parts of the mold, where the components of the green sand remain unaffected, serve to adsorb and/or capture the hydrocarbon gases generated during pouring. The gases re-condense in the mold away from the mold-metal interface, preventing the HAPs from leaving the green sand mold. Volkmar further hypothesizes that "some of the materials in the pre-blend oxidize these hydrocarbon condensates that are in the sand, thus reducing the amount of gases being emitted from the molding sand" (Volkmar, *et al.*, 1997).

Volkmar's hypothesis of green sand emissions adsorbed within the mold is supported by other independent research. Several papers discuss the role of sand-to-metal ratio in the emissions of full-scale foundries. A larger green sand-to-metal ratio lowers benzene and total volatile organic compound (VOC) emissions (Kauffman and Voigt, 1997; LaFay, *et al.*, 1999b; Crandell and Glowacki, 2001). A study by LaFay, *et al.* (1998a) showed that the lower the sand-to-metal ratio, the higher the benzene emission rate. Kauffmann and Voigt (1997) found that increasing the sand-to-metal ratio decreased overall emissions. Their study also showed that an increased amount of coal in the green sand resulted in an increase in VOC emissions, but did not affect the benzene emission rate. Kauffmann and Voigt concluded that sand-to-metal ratio and coal content most influence VOC emission rates, while the benzene emission rate is most reduced by increasing the sand-to-metal ratio.

**Table 2.2-1: Foundry related hazardous air pollutants, as determined by CERP/Technikon (Technikon, 2001).**

| | |
|---|---|
| Acetaldehyde | Methanol |
| Acrolein | Methyl isobutyl ketone |
| Aniline | 4,4- Methylenediphenyl diisocyanate |
| Benzene | 4,4- Methylenedianiline |
| Biphenyl | Napthalene |
| 2-Butanone | Phenol |
| Catechol | p-Phenylenediamine |
| Cresols/Cresylic | Polycyclic organic matter |
| o-Cresol | Propionaldehyde |
| m-Cresol | Styrene |
| p-Cresol | Toluene |
| Cumene | Triethylamine |
| N,N- Dimethylaniline | Xylenes |
| Ethylbenzene | o-Xylene |
| Formaldehyde | m-Xylene |
| Hexane | p-Xylene |
| Isophorone | |

## 2.2.1 Emissions Measurement in the Foundry

LaFay, *et al*. (1998a, 1998b, 1999a, and 1999b) described a series of tests (under non-AO conditions) to determine benzene emission levels from coal and various coal supplements due to the metal casting process. These researchers found that the green sand mold tended to adsorb benzene emissions, however, the mold materials would readily release them when increased temperatures or steam conditions subsequently occurred. They also found that more benzene remained in the portions of the green sand that was farther from the sand-metal interface than that which was closer. This was determined by venting nitrogen gas through the sand and passing the effluent through a mass spectrometer. This was more pronounced at the lower sand-to-metal ratios (4:1) than at the higher ratios (11:1). With higher sand to metal ratios, the heat was dissipated more efficiently through the green sand and the high temperature isotherms did not extend as far from the metal interface, leaving more of the coal unaffected by temperature. The experiments described above were coupled with pilot-scale foundry pours. These pours mimicked the metal casting process with the exception of shakeout. Emissions were captured on gas absorption chromatography (GAC) during the pouring and cooling of the green sand mold. It was found that as the sand-to-metal ratio increased, the amount of benzene emissions decreased, primarily due to less carbonaceous material being affected by the heat (Lafay *et al*., 1998a).

### 2.2.2 Emissions Measurement in the Laboratory

In bench-scale foundry emissions studies, researchers face the daunting task of mimicking the metal casting process. This is difficult due to the high temperature ramping and complex nature of a sand mold. Experimenters have broken down the green sand mold into its constituents and tested them individually. Several tests have been designed to subject test samples to the temperatures that green sand would experience in the metal casting process, including thermogravimetric analysis (TGA) and analytical pyrolysis.

Landis (1996) conducted TGA tests of eight different coal deposits and found that benzene levels for the same mass of coal varied from 45 to 110 ppm. This means that the potential of coal to emit benzene varied significantly from one coal deposit to the next.

## 2.3 GREEN SAND PERFORMANCE

This section of the report presents an introduction to molding with green sand, a detailed description of green sand components and testing parameters, and a description of mulling, molding, and control issues related to green sand molding processes.

In the green sand molding process, a mixture of sand, clay, and water are formed into a mold around a pattern of a cast component. Molten metal is poured into the mold and allowed to solidify. After sufficient cooling, the mold is broken down, the metal casting is removed, and the mold materials are collected and recycled. New ingredients are added to the re-circulated material, and all mold materials are mulled together thoroughly and re-used in a continuous molding process.

Additional materials such as clay, coal and soda ash are added to promote desirable molding, casting and shakeout characteristics in the green sand mold. A number of physical property tests and calculated empirical parameters are monitored to maintain control of the molding process.

### 2.3.1 Green Sand Components

Green sand consists of silica sand (80-85%), clay (8-10%), coal (3.5-6%), water (3-4%) and other minor components. Silica ($SiO_2$) sand is an inexpensive refractory material capable of withstanding the temperatures of molten metal. The shape, size, and distribution of the sand grains all affect the properties of the mold. Sand grains can be present in a number of shapes, including rounded, angular, sub-angular, or compound (Green Sand Molding Committee, 1994). To obtain the best overall mold properties, a distribution of both coarse and fine grains is typically used in foundries.

Green sand typically consists of about 8-10% bentonite clays. The foundry industry mainly uses sodium (western) and calcium (southern) bentonites. The bentonite clay is a mixture of mainly montmorillonite, along with a few other clay minerals. The use of calcium bentonites leads to the development of higher green strength values in molds, while the use of sodium bentonites leads to higher dry compressive strength values (Diran and Taylor, 1952). Iron foundries may use mixtures of both bentonite types to optimize the performance of their green sand system.

Bentonite clays have a very small, plate-like structure with a large surface area-to-mass ratio. Bentonites can swell tremendously, particularly the sodium bentonites. Bentonite clays are often capable of absorbing many times their weight in water. This swelling governs many of the physical properties of sand molds.

The coal within green sand is essential in that: (i) the coal improves the surface finish of the resulting castings (ii) the carbon consumes oxygen at the molten metal surface preventing adverse reactions of the metal with oxygen, (iii) at high temperature, the coal forms a malleable coke that prevents the penetration of gases and molten iron into the pores in the sand, (iv) the coal facilitates shorter cooling times for the molten metal, (v) both coal and sand swell while clay shrinks at high temperature, thus balancing the volume changes to maintain dimensional tolerances, (vi) in AO systems, a significant portion of the coal can become activated, serving as a VOC and HAP adsorbent and/or capturing bed.

Coal undergoes several different transformations that are dictated by their proximity to the molten metal interface. In the immediate vicinity of this interface, where the temperatures rise to 1100-1400°C, the coal combusts with residual oxygen and creates a reduced gas atmosphere of CO that protects the molten metal surface from becoming oxidized. After all the oxygen becomes consumed, these temperatures cause the remaining coal to become coked, and the coke expands as it engulfs bubbles of released gases. In the second zone, characterized by a temperature regime of 700-1100°C, the coal pyrolyzes to form an activated carbon, but in the process releases VOCs. This is the same temperature regime, raw material source, and pyrolyzed/steam gas environment that an activated carbon manufacturer would employ to produce activated carbon. In a third zone, between 200-700°C, the coal releases VOCs and perhaps participates in retaining VOCs via radical reactions (when AO is employed). In the outer zone, with temperatures of ambient to 200°C, the coal transforms only slightly.

Water is a critical component of the green molding sand because it both "activates" the adhesive properties of the clay, and it can be used to control the properties of the sand mold mixture. Moisture in green sand mixtures may occur as absorbed water and as free water. The absorbed water is responsible for chemically "activating" the adhesive properties of the clay/sand/water mixtures. Free water is considered as the excess water that is unabsorbed by the clay mixture.

Water molecules are asymmetrical – the oxygen atom carries a net negative charge and the hydrogen atoms carry a net positive charge. This dipolar characteristic ultimately allows water molecules to bond to clay particles (Draper, *et al.*, 1965). When clay absorbs water, the water disassociates into a negatively charged hydroxyl ($OH^-$) ion and a positively charged hydrogen ion ($H^+$) (Diran and Taylor, 1952). The hydroxyl ion adheres to the clay platelets, making them negatively charged. The water molecules that are closest to the clay platelets are numerous, aligned, and evenly spaced, while those farther away from the clay platelet are less rigidly bonded, random, and scattered (Wenninger, 1963). In the presence of a charged particle, such as silica sand, randomly oriented water layers can form between the particle and the clay. The spacing, or gap, between the clay platelets and any charged particle are a function of the type of exchanged cation (sodium or calcium), the absolute amount of water absorbed, and the acidity of the water (Newman, 1987). This interlayer spacing controls the strength of the electrostatic bonding between clay platelets and charged particles, which in turn governs the visco-elastic properties of clay-water solutions. The physical properties of a greensand mold result mainly from these fundamental clay-water interactions.

The chemical composition of the absorbed water greatly affects green sand mold properties. The bonding action of clay stems from the chemical attraction between the layers of clay, water, and sand grains, as discussed earlier. The aqueous environment that these interactions occur in governs the properties of these attractions. The water hardness and salinity, the presence of soluble organics, ions, and trace metals all affect the behaviors of clay-water solutions and the physical properties of green sand molds. However, the most critical water property affecting clay-water interaction is pH (acidity or alkalinity). Green sand mold properties are directly linked to the visco-elastic behavior of clay/water mixtures, and this clay/water rheology is strongly affected by pH. Simple experiments have shown significant increases in clay-water viscosity with increasing pH, or alkalinity. In foundries, a common green sand additive, soda ash (NaOH), is simply a water pH modifier. The influence of soda ash (and thus of pH) on the properties of green sand has been extensively studied. Shih, *et al.*, (1989) found that the addition of NaOH causes green compressive strength to increase and compactibility to decrease at constant moisture content.

Surfactants or wetting agents are sometimes also added to the molding water to reduce surface tension, allowing more efficient and faster wetting of clays. These typically organic chemicals have been reported to increase the green strength and dry compressive strength of molding sands while decreasing the amount of clay required (Lafay, 1993). Additionally, surfactants can sometimes reduce mulling times and raw material requirements; however, most surfactants continually build-up in the sand system, and in the long run may not significantly enhance sand system performance.

Water that has been ultrasonically treated has also been found to "enhance the bonding properties of the clays" (Anisovich and Gamov, 1975). This is most likely due to effects on the wetting angle, the surface tension, and on the pH of the molding water. Anisovich and Gamov suggested that ultrasonic treatment increased the number of stable molecules that are paired together, which in turn increased the green compressive strength of the sand.

Other additives used in green sand can be grouped into four categories: cellulose, organics, polymers, and inorganic materials (Green Sand Molding Committee, 1994). Cellulose and other organics are used to widen the acceptable range for water additions. Polymers and inorganics assist in sand flowability and clay/water dispersion in the mixture. These additive materials all tend to be much finer and have more surface area than the sand grains; increasing the clay and water percentages needed to produce molds.

Other contaminants enter the system because of the recycling of the sand. These constituents include dead (calcined) clay, ash, slag, and other oxides. Not only do these materials lower the fusion point of the prepared sand, but contaminants and silica fines also reduce the permeability of the greensand (Carey, 1999). These reductions in permeability can be controlled by disposing a portion of the system sand and continually adding new sand and bond to the system.

### 2.3.2 Green Sand Properties

Extensive sand testing is performed in foundries to monitor the critical sand properties that ensure casting consistency. The principle sand tests used by foundries include percent compactibility, green compressive strength, percent moisture, and percent methylene blue (MB) clay. In addition, other calculated sand system performance measures based on these fundamental properties are important. These sand tests are explained and the key green sand system performance measures are presented and discussed in the following paragraphs.

The compactibility test (%TC = % test compactibility) measures the percent compaction of a standard 2x2x2 in. 3-ram sample under a fixed energy load. The compactibility test mimics molding performance and is also used as a sand system control parameter. Compactibility is a quick, repeatable test and maintaining constant compactibility is often the most common process control strategy.

The green compressive strength (GCS) or test green strength (TGS) is defined as the maximum stress during the deformation of the sand sample. The GCS is shown schematically on the compressive stress-strain curve given in Figure 2.3-1. GCS is often the only property measured from a stress-strain test, but additional measurements such as modulus, falling slope, and strain at maximum load can also be measured from a stress-strain curve (Monroe, *et al.*, 2002). Many factors affect the green compressive strength, including sand size, shape, and distribution, the process mulling time, moisture level, and the types and amounts of coal, cereal, soda ash and other additives.

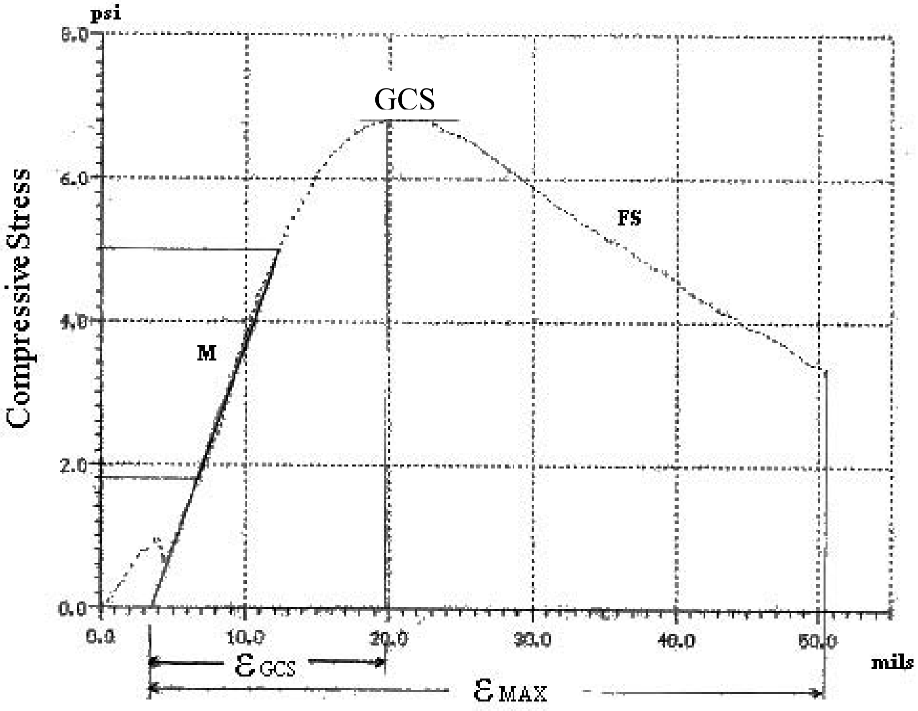


**Figure 2.3-1: A typical compressive stress-strain curve for greensand (Monroe, 2001).**

The percent moisture test (%TM) measures the mass percent of water present in a standard sample of green sand. Controlling the moisture content of green sand within tight limits is critical to maintain mold properties. Since water interacts with different clay types and clay percentages differently, the best combination of clay type, clay amount and moisture is chosen by each individual foundry to achieve the desired properties (Granlund, 1999).

The methylene blue (%MB) clay test estimates the amount of active or live clay in the sand system. The methylene blue dye is only absorbed by clays that can undergo cation exchange (i.e. they can still be activated by moisture). MB dye is not absorbed by dead (or calcined) clay, which is clay that was directly exposed to very high temperatures during molten metal casting and can no longer be reactivated with water (Krysiak, 1994). Injured clays are active clays that, although give a methylene blue indication, are not as easily reactivated during typical mulling cycles. Difficulties in reactivation during mulling are thought to be due primarily to organic contamination on the surface of the clays caused by decomposition of carbonaceous additives and core binders. The intensity of the ultrasonic stirring during MB clay testing is sufficient to activate some injured clays even though typical mulling may not fully activate these injured clays. Because of this, measurements of MB clay may sometimes overestimate the clay percentages that are effectively activated during foundry mulling cycles. In addition, methylene blue can also be adsorbed by activated carbon. Activated carbon produced by the advanced oxidation process will also create overestimations of the amount of live clay in the system.

The four primary green sand tests, %TC, TGS, %TM, and %MB, are the principle indicators of sand system performance. Additionally, many secondary empirical performance parameters have been developed and are used in conjunction with the primary sand tests to further characterize system performance. Table 2.3-1 provides a list of these parameters, their formulas, and a description of what they measure.

**Table 2.3-1: Additional green sand system performance measures.**

| | |
|---|---|
| **Test Properties:** | 1. Methylene Blue (**%MB**); 2. Test Moisture (**%TM**); 3. Test Compactibility (**%TC**);<br>4. Test Green Strength (**TGS**), psi |
| **Reference Properties:** | |
| 5. Available Clay or Available Bond (**%AC**,**%AB**) | %AC = 0.105 x **TGS** + (1.316 x **%TM**)<br>Percent clay based on %TC and TGS curves developed from new clay and silica sands. Estimates the %clay in the sand that **is available** for developing molding properties for a given %TM and TGS. |
| 6. Effective Clay or Working Bond (**%EC**, **WkB**) | %EC = (15.29 x **TGS)** / (132.1 - **%TC**)<br>Percent clay based on %TC and TGS curves developed from new clay and silica sands. Estimates **the actual** %clay in the sand that is producing the molding properties for a given %TC and TGS. |
| 7. Moisture Green Strength (**%MGS**) | %MGS = (4.52 x 10^(1 / (2.5887 - 1.155 x log(**%TM**) - 0.5635 x log(**TGS**))) + 4.075) / 6<br>Percent clay that is based on an extension of the %AC equation to include a wider % clay range, coal additions, and improved mulling. Estimates the %clay in the sand that **is available** for developing molding properties from a given %TM and TGS. (equivalent to available clay) |

| | |
|---|---|
| 8. Compacted Green Strength (**%CGS**) | $\%CGS = [(\mathbf{TGS} + 9.56 - 0.0971 \times \mathbf{\%TC}) / (11.25 - 0.1 \times \mathbf{\%TC})] \times 100$<br>Percent clay that is based on an extension of the %EC equation to include wider % clay range, coal additions, and improved mulling. Estimates **the actual** %clay in the sand that is producing the molding properties from a given %TC and TGS. (equivalent to effective clay) |
| 9. Equilibrium Moisture (**%EM**) | $7 < \%MB < 11$ and $\%TC > 47.5$: $\%EM = \mathbf{\%MB} / (3.213 - 0.02525 \times \%\mathbf{TC})$<br>$7 < \%MB < 11$ and $\%TC < 47.5$: $\%EM = \mathbf{\%MB} / (2.583 - 0.01185 \times \mathbf{\%TC})$<br>The moisture in a fully processed sand at a specific %TC. In a fully processed sand, %TM = %EM. |
| 10. Equilibrium Compactibility (**%EC**) | $7 < \%MB < 11$ and $TC\% > 47.5$: $\%EC = (\mathbf{\%MB} / \mathbf{\%TC} - 3.213) / (-0.02525)$<br>$7 < \%MB < 11$ and $TC\% < 47.5$: $\%EC = (\mathbf{\%MB} / \mathbf{\%TC} - 2.583) / (-0.01185)$<br>The compactibility of a fully processed new sand at a specific %TC and %MB. |
| 11. Equilibrium Clay-Water Ratio (**ER**) | $ER = \mathbf{\%MB} / \%EM$<br>$\%TC < 47.5$: $ER = 2.583 - 0.01185 \times \mathbf{\%EC}$<br>$\%TC > 47.5$: $ER = 3.213 - 0.02525 \times \mathbf{\%EC}$<br>The ratio required to produce a specific %TC for a fully processed new sand at a specific %MB and %TC. A good measure of the availability of moisture for producing compactibility. |
| 12. Equilibrium Green Strength (**EGS**) | $7 < \%MB < 11$ and $30 < \%EC < 60$:<br>$EGS = 224.5 / (\mathbf{\%TM} \times \log \%EC) + (4.13 \times \mathbf{\%MB} - 33.1)^{1.1}$<br>$7 < \%MB < 11$ and $30 > EC$:<br>$EGS = (143.1 + 13.5 \times \mathbf{\%MB}) / (\mathbf{\%TM} \times \log \%EC) + 2 \times \mathbf{\%MB} - 21$<br>$4 < \%MB < 6.5$ and $30 < \%EC < 50$:<br>$EGS = (12.76 \times \mathbf{\%MB} - 31.5)^{1.333} \times [1 / (\mathbf{\%TM} \times \log \%EC)] + 10.73 - 1.66 \times \mathbf{\%MB}$<br>$4 < \%MB < 6.5$ and $50 < \%EC$:<br>$EGS = (12.76 \times \mathbf{\%MB} - 31.5)^{1.333} \times [1 / (\mathbf{\%TM} \times \log \%EC)] + (14.48 - 2.445 \times \mathbf{\%MB})^{1.6}$<br>$4 < \%MB < 6.5$ and $\%EC < 30$:<br>$EGS = (12.76 \times \mathbf{\%MB} - 31.5)^{1.333} \times [1 / (\mathbf{\%TM} \times \log \%EC)] + 10.73 - 1.66 \times \mathbf{\%MB}$<br>Strength of a fully processed new sand at a specific %MB, %TC, and %TC. |
| 13. Test Ratio (**TR**) | $TR = \mathbf{\%MB} / \mathbf{\%TM}$<br>The tested clay-moisture ratio. |
| 14. Moisture Compactibility Clay (**%MC**) | $\mathbf{\%}MB > 6.8$ and $\mathbf{\%}TC < 47.5$: $\%MC = \mathbf{\%TM} \times (2.583 - 0.01185 \times \mathbf{\%TC})$<br>$\mathbf{\%}MB > 6.8$ and $\mathbf{\%}TC > 47.5$: $\%MC = \mathbf{\%TM} \times (3.213 - 0.02525 \times \mathbf{\%TC})$ |

## Calculated Parameters:

| | |
|---|---|
| 15. Mulling Efficiency (**%ME**) | %ME = %EC / %AC -or- %ME = %CGS / %MGS<br>Percent efficiency based on the extent of clay activation as defined by %EC or %CGS approaching %AC or %MGS. Measures the extent to which the properties of the processed sand approach the equilibrium properties of a fully processed new sand. |
| 16. System (Strength) Processing Efficiency (**%SPE**) | %SPE = %MGS / **%MB**<br>Percent efficiency based on the extent of clay activation as defined by %MGS approaching %MB. Measures the extent to which the properties of the processed sand approach the equilibrium properties of a fully processed new sand. |
| 17. Compactibility Efficiency (**%CE**) | %CE = **%TC** / %EC<br>Percent efficiency based on the extent of compactibility development (activation) as defined by %TC approaching %EC. Measures the extent to which the properties of the processed sand approach the equilibrium properties of fully processed sand. |
| 18. Green Strength Efficiency (**%GSE**) | %GSE = **TGS** / EGS<br>Percent efficiency based on extent of green strength development (activation) as defined by TGS approaching EGS. Measures extent to which the properties of the processed sand approach equilibrium properties of fully processed sand. |
| 19. Moisture Index (**%MI**) | %MI = ER / TR -or- %MI = **%TM** / %EM<br>An index to describe the moisture of the sand at any given compactibility as: moisture starved (MI<88%), moisture deficient (MI<100%), or moisture saturated (MI=100%) sands. Compares the %TC to the moisture of a fully processed new sand mixture of equal compactibility. |
| 20. Compactibility Index (**%CI**) | %CI = **%TC** / %EC<br>Compares the %TC with the compactibility of fully processed new sand mixtures of equal percent moisture. Similar to moisture index. |
| 21. Equilibrium Clay Parameter (**ECP**) | ECP = **%TM** x log %EC x EGS<br>4 < **%MB** < 6.63: ECP = 50.2 x **%MB** - 137<br>6.63 < **%MB** < 9.0: ECP = 22.6 x **%MB** + 46<br>**%MB** < 9.0: ECP = 27.85 x **%MB** – 1.25<br>Measure of the extent to which the clay has been activated by moisture and processing. |
| 22. Test Clay Parameter (**TCP**) | TCP = **%TM** x log **%TC** x **TGS**<br>Test parameter, related to the amount of **%MB** clay activated |

| | |
|---|---|
| 23. Available Methylene Blue (**%AMB**) | 4 < **%MB** < 6.63: %AMB = (TCP + 137) / 50.2<br>6.63 < %MB < 9.0: %AMB = (TCP +46) / 22.6<br>**%MB** < 9.0: %AMB = (TCP + 1.25) / 27.85<br>Closely related to %MGS but is a better measure of clay activation because it includes %TC in its calculation (see TCP). Will always be lower than **%MB**, except in a fully processed sand. |
| 24. Effective Methylene Blue (**%EMB**) | 40:1 Clay/Cereal Ratio: %EMB = 0.9331 x **%MB** – 0.3021<br>1% Cereal: %EMB = 0.667 x **%MB** + 0.7667<br>Percent clay corrected for the effect of cereal on **%MB** |
| 25. Clay Processing Efficiency (**%CPE**) | %CPE = %AMB / **%MB**<br>An improved efficiency based on a measure of clay activation by %AMB. A possible improvement on %SPE. |

## Additional Emission Parameters:

| | |
|---|---|
| 26. Active Clay Ratio (**ACR**) | %AMB / AFS Clay |
| 27. Burnout Ratio (BR) | %AFS Clay / (100 - %AFS Clay) |
| 28. Fixed Carbons | LOI@1800 - Volatiles@1200 |
| 29. Inorganics | AFS Clay + Post Wash LOI - LOI@1800 |
| 30. Dead Clay | Inorganics - MB Clay |
| 31. AFS Clay – MB Clay | AFS Clay – MB Clay |

**References:**

1. Heine and Green, 1989.
2. Heine, Green, and Shih, 1990.
3. Green and Heine, 1990.
4. Green and Heine, 1991.
5. Heine and Green, 1992.
6. Heine, Green, and Kotschi, 1993.
7. Headington, Rothwell, Green, and Heine, 1998.

### 2.3.3 The Green Sand Molding Cycle

A metal casting process utilizing green sand molding consists of four primary steps—sand mulling, molding, pouring, and shakeout/return. New molding materials are added to the recycled sand and mulled (mixed) to recondition the sand and develop mold properties. The sand is pressed and shaped into a mold, cores are added if required, and the molten metal is poured. The heat from the molten metal raises the temperature of the mold sand. In the areas around the mold-metal interface where the temperatures are especially extreme, the clay, which is "calcined" above 600-700°C, and coal can be degraded or destroyed. After casting, the molds travel through a cooling line where most of the gaseous emissions from coal and core binder decomposition are released. The molds are then shaken out and a vibratory shaker or drum is used to separate the sand from the metal casting. The hot, dry sand from the drum is sent to a cooler where it is further cooled and re-moisturized through water additions. The cool, moist sand is returned to the muller where clay, coal, and water are added to make up that which was lost in the casting process, and the entire process is repeated. Figure 2.3-2 depicts the typical routing of green sand through the casting process.

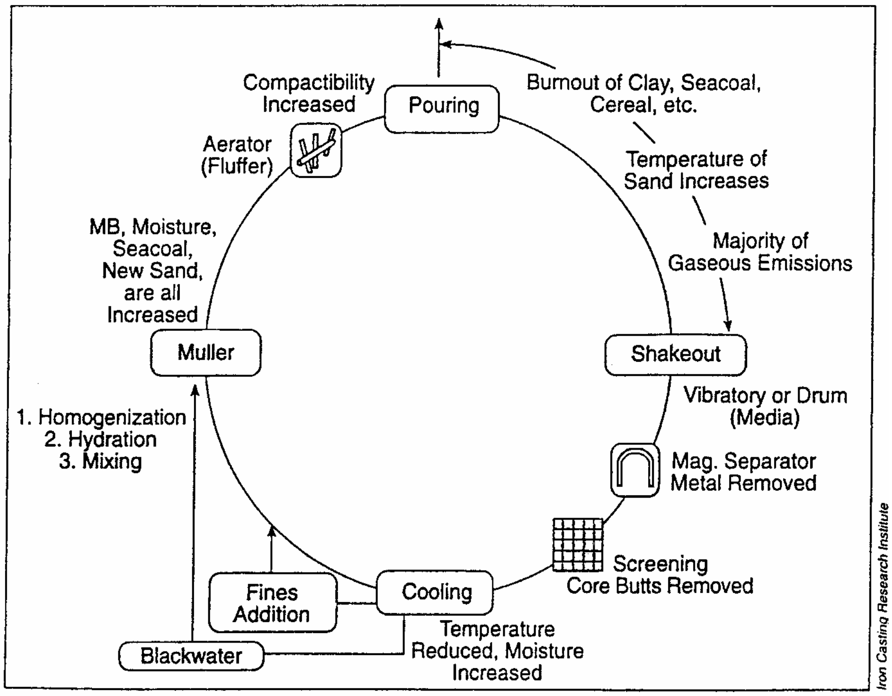


Figure 2.3-2: The molding cycle (Green Sand Molding Committee, 1999).

Proper mulling is required to thoroughly incorporate new raw materials, to reactivate clay, and to recondition the molding sand. The mulling time is critical in the development of mold properties. "Undermulling" does not allow the sand to develop its full properties, while "over-mulling" is costly and can also degrade the sand and the sand processing equipment. The mulling time has to be long enough to disperse the water into the clay and develop the bonding mechanisms to the proper extent (Carey, 1999).

Mull-down curves show the development of green sand properties as a function of mulling time at given moisture levels. Full properties are developed only after "complete" mulling. Figure 2.3-3 is an example of a typical mull-down curve showing compactibility development with time. The development of green compressive strength over time shows a similar relationship.

The percentage of moisture in green sands is another critical element of property development. The water content affects every property of a molding sand mixture. Green and Heine (1991) and other researchers have classified green sands as either moisture starved, moisture deficient, or moisture saturated. The correct amount of water gives the sand its best workability and moderate deformation. Excessive water not only leads to steam and gas formation within the mold cavity, but it also leads to overweight and oversized castings. Excess water can also create extreme oxidizing conditions, as well as unfavorable mold properties such as low permeability, high dry strength, low hardness, poor flowability, and high hot compressive strength.

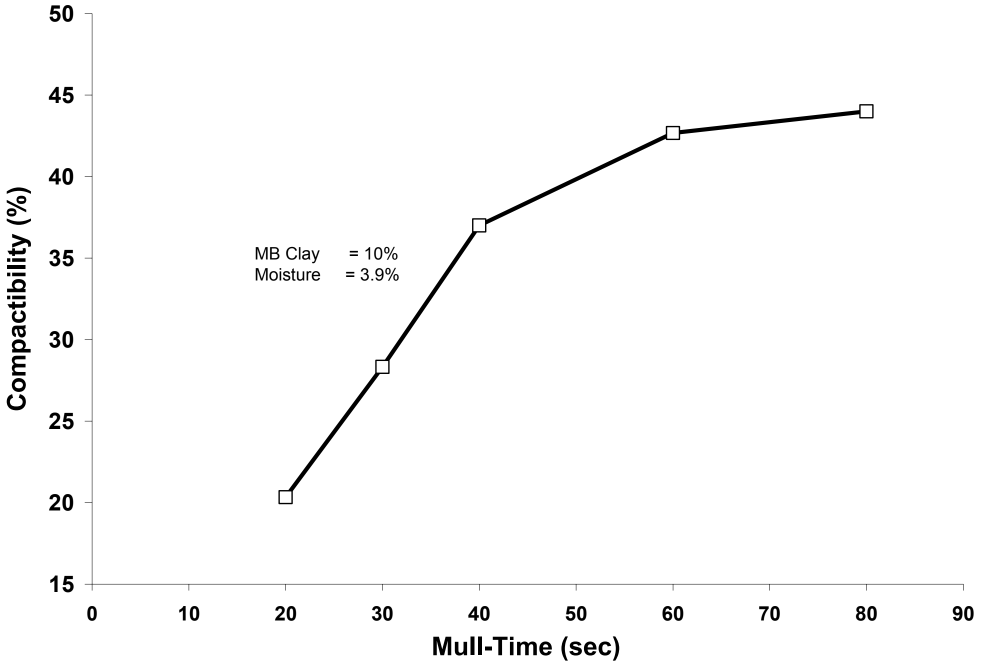


**Figure 2.3-3: Typical compactibility mull-down behavior for a greensand.**

Maintaining proper water/clay relationships is critical to the control of mold properties. The plasticity of clays is intimately linked with the amount of water associated with the clay. The proper water percentage required in green molding sand is a complex relationship that depends on the amount and type of clay present and the desired mold properties. Optimum water/clay ratios for western bentonite bonded green sand systems are typically between 35 and 45% by weight.

Temper curves illustrate the influence of moisture content on the properties of fully mulled green sands. Figure 2.3-4 shows typical compactibility temper curves for sands using two different types of clay. By characterizing both the mull-down and temper curve behaviors of green sands, sand system performance and control can be better understood.

## 2.3.4 Sand system control

Each green sand system in the foundry industry is unique. The best way to control a sand system is to determine the properties of the green sand when the system is running well and good castings are being produced. Operational difficulties can in foundries if the sand is not fully characterized until casting problems begin (Hoyt, 1996). Regular sand system testing and control helps to reduce the variability in the system, and ultimately results in higher quality castings.

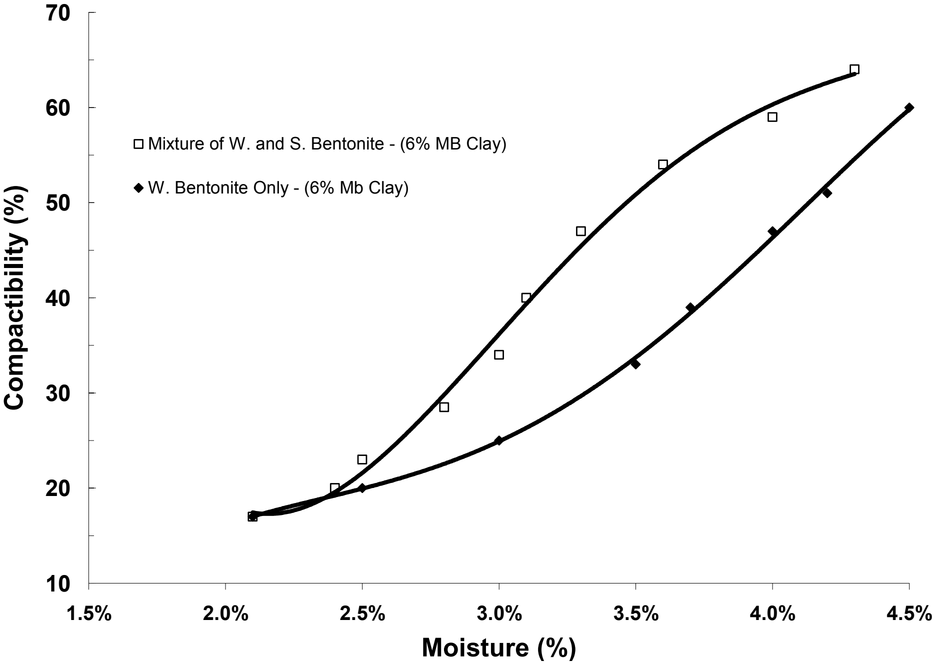


**Figure 2.3-4 Effect of percent moisture on compactibility on sands with different clay types after eight minutes of mulling (R. W. Heine and J. S. Schumacher, 1977).**

Five main sand properties—green compressive strength, moisture, compactibility, calculated clay, and moisture-to-methylene blue clay ratio are used in combination as process control parameters. The interaction of these five properties is very important. Heine and Schumacher (1977), Shih, *et al*. (1986), and Heine, *et al.* (1990) have done extensive research to develop fundamental relationships between these properties. These relationships are extremely useful for tracking and controlling the green sand molding process.

Green sand control is typically aimed at controlling compactibility in a range suitable for molding. However, many different green sand formulations can have similar compactibilities, even though the resultant mold and casting qualities can be drastically different. Thus, compactibility control alone is not always sufficient. Green and Heine (1990) have developed a number of empirical relationships, based on the above primary sands tests, to fully characterize green sand and its molding properties. They propose that these parameters (included previously in Table 2.3-1) can be used in control strategies to accurately characterize green sand and provide consistent molds and castings.

# 3. RESULTS

The research results for this initial study of the effects of advanced oxidation on green sand systems will be presented individually for each phase of the overall research effort as follows:

3.1 – Emissions Performance — Pilot-Scale Laboratory Studies
3.2 – Emissions Performance — Bench-Scale Studies
3.3 – Emissions Performance — Plant Trials and Pre-Production Tests
3.4 – Sand System Performance — Laboratory Studies
3.5 – Sand System Performance — Plant Trials

## 3.1 EMISSIONS PERFORMANCE – PILOT-SCALE LABORATORY STUDIES

The Penn State University laboratories have been equipped with a pilot-scale foundry that is capable of producing green sand molds and melting iron. The Penn State team adapted this facility so that it could generate advanced oxidant treated water and monitor emissions during the metal casting process. Tests compared the use of tap water versus advanced oxidant treated water as the source of moisture in greensand. Molten metal was poured into the green sand molds, and the emissions were monitored during pouring, cooling and shakeout.

### 3.1.1 Initial Emissions Capture Studies

#### 3.1.1.1 Introduction

Full scale parametric testing of advanced oxidation may only be taken to a limited level of departure from standard operating conditions because of the underlying issues of production and cost. For example, a high-production foundry that is generating 500-700 tons of castings a day would not be able to operate its green sand system with an excessively high moisture level, because such action might cause excessive scrap, even if important research questions could be answered. However in contrast, our Penn State laboratories do not face these "final product" issues, so castings can be made while employing a broader range of molding and casting protocols. It was with this thought in mind that pilot scale experiments were designed to test the effect of AO on green sand emissions. The Penn State team built an emissions capture chamber that borrowed from earlier designs used by CERP-Technikon and LaFay, *et al*. The final design of the capture chamber was tested for reproducibility and repeatability in a series of several tests.

### 3.1.1.2 Material and Methods

The advanced oxidation system at Penn State allowed the team to combine hydrogen peroxide, ozone, ultrasonics, and underwater plasma (UWAP) treatment to tap water. These treatments could be tested separately or in combination with one another.

### 3.1.1.3 Results and Discussion—Accuracy and Repeatability Assessment

Penn State conducted pilot-scale foundry pours to meet several objectives. First, the initial pours helped develop a method of emissions capture that prevented breakthrough of emissions in the granular activated carbon (GAC) slipstream tube. Second, pilot-scale pours helped develop a method of emissions collection that generated repeatable results in slipstream capture. This was to prepare the way for pilot scale tests that compared AO versus non-AO conditions. The full materials, methods, and protocol for these pilot tests are described in the Masters Thesis of Neill (2001) and Hoffman (2002).

To properly monitor foundry stack emissions, GAC slipstream tubes must capture emissions so that the back portion of the trap retains less than 10% of the total emissions (U.S. EPA Method 18 (2000)). Several initial pilot-scale foundry pours were conducted to determine the air flow rate and the volume of GAC that would prevent breakthrough. The green sand for these experiments originated from Wheland foundry in Chattanooga, TN. This green sand had been used in an advanced oxidation blackwater system, and it contained a loss on ignition (LOI) of 3-3.5% (thus 3-3.5% of the green sand is coal or other organic materials and hydrated water). The Penn State group air-dried this green sand to 1-1.5% moisture, and then employed the pilot-scale advanced oxidation-underwater plasma (AO-UWAP) system to moisturize these green sands to 3.5-4% moisture. Iron was poured into these molds with a flat plate shape; (9” x 7” x 3/4”); and a sand-to-metal ratio of 65:17 lbs. Slipstream analysis showed that no emissions were collected on the back section of the GAC tube. Therefore, the flow rate of 60 milliliters (mL) per minute through 1.5 mL of GAC in the slipstream tube was appropriate for emissions capture.

An important fact to mention about the slipstream emissions data is that it has been normalized to the air volume that passed through the full capture GAC. Specifically, the mass of emissions collected on the slipstream GAC tubes have been multiplied by 3,000 to normalize the data. Slipstream repeatability data, as determined by gas chromatography-flame ionization detection (GC-FID), is shown in Figures 3.1-1 and 3.1-2 for total VOC and benzene emissions. As observed from these figures, total $VOC_{H-(C6-C14)}$ emissions averaged 0.1 lb/ton of metal poured, and benzene emission averaged 0.014 lb/ton of metal poured. Thus, benzene emission represented 14% of all monitored emissions.

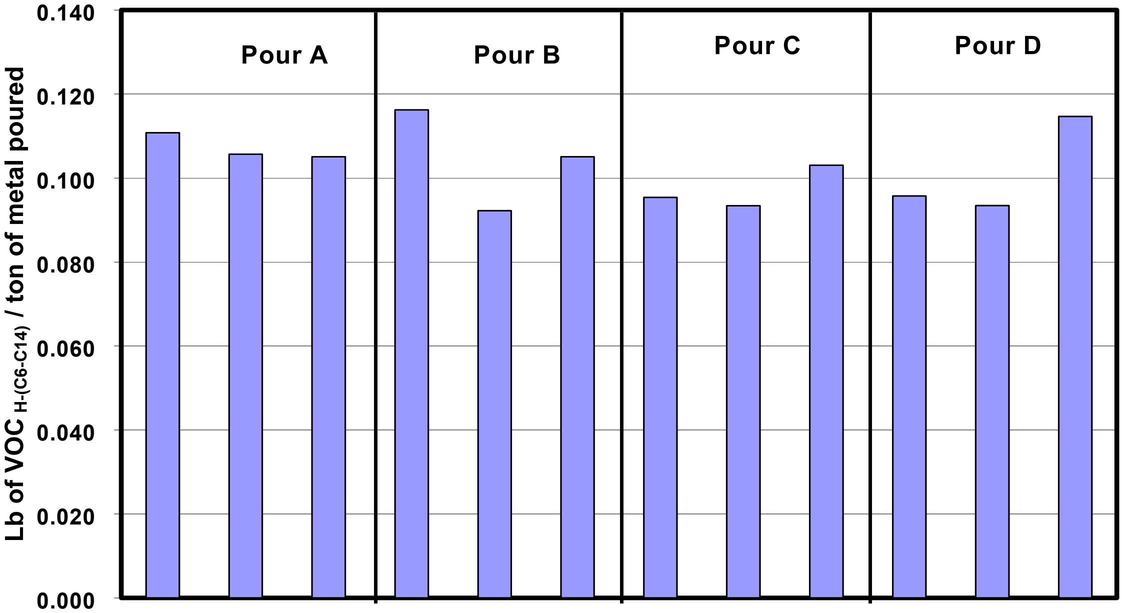


**Figure 3.1-1: Slipstream VOC H-($C_6$-$C_{14}$) emissions (lb/ton of metal poured) from repeatability test trials.**

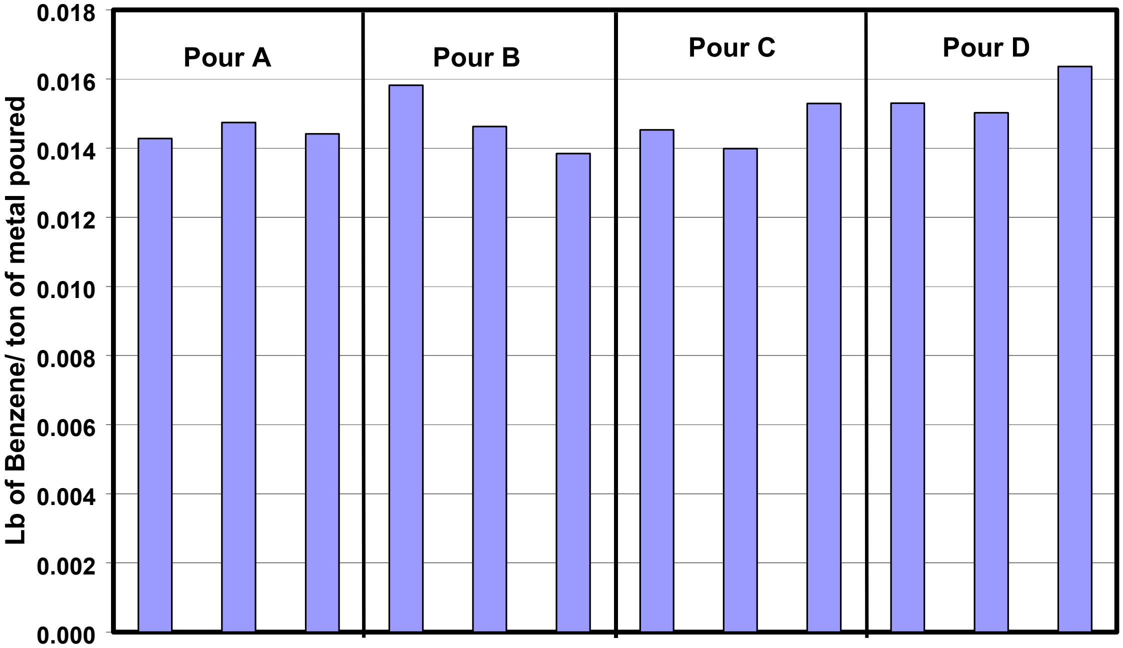


**Figure 3.1.-2: Slipstream benzene emissions (lb/ton of metal poured) from repeatability test trials.**

A statistical analysis of the emissions data from the slipstream capture was conducted to determine sample and total experimental error. The coefficient of variance (CV) was determined for each experiment and the total set of experiments to quantify the errors. CV is the sample population standard deviation divided by the sample mean times 100. Table 3.1-1 displays the summary of the statistical analysis of the reproducibility and repeatability experiments.

**Table 3.1-1: Within sample and among-sample coefficient of variance (CV) for slipstream repeatability experiments A, B, C, and D.**

| Experiment | Slipstream Sample CV (VOC) | Slipstream Sample CV (Benzene) |
|---|---|---|
| **Within A** | 2.94 | 1.67 |
| **Within B** | 11.51 | 6.72 |
| **Within C** | 5.24 | 4.49 |
| **Within D** | 11.52 | 4.55 |
| **Among Sample (among A-D)** | 8.30 | 5.01 |

Overall, the repeatability of the experiment proved satisfactory. Within the casting and emissions capture processes, slight variations in the myriad of variables can have a considerable influence over the final results. The sand is a very heterogeneous mixture and two molds from the same batch of green sand could have different properties. By quantifying the error that could be expected from the experiments and including it in future analysis, sounder conclusions on the emissions differences could be drawn. The next stage of testing involved thermally treating green sand prior to pouring.

## 3.1.2 Thermal Treatment Trials

### 3.1.2.1 Introduction

As green sand is recycled through the metal casting process a fraction of it undergoes fundamental changes: a small fraction of the coal is changed to GAC (Landis 1996), some of the clays are inactivated, and some of the organics (coal, core resin and cereal) are pyrolyzed. The full effect of a system change may not be seen through one turn (cycle) or even several turns of the metal casting process. A turn represents the cycle of moisturizing the green sand, forming the mold, pouring the gray iron into the mold, shaking the mold out, and then adding make-up materials for the next cycle. For example, Volkmar, *et al*. (1997) felt that it was appropriate to allow a system to stabilize for three months before data analysis. This would have allowed for hundreds of turns of the system. Many turns are not possible in the pilot setting since the tests are often labor-intensive and costly; however the benefits of turns need to be quantified. It was with this in mind that Penn State researchers decided to try a heat pre-treatment protocol to simulate exposure to the temperatures of the mold environment.

### 3.1.2.2 Materials and Methods

Portions of the green sand were placed in an oven and exposed to three different temperatures (ambient, 350°C and 675°C) to partially simulate some of the elevated temperature effects that green sands experience during molten iron pouring. This was done rather than actual cycle experiments in an effort to save time, as the research team was soon going to loose access to the pilot foundry (for 18 months) until a new one was built. The green sands were immersed in a nitrogen atmosphere during the thermal treatment to prevent combustion of the organics. The green sand was separated into three approximately equal batches, each receiving a different thermal treatment: ambient, 350°C or 675°C.

These experiments used a non-AO treated green sand from Wheland Foundry's Broad Street plant with an LOI of 4.5%. The green sand was air-dried to 1-1.5% moisture as before, and excessive moisture (6%) of either tap ("TAP"), AO-treated ($H_2O_2$-150 ppm and ozone) or AO-Under Water Plasma (UWAP) treated water was added to the green sand. The moisturized sand was mulled, packed into stainless steel drums and attached to a nitrogen gas feed. For the 350°C thermal pre-treatment, the assembly was placed in a nitrogen-atmosphere furnace, heated to 350°C, held for 20 minutes, then cooled to room temperature. This thermal pre-treatment was repeated for a total of three cycles. The process for the 675°C treated sand was the same as used for the 350°C sand, however only through one cycle.

After the heat treatments, the thermally-treated sands were mixed together to create nine separate molds, three each for TAP, AO (hydrogen peroxide and ozone), or AO-UWAP treated waters. The molds were therefore comprised of one third untreated sand, one third 350°C-treated sand and one third 675°C-treated sand. For example a tap water mold was made from 21.67 lb of ambient treated green sand, 21.67 lb of 350°C TAP-treated green sand and 21.67 lb of 675°C TAP-treated green sand. After this blend of green sand was created, additional treated water was added to raise the moisture level to 3.5%. The moisture that was used in the thermal pre-treatments was the same as the moisture added. For example, if the green sand received AO water during thermal pre-treatments, AO water was used to form the green sand mold. The molds were shaped the same as for the repeatability experiments.

### 3.1.2.3 Results and Discussion – Thermal Treatment Trials

The results from the slipstream capture of emissions are presented in Figures 3.1-3 and 3.1-4. The figures contain the average result from GC-FID analysis of the emissions captured on the GAC; each bar on this plot represents an average of three injections into the GC-FID. As shown, the $VOC_{H-(C6-C14)}$ emissions for the tap-treated green sands were slightly higher than for the AO-treated or AO-UWAP-treated green sands, and all of these emissions were in the range of 0.6 to 0.9 lb $VOC_{H-(C6-C14)}$ per ton of metal poured. The benzene emissions for the tap-treated green sands were slightly lower than for the AO-treated or AO-UWAP-treated green sands.

The data were examined using the statistical tool, the "t-test." The data from each injection were included in the statistical analysis, not just the average values. The t-test determines whether two samples' means are distinct. The t-test can be used when there is a natural pairing of observations in the samples, such as when two sample groups are tested with only one variable changed (i.e. tap water vs. AO water). This test factors in the within sample error by including the standard deviation in the determination of the critical t-value.

The VOC $_{H-(C6-C14)}$ emissions were analyzed statistically and both the AO treated green sand and AO-UWAP treated green sand were significantly lower, to the 95% confidence level. The AO treated green sand was 11 % lower than the tap treated green sand and the AO-UWAP treated green sand was 20.5% lower than the tap treated green sand. The emission differences are summarized in Table 3.1-2 and presented in Figures 3.1-3 and 3.1-4.

**Table 3.1-2: Summary of results from Penn State thermal pre-treatment experiments.**

| | **Slipstream VOC$_{H-(C6-C14)}$ (lb/ton metal)** | **Slipstream Benzene (lb/ton metal)** |
|---|---|---|
| **Tap** | 0.844 | 0.0347 |
| **AO** | 0.751 | 0.0389 |
| Difference from tap | -11.0%* | 12.1% |
| **AO-UWAP** | 0.671 | 0.0427 |
| Difference from tap | -20.5%* | 23.1% |
| ** Differences that were statistically significant to the 95% confidence level* | | |

The differences between benzene emissions for the TAP and AO-treated greensands were not statistically significant. The Penn State group also conducted full-capture emissions monitoring, which has been presented by Neill (2001). The full-capture trends showed that for both VOCs and benzene, the tap treated greensands exhibited more emissions than either the AO-treated or AO-UWAP-treated green sands.

There are several theories as to why differences were experienced between TAP treated green sand and AO or AO-UWAP treated green sands. The generation of emissions-absorbing material may have the effect of reducing emissions. As mentioned in Chapter 2, activated carbon may be formed from coal in the green sand. The activated carbon can absorb emissions and allow AO reactions to oxidize or completely degrade them to $CO_2$ and water. Reactions may also be taking place with the emissions as they are formed. The oxidant-rich water can react with emissions as they are formed, degrading them via combustion reactions (Kuo and Chen 1996). Another possibility is

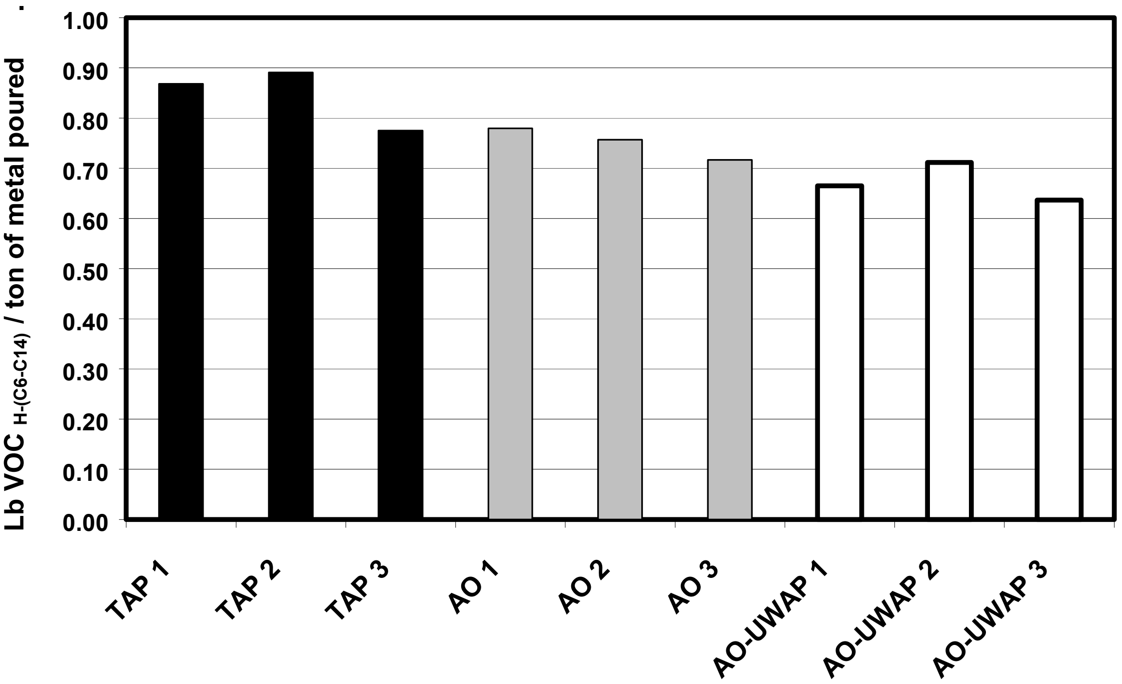


**Figure 3.1-3: Slipstream VOC H-($C_6$-$C_{14}$) emissions (lb/ton of metal poured) from thermally treated green sand test trials.**

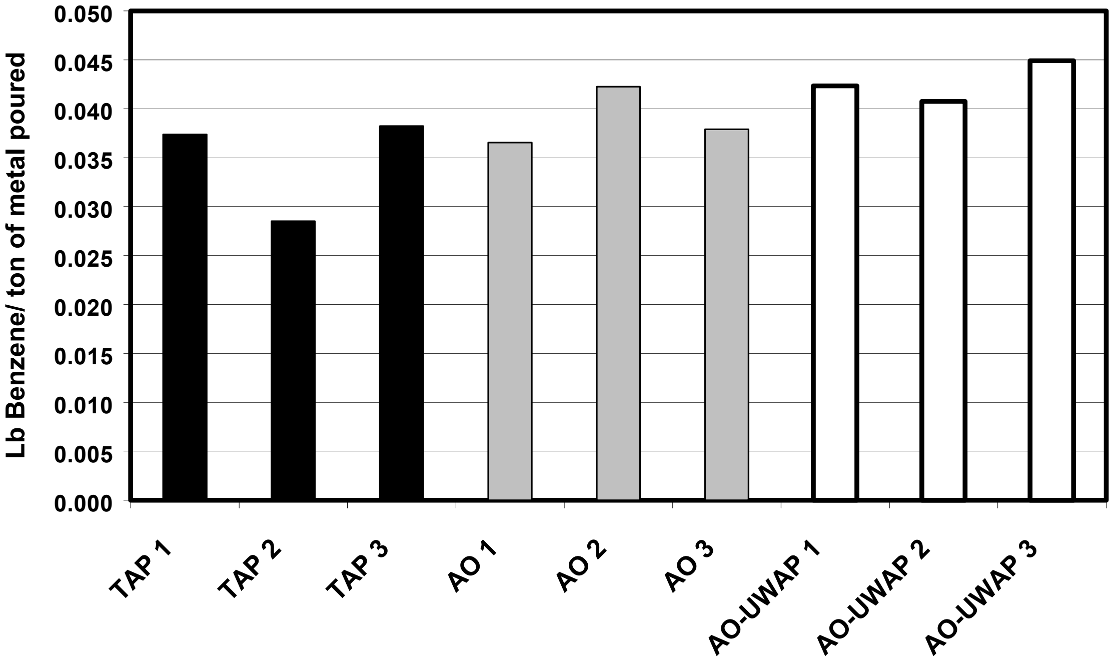


**Figure 3.1-4: Slipstream benzene emissions (lb/ton of metal poured) from thermally treated green sand test trials.**

that radicals were reacting with the green sand after the fresh AO or AO-UWAP moisture was added. These reactions may have fundamentally changed the coal and core resins by fixing some of the volatile emissions into the coal and/or clay matrix.

The difference between AO and AO-UWAP emissions is another interesting issue. AO-UWAP treated green sands had lower $VOC_{H-(C6-C14)}$ emissions than the AO treated sands. This may be due to the compounding effect of multiple advanced oxidation processes. The UWAP assists in the production of radicals and it adds to the total concentration of these radicals in the water. The AO system only utilizes $H_2O_2$, $O_3$ and ultrasonication, and although effective at reducing emissions, it can be enhanced with the addition of UWAP treatment.

It is also interesting to compare the pilot-scale tests that employed the Wheland green sands that had been incorporating an advanced oxidation blackwater (AO-BW) system with the Wheland green sand that had been employing merely municipal (TAP) water. Emissions from Wheland AO-BW green sand that was further treated with AO-UWAP at Penn State were compared to Wheland TAP green sand that was further treated with tap water and some thermal conditioning at Penn State. Both of these green sands were formed into molds; and molten iron was poured into them. The comparison of the emissions that occurred during the resultant pouring, cooling, and shakeout are summarized in Table 3.1-3.

**Table 3.1-3: Comparison of emissions from Wheland AO-BW green sand which was treated with AO-UWAP at Penn State versus Wheland non-AO green sand which was treated with TAP water and some thermal treatment at Penn State.**

| Condition | Slipstream $VOC_{H-(C6-C14)}$ (lb/ton metal) | Slipstream Benzene (lb/ton metal) | Loss-on-Ignition (LOI) |
|---|---|---|---|
| **Non-AO; TAP** | 0.844 | 0.0347 | 4.5% |
| **AO-DBW; AO-UWAP** | 0.105 | 0.0145 | 3-3.5% |
| % Change | 88% | 58% | 20-35% |

This comparison shows that the AO-DBW (sand) / AO-UWAP (water treatment) emissions for total $VOC_{H-(C6-C14)}$ diminished 88% when compared to the non-AO (sand) / tap water green sands, while the benzene emissions diminished 58%. The LOI was only lower by 20-35% for the AO-DBW / AO-UWAP system. It should be noted that this comparison is somewhat confounded: some of the non-AO / tap water green sand also experienced thermal treatments (which should have diminished subsequent emissions – without this confounding effect, the differences in emissions would have been even greater between the non-AO and the AO green sands). Moreover, good records are not available regarding how much core had been used in these two lines just prior to sampling. However, it is known that the two lines made similar parts, and the fraction of core following multiple sand re-circulations was likely similar.

#### 3.1.2.4 Summary of the Thermal Treatment Trials

1. The overall synopsis from these tests was that full-scale green sands did manifest a considerable emission difference between AO versus non-AO conditions.
2. The thermal treatment protocol of exposing the green sand to oven temperatures of ambient, 350°C, and 675°C did not adequately serve as a "short-cut" to mimicking emissions behavior following the multiple turns that a full-scale foundry would experience.
3. Immediately following these tests, the Penn State team lost access to the pilot-scale foundry for 1.5 years, as it was relocated to another building, therefore tests were subsequently focused on bench-scale tests (as discussed in section 3.2).

### 3.1.3 TGA of Mold Autopsies and Full-Scale Foundry Green Sands

Sand testing to evaluate the mass loss response as a function of heating in nitrogen was performed using a Cahn Instruments TG-131 thermogravimetric analyzer (TGA). Inside the TGA, shown schematically in Figure 3.1-5, a computer controls the temperature to follow a pre-seclected program up to 1000°C, while an electronic balance continuously measures the mass of the sample. During tests, the mass loss as a function of temperature and its derivative were used as indicators of the amount and location for emissions or released waters of hydration.

Figure 3.1-6 is a plot of the weight loss and its derivative as a function of temperature for a representative foundry green sand sample. In the region from 25-200°C, a large mass loss occurred due to the release of loosely bound moisture in the sand. Little mass loss occurred between 200-350°C resulting in a plateau in temperature regime. To account for the moisture in the sample, the sample mass at 230°C was defined as the "dry mass". From 350 to 1000°C, the sample mass loss represented the release of (a) VOCs from the organics, (b) strongly bound waters of hydration from the clay, and (c) possibly some oxygen group release from the carbon in the sample. The derivative plot in Figure 3.1-6 shows the three main mass loss regions that were centered at 100, 450, and 625°C.

#### 3.1.3.1 TGA Tests on the Green Sand Constituents

Initial TGA tests monitored mass loss behavior of the individual green sand components. The green sand is typically comprised of silica sand (70-80%), clay (8-10%), coal (2-5%), water (3-4%), and organic filler such as cereal (<0.5%). Figures 3.1-7 to 3.1-9 identify the mass loss behavior of these individual green sand constituents. The data in Figure 3.1-7 is presented in the format of mass loss, while Figure 3.1-8 depicts the derivative of mass loss. The primary mass loss of coal (which causes much of the VOC and HAP emissions) occurred between 400 and 500°C. The mass loss from the

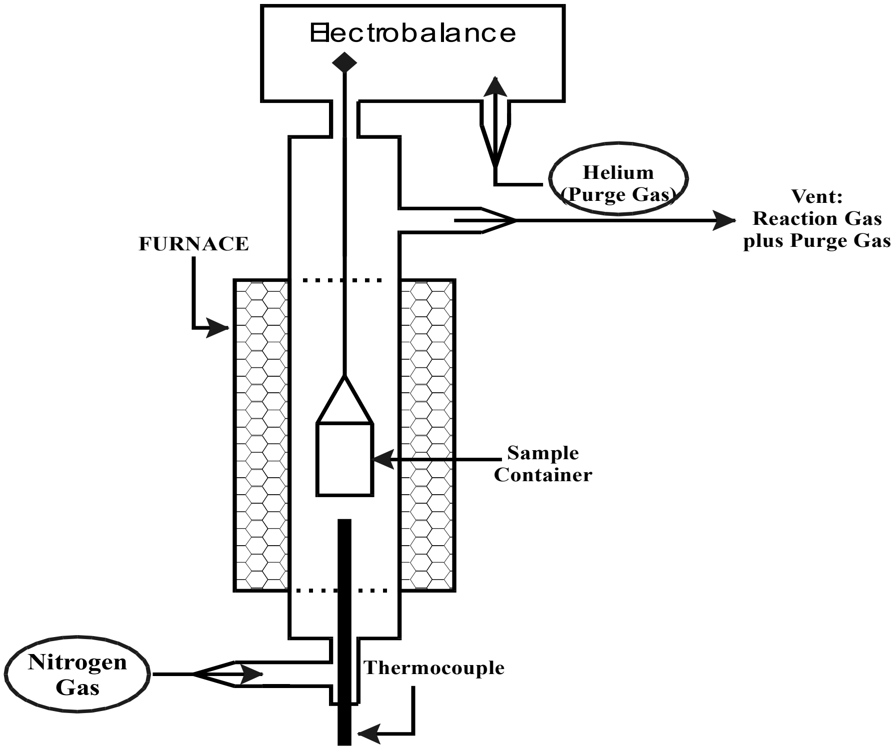


Figure 3.1-5: Schematic of a thermogravimetric analyzer.

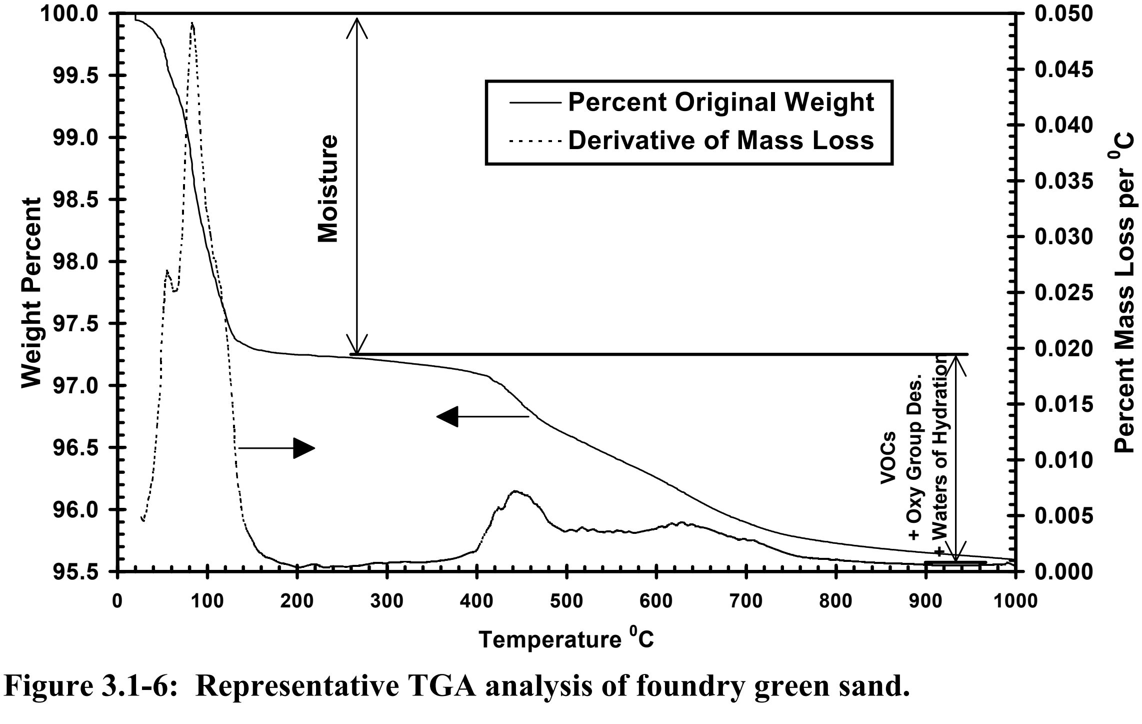


Figure 3.1-6: Representative TGA analysis of foundry green sand.

clay represented mostly the loss of waters of hydration and it occurred between 500 and 800°C. As can be seen from Figure 3.1-9, a TGA derivative mass loss plot for a foundry green sand, the coal mass loss corresponded to the peak at 450°C and the clay mass loss corresponded to the peak at 625°C. The cumulative losses at 550°C and 1000°C and the derivative at 450°C were used as a relative indicator of the green sand's ability to emit VOCs and HAPs. The derivative at 625°C was used as a relative measure of the waters of hydration bound in the clay in the green sand.

- Tracking Potential Sand Testing Emissions at Operating Foundries:

The capacities for green sand emissions for two casting lines at Neenah Foundry were tracked using TGA testing. Both casting lines operated with the same sand mixing and sand molding equipment, but one line (Plant 3) had integrated AO-CW treatment into the molding process. The other process line (Plant 2) had not yet been equipped with an AO system at the time of these comparisons (but it has subsequently been equipped with an AO-DBW system). The green sand from the casting line that used AO treatment averaged roughly 10% less mass loss than the one without AO treatment, as shown in Figure 3.1-10. The decreased mass loss occurred in the 400-500°C temperature region (the region best correlated to mass loss from the coal) as exhibited by the derivative comparison in Figure 3.1-11. In the region where mass loss is expected from the release of waters of hydration (centered at 625°C), little difference was observed in the mass released.

### 3.1.3.2 Autopsies of Pilot-Scale Molds

Iron casting tests were performed in order to evaluate the effect that advanced oxidants have on emissions. Iron was poured into a pair of green sand molds that had been moisturized with either TAP water or AO water. After cooling, the green sand was autopsied with respect to distance from the mold. These were open-faced molds and samples were taken from both sides of a casting in order to provide duplicate samples. Naturally, the temperature experienced during casting by the sand decreased with distance from the casting. The temperatures experienced by the mold dropped off quickly with distance from the casting surface, as shown by the results in Table 3.1-4.

TGA analysis of autopsy sand samples determined the change in volatile content of the sand as a function of distance from the mold surface. The autopsy analysis was determined for untreated and AO-treated green sands. The pair of molds used here were formed from green sand from a Neenah foundry line that did not incorporate an AO system. At Penn State, the AO water that was added contained hydrogen peroxide (300 ppm) and dissolved ozone (but no sonication). TGA tests on the autopsy samples determined the mass loss as a function of increasing temperature as shown in Figures 3.1-12 (TAP-treated sand) and 3.1-14 (AO), and its derivative with respect to temperature as shown in Figures 3.1-13 (TAP) and 3.1-15 (AO). The derivative of mass loss at 450°C was used to compare the relative potential for emissions of the autopsied sand in Figure 3.1-16.

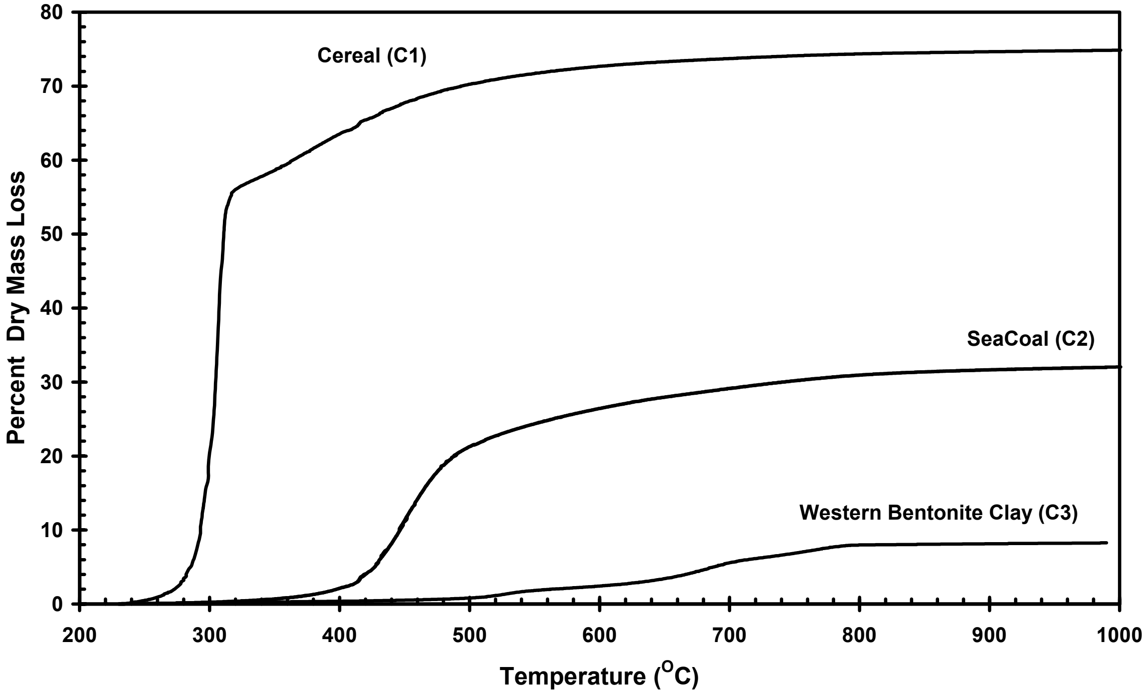


Figure 3.1-7: Dry mass loss of green sand constituents.

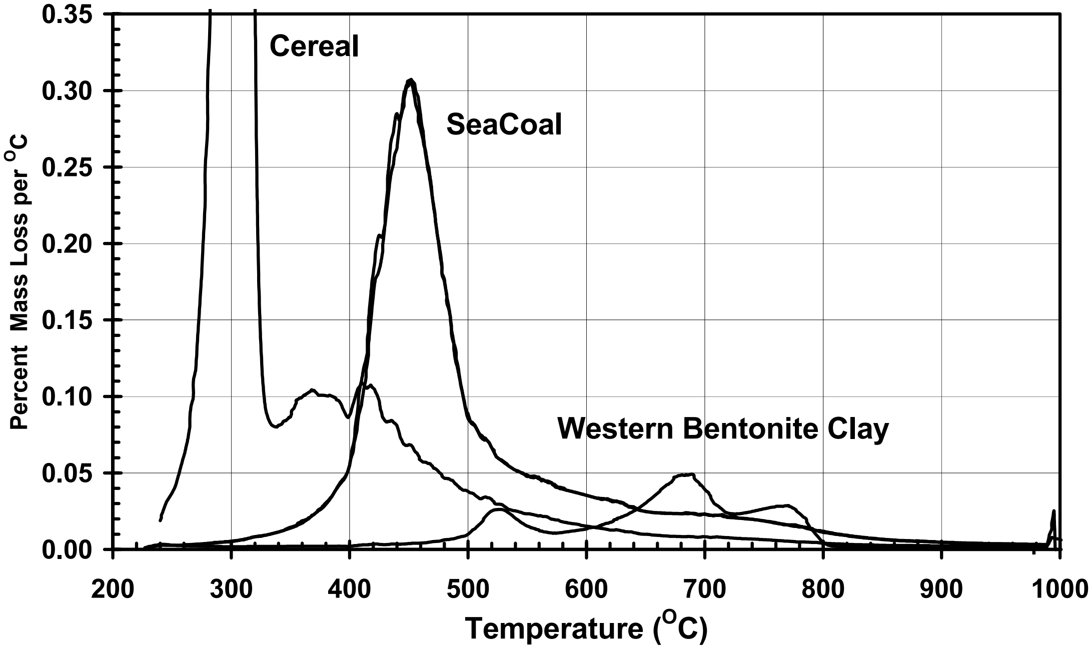


Figure 3.1-8: Derivative mass loss rate of green sand constituents.

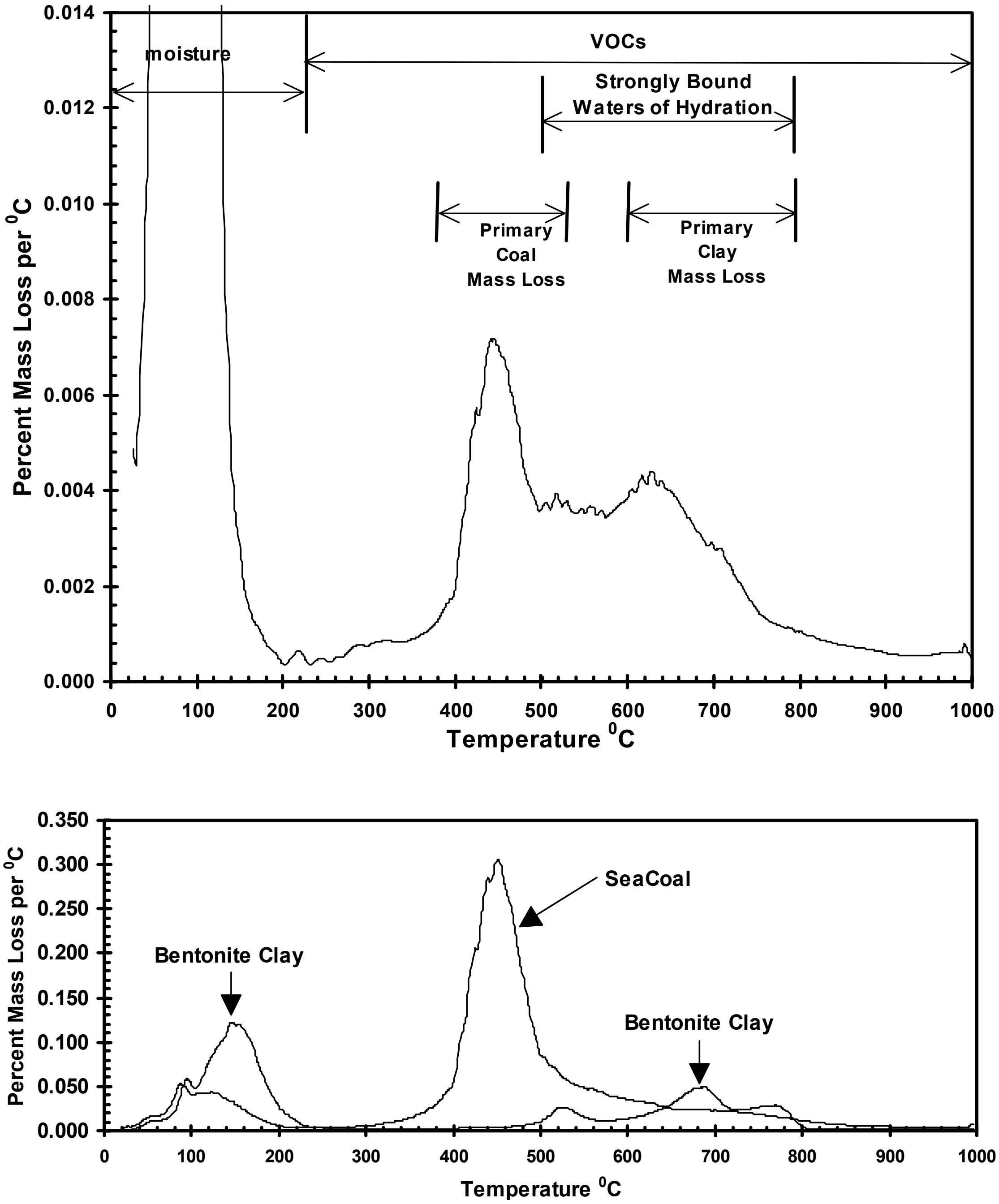


**Figure 3.1-9: Comparison of a TGA derivative mass loss plot for a foundry green sand.**

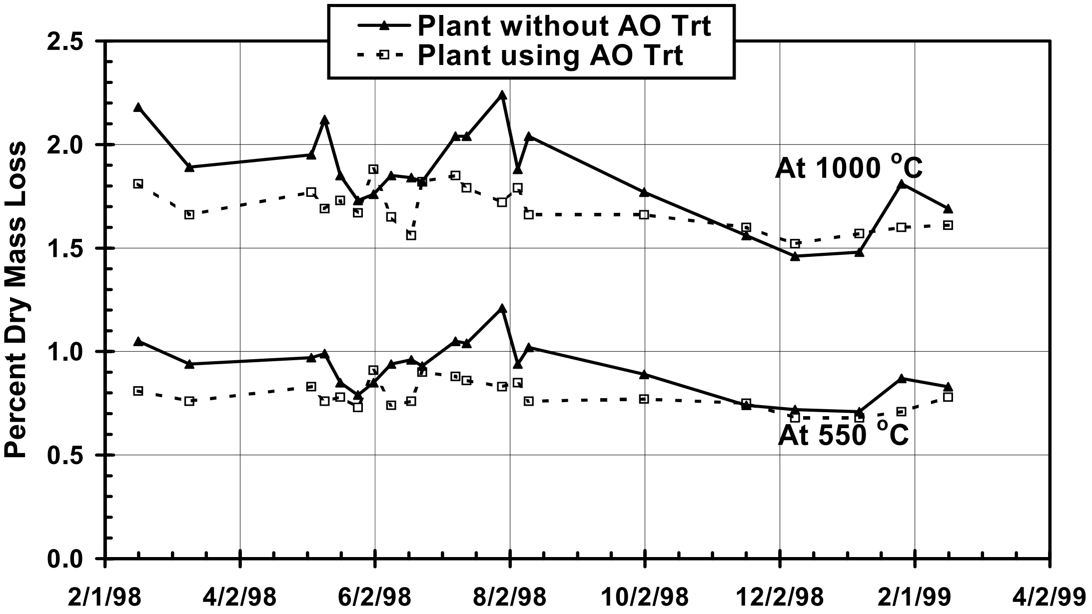


**Figure 3.1-10: Cumulative dry mass loss of Neenah Foundry DISA line green sand samples: total TGA dry mass loss up to 550°C (attributed to VOC release from coal), or up to 1000°C (attributed to VOC release from coal plus released waters of hydration from the clay).**

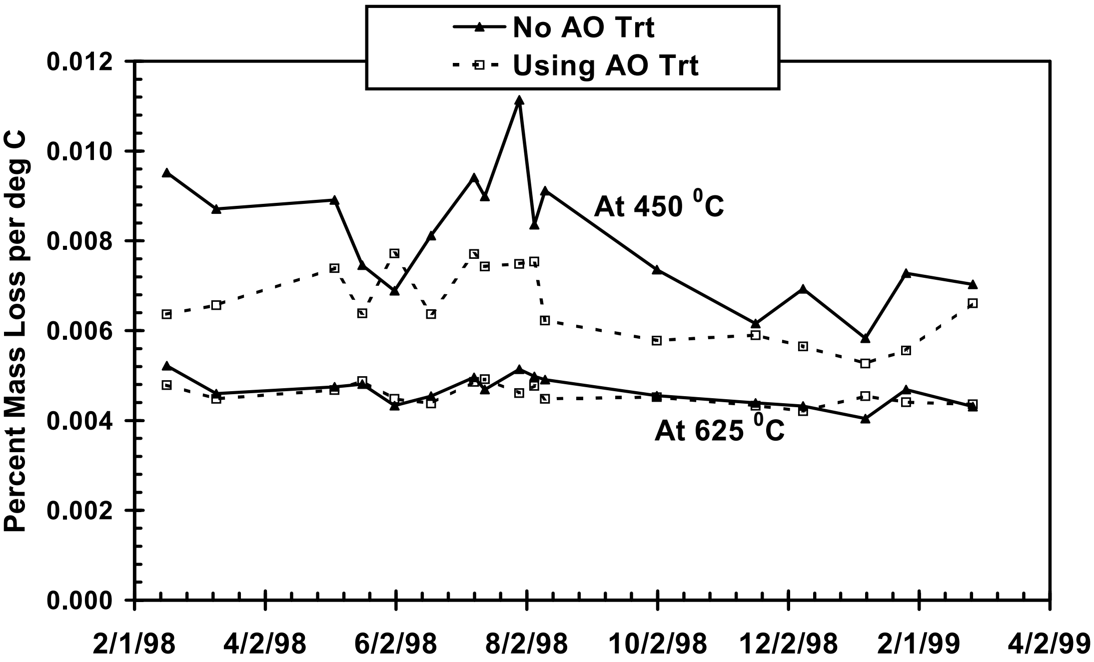


**Figure 3.1-11: Derivative mass loss rate of Neenah Foundry green sand samples: derivative at 450°C (attributed to VOC release from coal) or at 625°C (attributed mainly to waters of hydration release from clay).**

**Table 3.1-4: Temperatures experienced in the autopsy green sand mold as a function of distance from the casting surface.**

| Distance from Surface | Temperature Exposure |
|---|---|
| within 1 cm | 800-1400°C |
| 1-2 cm | 500-800°C |
| 2-4 cm | 300-500°C |
| 4-6 cm | 160°C |
| 6-8 cm | 100-160°C |
| 8-10 cm | < 100°C |

The derivative at 450°C corresponded to the mass loss peak for coal emissions as discussed above. The AO-treated sand had lower mass losses for the samples autopsied 2-4 cm from the casting (where it had experienced 300-500°C during metal pouring) when compared to the TAP-treated sand. Moreover, these results mean that when green sands experience this 300-500°C temperature regime the second time (i.e., during the TGA analysis), the AO-treated green sand exhibit fewer emissions than did the non-AO treated green sand. Since both molds used the same initial sand, the difference in mass loss between the two autopsied molds represented either AO destruction of VOCs or AO-induced binding of these VOCs into the sand's carbon matrix such that heating could no longer cause their release.

The mass loss derivative at 625°C has been plotted in Figure 3.1-17. The AO-treated sand's mass losses were also lower for the 1-2 cm sample distance at the 625°C point. This means that when the green sands experienced this 500-800°C temperature regime the second time, the AO-treated green sand exhibited fewer emissions than did the non-AO treated green sand.

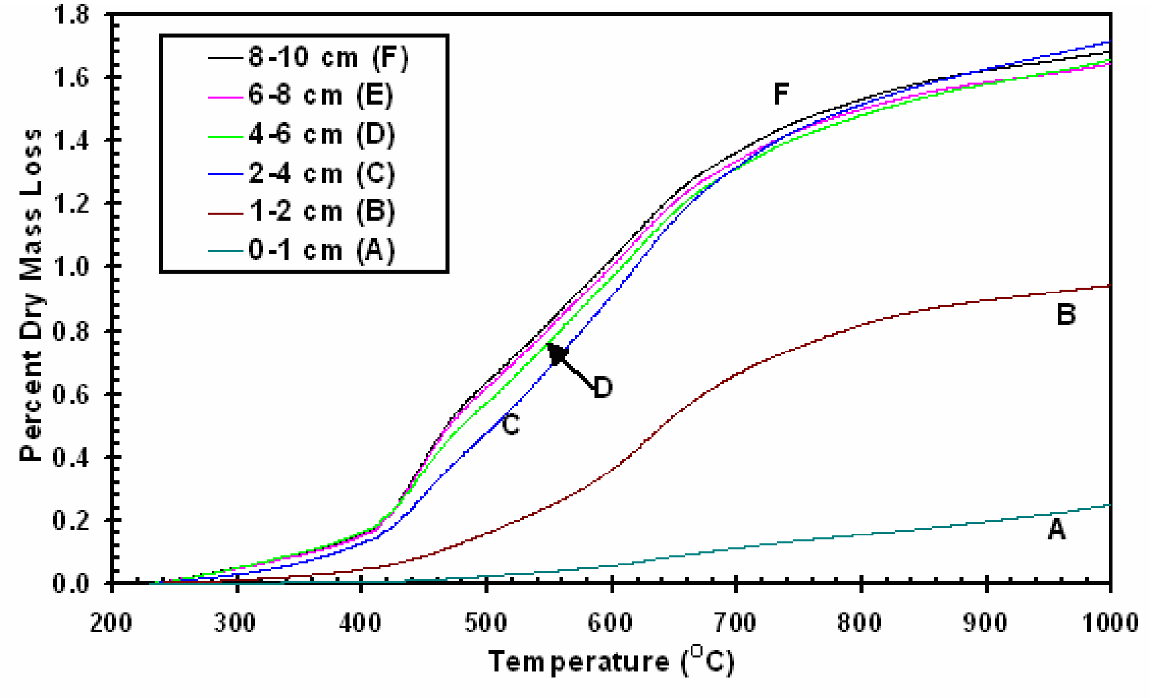


Figure 3.1-12: TGA analysis of a green sand mold as a function of distance from the casting surface: no AO-treatment.

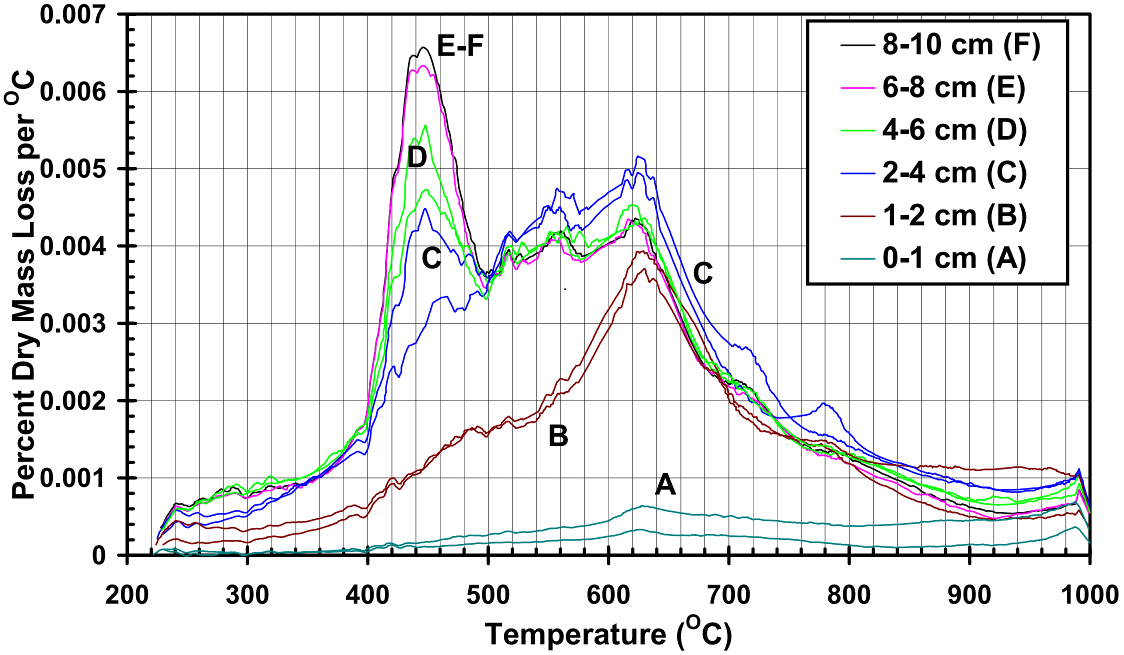


Figure 3.1-13: TGA derivative analysis of a green sand mold as a function of distance from the casting surface: no AO-treatment.

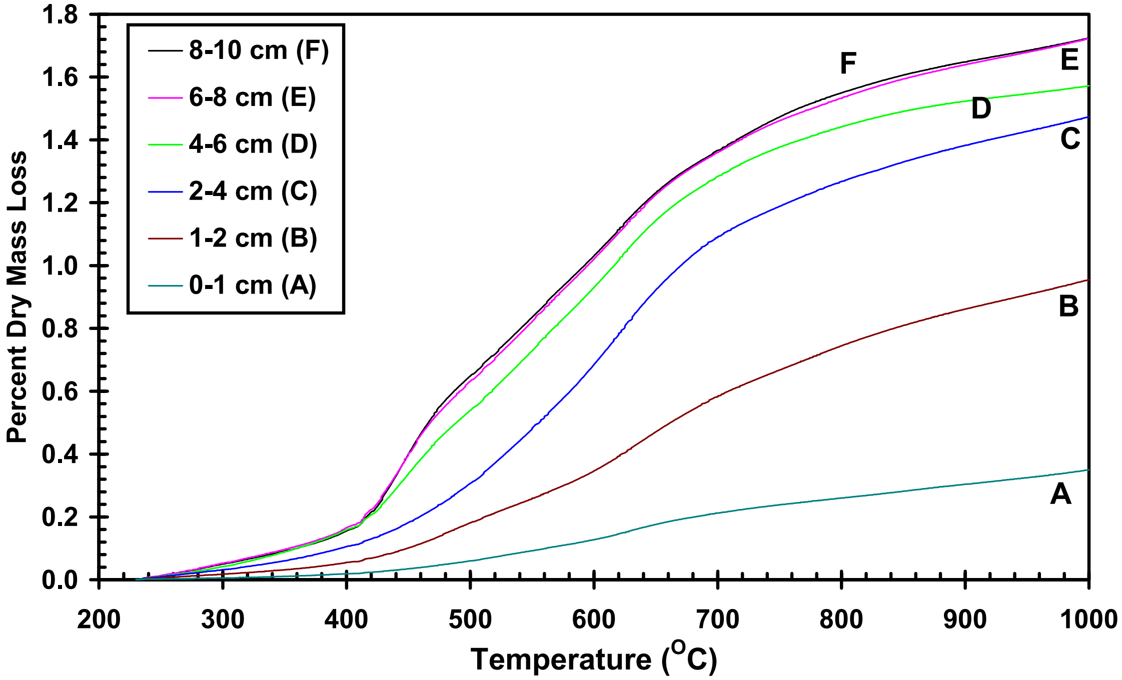


Figure 3.1-14: TGA analysis of a green sand mold as a function of distance from the casting surface: AO water added to foundry sand previously untreated by AO.

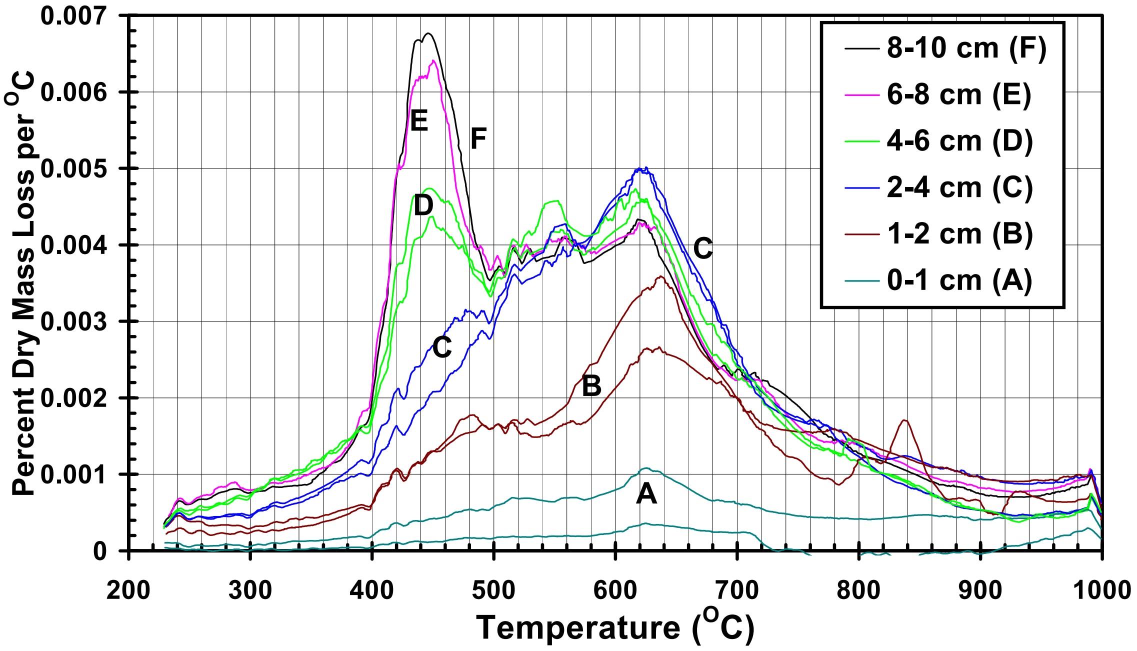


Figure 3.1-15: TGA derivative analysis of a green sand mold as a function of distance from the casting surface: AO water added to foundry sand previously untreated by AO.

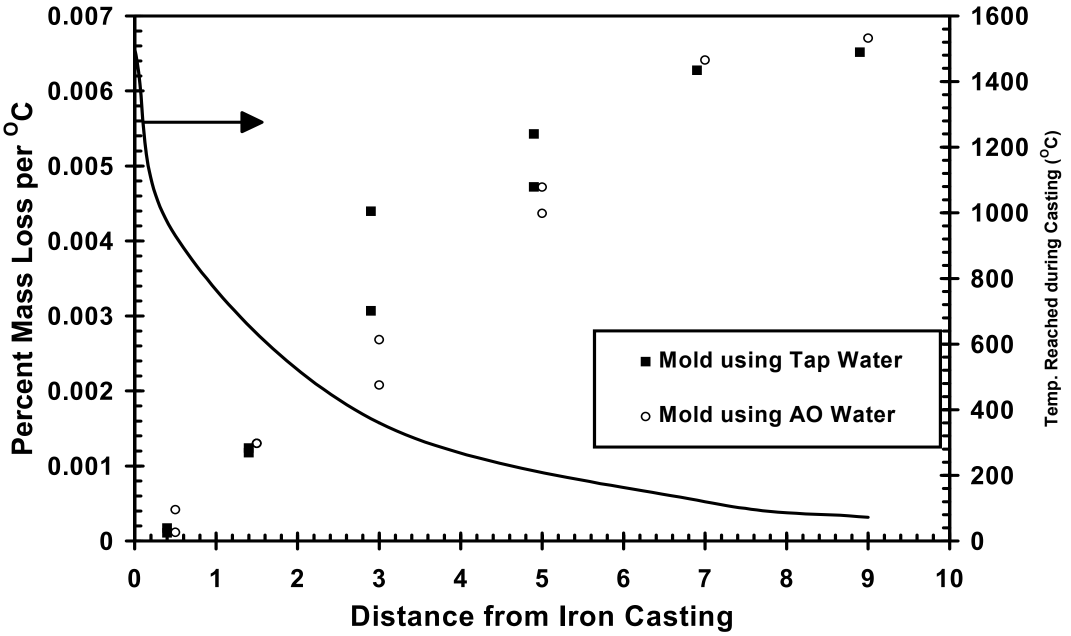


**Figure 3.1-16: Mass loss rate at 450°C for green sand as a function of the distance from the casting surface.**

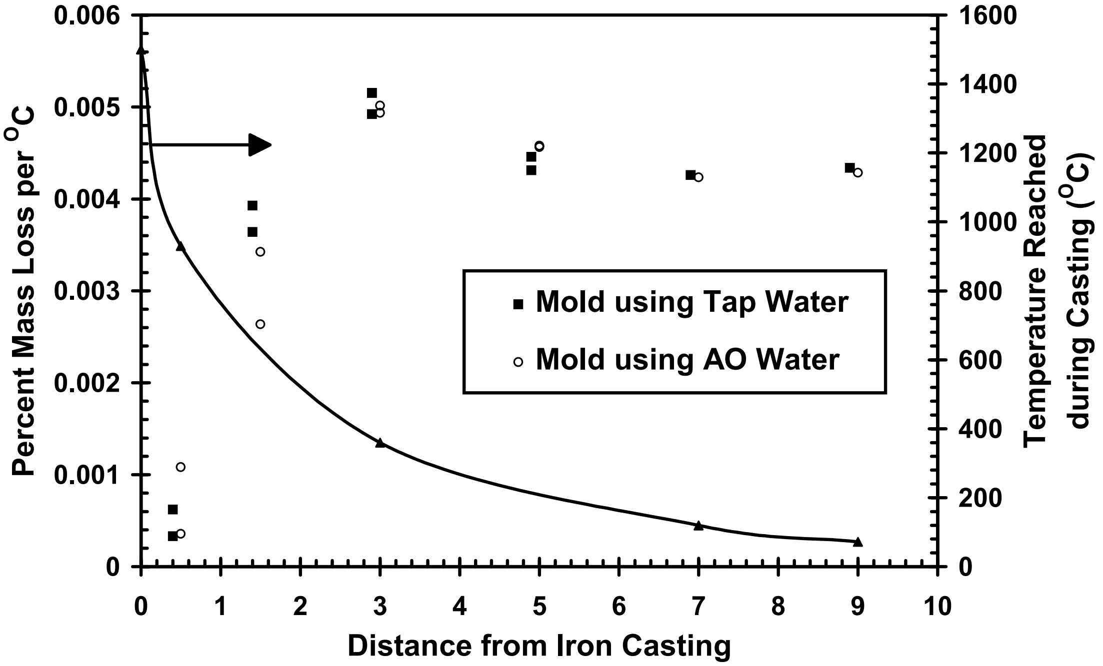


**Figure 3.1-17: Mass loss rate at 625°C for green sand as a function of the distance from the casting surface.**

## 3.1.4 Summary of Section 3.1:

1. Emissions capture testing using the Penn State emissions hood stack system has been successfully demonstrated. The repeatability and reproducibility of VOC and benzene emissions during hood stack tests are similar to the repeatability and reproducibility reported for other similar testing at other air emissions testing facilities.

2. When conducting pilot-scale mold-and-pour tests at Penn State, it was found that Wheland foundry green sands that were sampled from an AO-blackwater system generated 88% less VOCs and 58% less benzene than did the Wheland green sands that were sampled from a non-AO system. The AO green sand also contained 20-35% less LOI than did the non-AO green sand, and this would have partially contributed to the lower emissions from the AO green sand, as discussed in section 3.3.4.

3. TGA analysis of autopsied green sand mold temperature regions after iron-pouring tests have characterized the mass loss (emissions) potential remaining in the sand for both non-AO and AO-CW treated system sands. Reduced TGA mass loss in the 400-500°C temperature range have been observed for autopsied sands that were 2-4 cm from the mold-metal interface where the green sands had experienced 300-500°C temperatures during metal pouring. Likewise, reduced TGA mass loss in the 600-700°C range have been observed for autopsied sands that were 1-2 cm from the mold-metal interface, where the green sand had experienced 500-800°C temperatures during metal pouring. These results indicated that when the green sands experienced temperatures in these ranges a second time, the AO-treated sand exhibited fewer emissions than did the non-AO treated green sand.

4. When comparing TGA testing of Neenah green sands that were sampled over the course of a year, the AO-CW green sands exhibited less TGA mass loss in the 400-500°C range than did the non-AO green sands. This is a temperature range where mass loss is attributed to VOC release.

## 3.2 EMISSIONS PERFORMANCE – BENCH-SCALE STUDIES

### 3.2.1 Introduction

Bench-scale experiments that are designed to mimic foundry operations are quite difficult to devise, due to the rapid thermal heating and relative complexity of the foundry green sand mold. In an effort to determine the effect of advanced oxidation (AO) on the green sand, Thermogravimetric Analysis (TGA) was used to perform a variety of experiments at Penn State on green sand samples. TGA was coupled with granular activated carbon (GAC) absorption to capture emissions, and solvent extraction followed by gas chromatography flame ionization detection (GC-FID) was used to analyze these emissions. The mass loss profiles of green sands were also examined for a possible correlation with the emissions generated. Many experiments were conducted using green sand samples from full-scale foundries and from pilot-scale experiments. These samples were tested in the “as-received” condition (i.e. without fresh moisture added), and also in a condition where fresh moisture had just been applied to them. This moisture either did or did not contain advanced oxidants (AO) from a Sonoperoxone$^{TM}$ system that included hydrogen peroxide, ozone, sonication, and (in some cases) under water plasma.

### 3.2.2 Materials and Methods

Several different foundry green sands were tested. All sands were tested using the same protocol for the TGA. 1-gram samples were placed in a Cahn TG-131 TGA with a quartz-glass reaction chamber and heated at 6°C/min from ambient to 1000°C under a nitrogen and helium atmosphere. This temperature ramping took about two hours and 45 minutes for completion. It is important to note that the TGA experiments were conducted under nitrogen, and in the absence of oxygen, so combustion could not take place. This simulated some of the key features of the foundry green sand mold conditions. Researchers have conducted studies on the gases within the foundry mold and have determined that the hydrocarbons that were generated react with the oxygen, completely converting it to carbon monoxide (CO) and carbon dioxide ($CO_2$), and also creating an inert and reducing atmosphere in the mold. This inert and reducing atmosphere can contain nitrogen ($N_2$), CO, $CO_2$, hydrogen ($H_2$) and other gases (Peterson and Blanke, 1980). The relatively inert gas nitrogen was chosen as the carrier gas in the Penn State TGA tests. $CO_2$ was avoided since it is an endothermic oxidant that could have confounded emissions results. Carbon monoxide and hydrogen were avoided as they can be dangerous to work with. All experiments were run with a nitrogen flow rate of 60 mL/min through the TGA furnace, plus 60 mL/min helium blended in above the furnace.

The TGA heating rate, though much slower than the green sand mold experiences during metal pouring, is useful because individual temperature regimes may be analyzed relative to emissions generated and mass loss characteristics over those regimes. The largest amounts of mass loss are due to: (a) removal of loosely bound or free water, (b) pyrolosis of coal, core material and coal supplements and (c) the driving out of tightly bound waters of hydration from the clay.

Several modifications were made to the "standard" TGA apparatus to decrease experimental error. First the gas flows were closely regulated using Porter Instrument Series 200 thermal mass flow controllers. The flow controllers were accurate to ±2 mL/min. The second modification was made to ensure that the entire green sand sample was exposed to the nitrogen atmosphere, so that volatiles could uniformly diffuse out of the green sand matrix. Originally, the sample container in the TGA was a non-porous quartz glass bucket that could hold approximately two grams of sand. The modified basket was made from 20-micron stainless steel mesh, and it was formed in a conical shape that could hold approximately 1.5 grams of green sand. This design allowed for more of a free flow of nitrogen into and out of the green sand sample, ensuring that diffusion issues were minimized. Thus the pyrolysis products that were released by the green sand sample could be exhausted and analyzed.

The data generated directly by the TGA are mass loss profiles versus temperature curves. These TGA output curves are informative, however they require some mathematical computation for complete evaluation. First, the mass loss curves were normalized to the "dry mass" (the mass at 230°C). This was necessary because each green sand sample has different initial moistures. Our experiments have shown that prior to 230°C, emissions are not generated; therefore all mass loss is due to loosely bound water. It is also convenient to find the incremental mass loss (the derivative) over the temperature intervals of interest. This data is presented as the percent mass loss per degree Celsius.

The other important data that were collected during TGA experiments were the emissions that were released while the green sand was being heated. The emissions were captured from the TGA experiments on GAC tubes. The tubes were Supelco ORBO 32 GAC tubes with 0.10 and 0.05 grams of activated carbon on the front and back sections, respectively, and were the smaller version of the slipstream tubes used in the experiments described in section 3.1. The emissions were captured over different temperature intervals in replicated experimental trials. The initial intervals were ambient-to-230, 230-343, 343-510, 510-650 and 650-1000°C. It was determined after the first trial of analysis that these intervals could be simplified to ambient-to-343, 343-510 and 510-1000°C.

The flame ionization detector (FID) is a valuable tool in the quantification of emissions. The FID can be operated in tandem with a gas chromatograph (GC) or in the stand-alone condition. When coupled with a GC, the concentration of specific emission species can be determined. A FID works by burning organic compounds in a hydrogen/air atmosphere and generating ions. These ions can be positively or negatively charged. A positively charged electrode collects the ions and the voltage generated by this collection of ions is amplified and recorded. Stand-alone FID analysis is also used by the U.S. EPA for the determination of total pollutant concentrations from stack gases.

Specifically, the U.S. EPA Method 25A (2000), "Determination of Total Organic Concentrations Using a Flame Ionization Analyzer (or Detector)," samples stack gases and calibrates them to a standard gas (propane) on the basis of carbon (U. S. EPA, 2000). The Penn State method for TGA-stand-alone FID analysis borrowed from the EPA method.

The FID that was used in these experiments was a SRI Instruments, Model 110 stand-alone FID. The effluent flow from the TGA (120-mL) was passed through a heated transfer line (200°C) to the FID assembly. The gas was burned in a hydrogen/air (30-ml/250-mL) atmosphere and the voltage was recorded. One limitation with the TGA-FID analysis was that individual emissions species could not be determined, only a total gaseous organics measurement. However the advantage of this FID process is that it will not measurably monitor $H_2O$, CO or $CO_2$. Thus the FID allows us to distinguish mass loss that is related to organic compounds, from mass loss that is related to water, CO and $CO_2$ release. A sample TGA mass-loss, FID response curve is found in Figure 3.2-1. This curve is from typical foundry green sand.

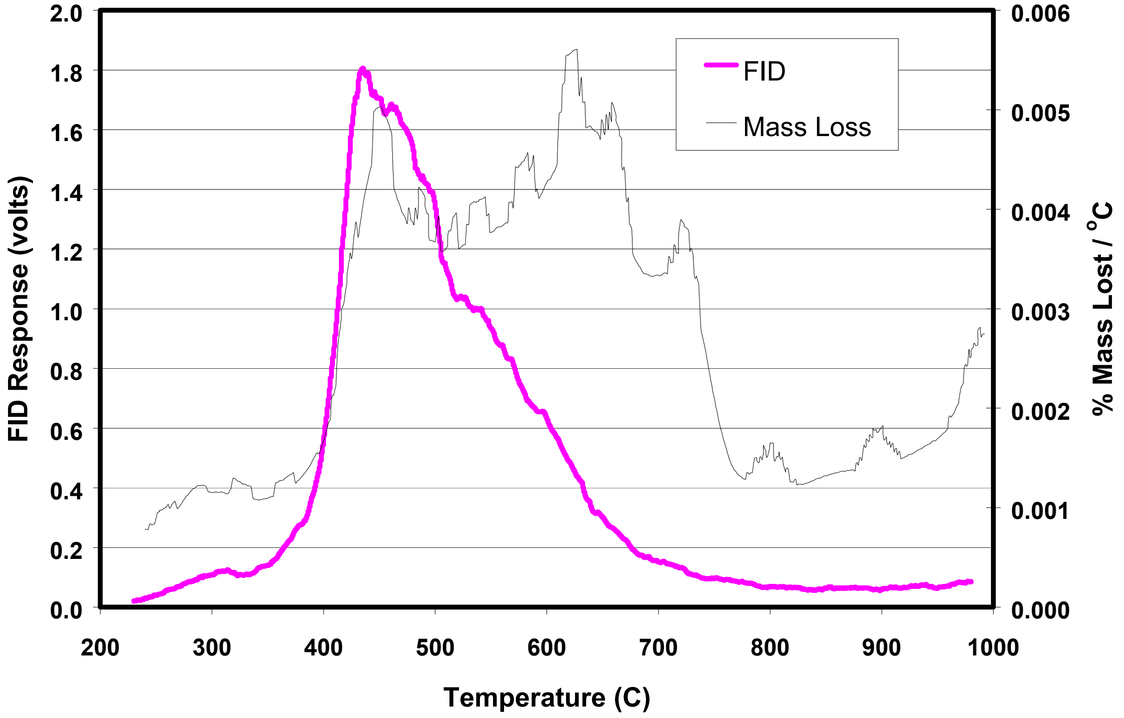


**Figure 3.2-1: Thermogravimetric analysis: derivative mass loss curve vs. flame ionization detector response for typical foundry green sand.**

Figure 3.2-1 shows that the FID response starts at 230°C and peaks at 450°C, which is the point where the coal is pyrolyzing. The voltage reading from this experiment could be standardized with propane or some other organic gas and a mass quantity could be determined. This calibration to a standard gas was the next step in the TGA-FID protocol.

### 3.2.2.1 Reapplication of Moisture Protocol

For some of the TGA experiments, it was desired to test the sand after fresh moisture had been added. This moisture was either tap water, AO treated water (350 ppm hydrogen peroxide ($H_2O_2$)), AO treated blackwater (350 ppm $H_2O_2$) or AO-UWAP treated blackwater (350 ppm $H_2O_2$). The blackwater in these experiments originated from Neenah Foundry Plant 2, which has been operating an AO-black water clarifier system since January 2000. The black water contained 10-15% solids by weight and these solids contained 51% MB clay and 21.7% LOI (organic materials or clay waters of hydration).

The AO machine was operated for five minutes to treat the water. The $H_2O_2$ was added at the beginning of the treatment. Either the treated moisture or tap water was added to 10-grams of dried green sand to raise the moisture level to 3.5%. The sands were then "mulled" using a mortar and pestle for one minute. The samples were placed in the TGA for testing within 15 minutes of moisture application. These samples were tested for mass loss profiles and emissions.

### 3.2.2.2 Thermogravimetric Analyzer Emissions Analysis by Gas Chromatography

The same gas chromatograph (GC) that was mentioned for pilot-scale testing analyzed the emissions from the TGA experiments. The GAC that was used to capture the emissions during the TGA heating experiments was removed from the tube and separated into front and back sections. The sections were desorbed with 1-mL solvent of 95% $CS_2$ and 5% methanol for 45 minutes. The addition of methanol helped to desorb the heavier weight organics. With 5% methanol, the "window" of compounds that eluted spanned between hexane ($C_6$) and hexadecane ($C_{16}$). Therefore the VOCs as hexane for these experiments will be referred to as $\text{VOC}_{\text{H-(C6-C16)}}$. One µL of the sample was injected in triplicate in the GC and results were compared to standards. The GC method for analysis of emissions was the same as that in the pilot-scale trials (section 3.1).

The TGA experiments were separated into two distinct trials, Trial 1 and Trial 2. For Trial 1, all injections were done manually using the solvent flush technique. This technique involved pulling 1-µL of clean solvent, 1-µL of air, 1-µL of the sample and finally 1-µL of air into the needle. This ensured that the entire sample was flushed out of the needle. This technique yielded experimental errors between 1-4%. For Trial 2, emissions analyses were done using the same desorption protocol and GC method, however an automatic sampler was used to inject the samples. The auto-sampler was an Agilent 6890 Series Injector (Palo Alto, CA). The major difference between the auto-sampler and the manual injections is the lack of the solvent flush technique in the auto-sampler. This meant that there was no step that flushed the entire 1-µl sample out of the needle and into the GC. An important effect of this was increasing the experimental error. This lack of flushing may also have yielded lower FID response when the auto-sampler was employed, and this represents an area of continued quality control testing. The auto-sampler injections varied 7-15%.

#### 3.2.2.3 Discussion of CERP/Technikon Samples

The Penn State research team also conducted bench-scale experiments with green sand samples that were generated at CERP/Technikon of Sacramento, CA, in informal collaboration with Penn State. CERP/Technikon, formerly the Casting Emissions Reduction Program (CERP), has tested a number of process and product changes to metal casting and they have monitored the effects that those changes have had on green sand properties and emissions. As part of an informal collaboration with Penn State, CERP/Technikon has tested the effects of the advanced oxidation system on foundry emissions in a pre-production-scale setting. The CERP/Technikon experiments employed an advanced oxidation system that was similar to the Penn State system, with the main difference being the CERP/Technikon system did not contain underwater plasma (UWAP). The CERP/Technikon pre-production-scale foundry has been described in detail elsewhere (Technikon, 2001). The pre-production pilot-scale foundry employed a 1300-1400 pound green sand mold with a horizontal parting line, into which was poured 225-245 pounds of gray iron. This was totally enclosed within an emissions capture device, which pulled air around the mold, and out an exhaust duct. The exhaust duct was fitted with 0.5 gram GAC tubes, which captured a slipstream of this exhaust airflow. Immediately after pouring the gray iron, the emissions capture device was closed and cooled for 45 minutes, and then the mold was shaken out for 15 minutes on a shaker table that allowed all of the green sand to fall away from the mold into a pit. The emissions were collected for another 15 minutes following shakeout. Emissions were captured during pouring, cooling and shakeout. After completing a turn (i.e. a cycle of mold preparation, pouring, cooling and shakeout), the next turn's mold was prepared by mulling together the previous turn's green sand, plus make-up clay and coal and tap or AO-treated water. Following mulling, a new mold was created and another turn was processed.

CERP/Technikon has processed several series of production and production-scale tests. However we have a specific interest in two series of trials that CERP/Technikon has identified as CH and CI. Although the CH and CI designations are merely site-specific sequential numbers, the authors herein have adopted them because they are no less confusing than any other acronym. These two trials were chosen because the results were well documented and green sand samples had been collected after each turn in the series. Both of the CH and CI green sands originated from the same full-scale foundry source. This was green sand that had been through multiple cycles of use in a full-scale foundry, 30% of its clay was southern (calcium) bentonite, while 70% of its clay was western (sodium) bentonite.

The CI AO-treated series was subjected to 24 turns to condition the sand with the AO treatment and to achieve a "pseudo-steady state" relative to sand properties and emissions. However, it is possible that true steady-state could take more than 24 turns. The initial six turns of the CI AO-treated series were excluded from analysis summary to allow for this pseudo-steady state to be met. Also, several turns from the middle of this trial were excluded because of electrical complications. This electrical problem affected both green sand properties and emissions. The specific cause of this problem was not discovered and rectified until after the 18th turn of the CI tests; so all emissions data from the CI turns, 13-18, were excluded as non-representative from the AO process. The data from these excluded turns is not included in the average values presented below.

A very important feature of these experiments is that they contained sodium silicate cores. The sodium silicate is not an organic based resin and therefore does not release VOCs or HAPs during thermal decomposition. The average process and stack parameters for all turns of the CH TAP-treated and CI AO-treated experimental trials are found in Table 3.2-1.

The green sand mold contained approximately 7% methylene blue clay, 5% LOI; and the gray iron was poured with a 5:1 to 6:1 sand-to-metal ratio condition. A slipstream of the emissions was collected on GAC and analyzed by a private laboratory (Clayton Labs). The average emissions results from the CH TAP-treated series and the CI AO-treated series are found in Table 3.2-2.

The emissions have all been normalized to pounds per ton of metal poured. HC refers to all hydrocarbons ($C_6$-$C_{14}$) as undecane, VOCs are all specific target compounds classified as volatile organic compounds. VOCs are a subset of HCs, and HAPs are all emissions classified as hazardous air pollutants and are a subset of VOCs. The results show that the total HCs, VOCs, HAPs and almost every emissions species are significantly lower when using the AO-treated water than when using tap water. The

**Table 3.2-1: Test plans at CERP/Technikon: CH (tap water, sodium silicate core) and CI (AO-treated, sodium silicate core) average process and stack parameters.**

| Mold and Pouring Process Conditions | Average of Test **CH** (Tap water, turns 1-6) | Average of Test **CI** (AO water, turns 1-24) | Target Range |
|---|---|---|---|
| Casting Metal Weight, lbs. | 239 | 248 | 225-245 |
| Total Mold Weight, lbs. | 1302 | 1319 | 1300-1400 |
| Total Core Weight, lbs. | 60.13 | 60.50 | 62-64 |
| Compactibility, % | 46 | 47 | 48-51 |
| Total Binder Weight, lbs. | 2.86 | 2.88 | 2.9-3.1 |
| Loss on Ignition %, 1000°C (in mold) | 5.28 | 5.02 | 4.7-5.3 |
| Loss on Ignition %, 1000°C (shakeout) | 4.89 | 4.82 | 4.3-4.7 |
| Loss on Ignition %, 1000°C (cores) | 0.50 | 0.55 | None |
| Methylene Blue Clay % (in mold) | 7.18 | 6.75 | 6.5-7.5 |
| Methylene Blue Clay % (shakeout) | 6.34 | 5.65 | None |
| Volatiles %, 480°C (in mold) | 0.75 | 0.62 | 0.7-0.85 |
| Volatiles %, 480°C (shakeout) | 0.70 | 0.59 | None |
| Pouring Temperature, °C | 1450 | 1443 | 1443 ± 6 |
| Water Type Used in Mold | Tap | AO | |
| Total Clay Added, lbs/mold | 2.84 | 3.71 | None |
| Coal Added, lbs/mold | 2.18 | 3.23 | None |
| Stack Conditions | | | |
| Average Stack Temperature, °C | 40 | 45 | 49 ± 6 |
| Average Stack Velocity, ft/sec | 15.95 | 16.21 | 17 ± 2 |
| Average Stack Pressure, in. Hg | 30.00 | 29.88 | 29.92 ± 1 |
| Stack Flow Rate, scfm | 688 | 686 | 700 ± 50 |

**Table 3.2-2: Average emissions results from CERP/Technikon pilot-scale experiments, CH turns 1-6 (tap water, sodium silicate core) and CI turns 7-12 & 19-24 (AO-treated water, sodium silicate core).**

| Analyte | Test CH (Tap Water) (Lb/Tn) | Test CI (AO Water) (Lb/Tn) | % Difference | *Is % Difference from Advanced Oxidation Effect?** |
|---|---|---|---|---|
| HC ref to Undecane | 0.3085 | 0.1674 | -46 | Yes |
| Sum of VOCs | 0.2060 | 0.1169 | -43 | Yes |
| Sum of HAPs | 0.1572 | 0.0888 | -44 | Yes |
| **Individual Organic HAPs** | | | | |
| Benzene | 0.0572 | 0.0358 | -37 | Yes |
| Toluene | 0.0375 | 0.0221 | -41 | Yes |
| m,p-Xylene | 0.0154 | 0.0087 | -43 | Yes |
| o-Xylene | 0.0072 | 0.0039 | -45 | Yes |
| Acetaldehyde | 0.0071 | 0.0058 | -18 | Yes |
| Napthalene | 0.0069 | 0.0029 | -58 | Yes |
| Phenol | 0.0060 | 0.0013 | -79 | Yes |
| 2-Methylnapthalene | 0.0051 | 0.0017 | -66 | Yes |
| Ethylbenzene | 0.0037 | 0.0022 | -41 | Yes |
| 1-Methylnapthalene | 0.0029 | 0.0010 | -66 | Yes |
| 2-Butanone | 0.0028 | 0.0013 | -51 | Yes |
| Formaldehyde | 0.0018 | 0.0018 | 0 | No |
| **Other VOCs** | | | | |
| Heptane | 0.0103 | 0.0071 | -31 | Yes |
| Octane | 0.0059 | 0.0050 | -16 | Yes |
| 1,2,4-Tirmethylbenzene | 0.0061 | 0.0033 | -46 | Yes |
| Nonane | 0.0043 | 0.0030 | -32 | Yes |
| Decane | 0.0036 | 0.0025 | -31 | Yes |
| Undecane | 0.0026 | 0.0015 | -42 | Yes |
| 1,2,3-Trimethylbenzene | 0.0019 | 0.0011 | -40 | Yes |
| 1,3,5-Trimethylbenzene | 0.0020 | 0.0011 | -42 | Yes |
| 3-Ethyltoluene | 0.0051 | 0.0008 | -85 | Yes |
| Dodecane | 0.0021 | 0.0004 | -83 | Yes |
| Cyclohexane | 0.0009 | 0.0003 | -64 | No |
| Indan | 0.0001 | ND | NA | NA |
| **Other Analytes** | | | | |
| Carbon Monoxide | 4.66 | 4.99 | 7 | No |
| Methane | 0.6474 | 0.5887 | -9 | No |
| Carbon Dioxide | 29.78 | 27.5 | -7 | No |

* Based on t-test of paired data at 95% confidence interval

statistical significance was appraised at Penn State by using the t-test as described above. These green sands, having experienced both advanced oxidant-treated water (CI) and tap (CH) water treatment, were valuable to Penn State for bench-scale analysis. The green sands were collected after every turn, and samples of the green sand were sent to Penn State. We used these green sands in our TGA analysis and subjected them to re-moisturization and emissions capture.

## 3.2.3 Results and Discussion

### 3.2.3.1 TGA Analysis – Mass Loss and Emissions

Initial experiments were run on virgin materials using the thermogravimetric analyzer (TGA). The mass losses for coal and western bentonite were examined to determine where the majority of mass loss could be expected. The first derivative mass loss for 5% coal and 95% silica sand is found in Figure 3.2-2 and that for 7% western bentonite clay and 93% silica sand is found in Figure 3.2-3. The clay, coal and silica sand (grain fineness number 60) originated from American Colloid Company.

The largest mass loss for the 5% coal sample occurred over the 400-500°C range, where the coal is releasing volatiles and pyrolyzing. The largest portion of mass loss for the 7% clay is observed over the 600-700°C range, where the waters of hydration are driven out of the clay matrix. The process of driving out the waters of hydration is called calcining. Different clays calcine at different temperatures, with western bentonite calcining at 650-800°C and southern bentonite calcining at 315-390°C. Following the experiments using the virgin materials, the CERP/Technikon CH and CI series sands were tested via thermogravimetric analysis.

The CH sands had been treated with tap water at Technikon, while the CI sands had been exposed to AO-treated water. TGA analyses were performed on "as-received" samples, and subsequently on remoisturized samples. The off-gas from the TGA was captured on GAC and the resultant solvent-extracted emissions and mass losses were examined over several temperature intervals. Distinct temperature intervals were developed to examine specific events. Example temperature intervals are: ambient to 230°C (loss of moisture), 230 – 343°C, 343 – 510°C (primary coal mass loss), 510 – 650°C, and 650 – 1000°C (primary clay mass loss). Figure 3.2-4 displays a sample graph of emissions analysis over these five intervals. The sample analysis shows that the largest amount of emissions is generated over the 343-510°C temperature range. This corresponds to large mass loss experienced when the coal pyrolyzes in the TGA as shown in Figure 3.2-2. In all experiments, 60-80% of the total emissions were generated over the 343-510°C temperature range. By examining these intervals it was determined that we could combine the emissions for the intervals below 343°C.

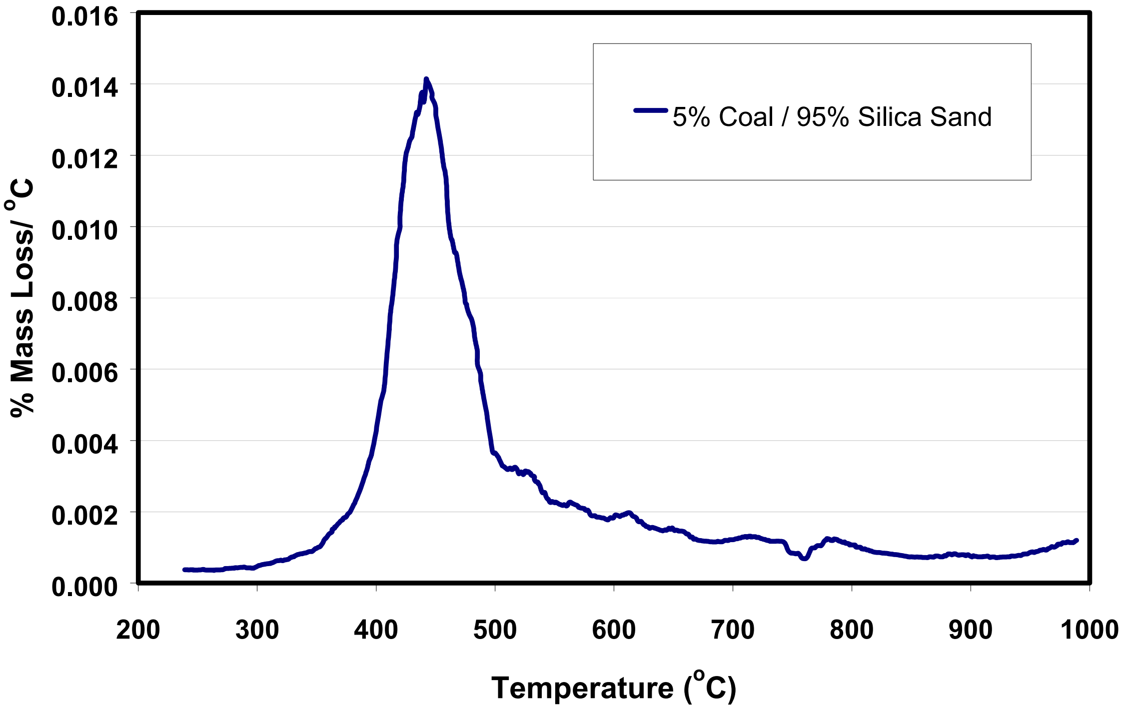


**Figure 3.2-2: Thermogravimetric analysis: derivative mass loss curve for 5% coal and 95% silica sand.**

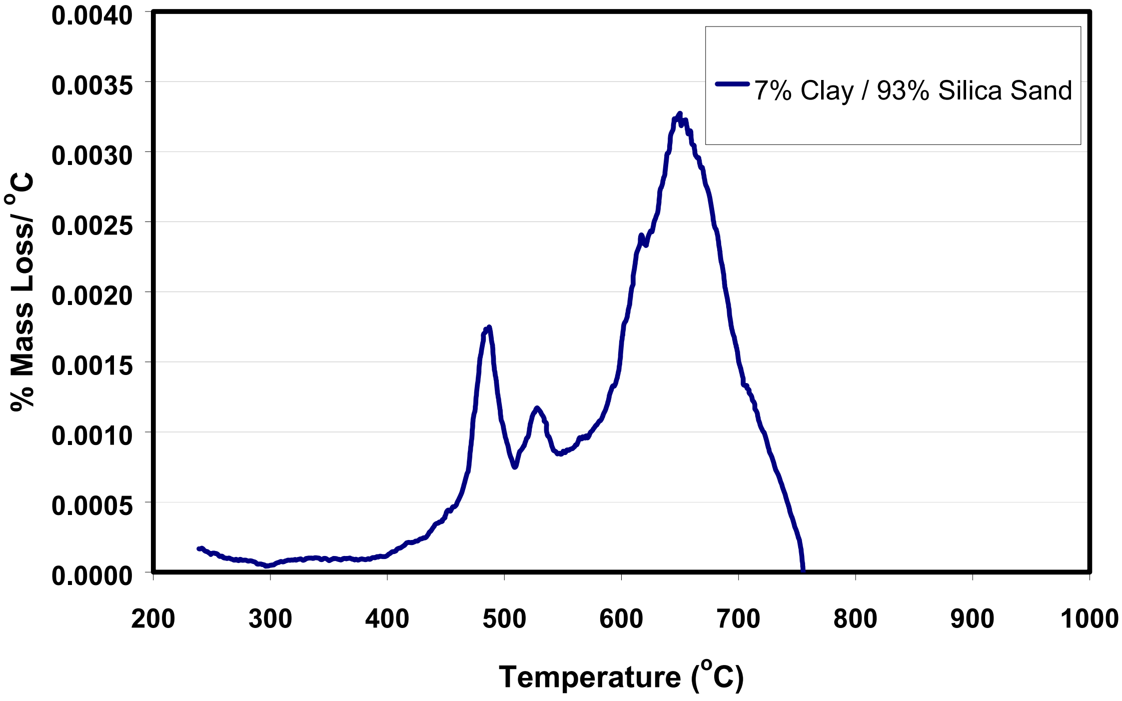


**Figure 3.2-3: Thermogravimetric analysis: derivative mass loss curve for 7% western bentonite clay and 93% silica sand.**

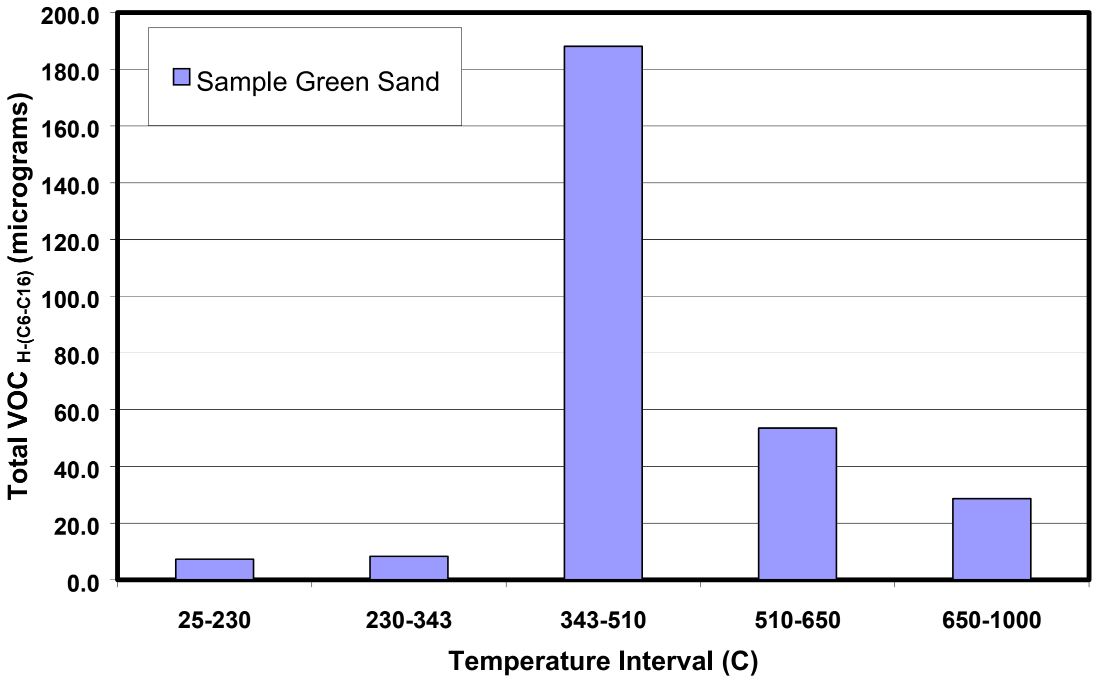
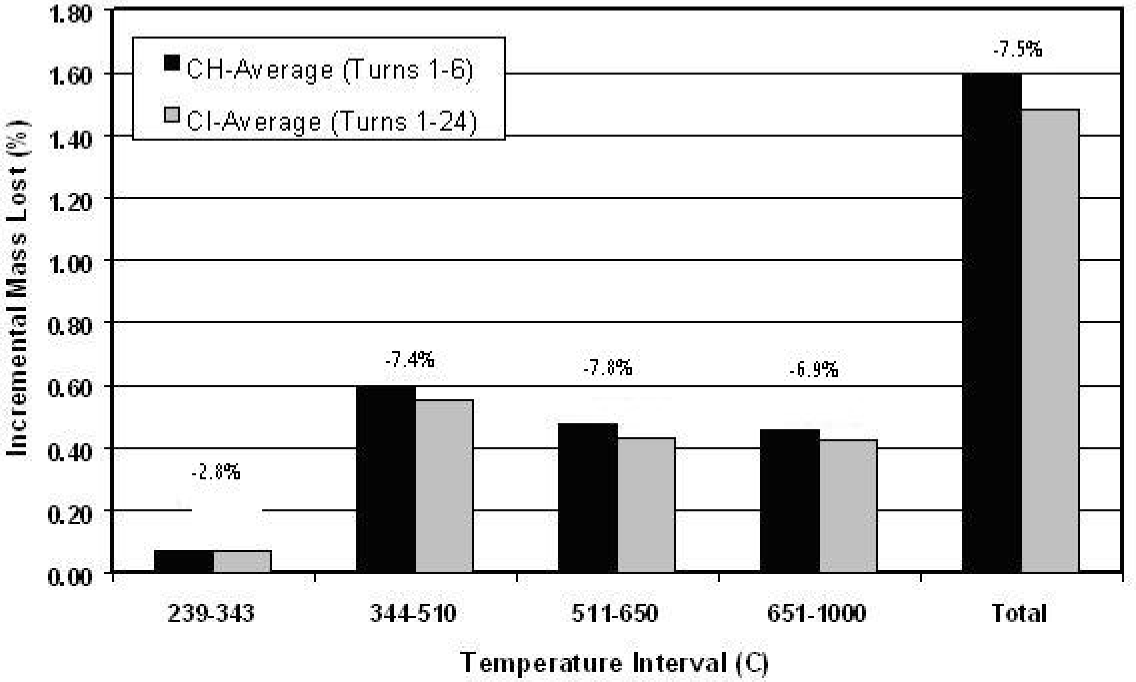


**Figure 3.2-4: Representative thermogravimetric analysis: total VOC H-($C_6$-$C_{16}$) emissions analysis of sample green sand as determined by GC-FID.**

The "as-received" system green sands, CH (mixture of turns 1-6) tap water-treated and CI (mixture of turns 1-24) AO-treated sands were examined by TGA. "As-received" means that no additional moisture was added to the sand after Penn State received the sand samples. The CI (turns 1-24, AO-treated) "as-received" system green sands lost less mass than the CH (turns 1-6, tap treated) "as-received" system green sand over each and every mass loss interval studied. Each "as-received" average sand was tested three times in the TGA and the mass loss results were averaged and recorded. Figure 3.2-5 presents the average incremental mass loss for the CH tap-treated and CI AO-treated "as-received" samples. The numbers over the intervals represent the percent change from CH to CI green sands.

More than a year had elapsed from the time that CERP/Technikon had conducted the CH and CI trials to the time that Penn State conducted these TGA experiments. Thus the differences in the interval mass losses of the average green sand samples tested at Penn State had to have been due to lasting fundamental changes that the AO treatment incurred on the green sand. The differences in LOI and MB clay would only account for a small portion of the difference in mass loss that was experienced at Penn State. The explanation of these fundamental changes is being evaluated in continued research; however, some theoretical and experimental interpretations are discussed later.

The CH and CI series sands were also re-moisturized at Penn State for additional experiments. Two distinct trials were conducted in which multiple samples were run for statistical comparison. Trial 1 consisted of comparing a mixture of CH green sand



**Percentages represent percent differences between CH and CI*

**Figure 3.2-5: Thermogravimetric analysis: incremental mass loss results for CH (turns 1-6) and CI (turns 1-24) "as-received" green sand samples for Trial 1**.

from turns 1-6 that was re-moisturized with tap water, versus a mixture of CI green sand from turns 1-24 that was re-moisturized with AO treated water (150 ppm $H_2O_2$). Table 3.2-3 displays the characteristics of the two average sands.

**Table 3.2-3: Average CH (tap, turns 1-6) and CI (AO treated, turns 1-24) system green sand characteristics for Trial 1.**

| Property | CH Average (Tap Water), Turns 1 to 6 | CI Average (AO Water), Turns 1 to 6 |
|---|---|---|
| Loss on Ignition, 1800°F, % | 5.28 | 5.03 |
| Methylene Blue Clay, % | 7.18 | 6.89 |
| Volatiles, 1200°F, % | 0.75 | 0.64 |

The green sand samples for Trial 1 were used for further emissions and mass loss analysis. For Trial 1a, emissions were analyzed over five distinct temperature intervals: ambient to 230°C, 230 – 343°C, 343 – 510°C, 510 – 650°C, and 650 – 1000°C. Trial 1b included the same average CH tap-treated and CI AO-treated green sands, however only three intervals were examined for emissions: ambient to 343 $^{o}$C, 343-510 $^{o}$C and 510-1000 $^{o}$C. The mass losses for this and all trials still focused on the five initial intervals. For mass loss analysis, Trials 1a and 1b are compiled into one examination because the same average green sand samples were used for both trials.

Trial 2 is distinctly different from Trial 1 in that the average CI AO-treated sand is from turns 19-24 as opposed to the 1-24 mixture that had been used in Trial 1. The sand from the last six turns was used to ensure that the system green sand had experienced the AO effect (i.e. when the AO system was running properly after experiencing electrical difficulties due to building-wide operations at the facility through turns 13-18). This blend had loss on ignition (LOI) that was more similar to the CH tap-treated average. The emissions were examined over the same temperature intervals used in Trial 1b. The mass loss data was still compiled in the five original intervals. Table 3.2-4 contains the data of the Trial 2 average CI AO-treated and CH tap-treated average system green sands.

**Table 3.2-4: Average CH (tap-treated, turns 1-6) and CI (AO-treated, turns 19-24) system green sand characteristics for Trial 2.**

| Property | CH Average (Tap Water), Turns 1 to 6 | CI Average (AO Water), Turns 19 to 24 |
|---|---|---|
| Loss on Ignition, 1800$^{o}$F, % | 5.28 | 5.29 |
| Methylene Blue Clay, % | 7.18 | 6.83 |
| Volatiles, 1200$^{o}$F, % | 0.75 | 0.64 |

The as-received green sands were next re-moisturized at Penn State with various treatments (non-AO and AO), and TGA tests were again performed. The CH (non-AO) sand was re-moisturized with tap water, while the CI (AO treatment at CERP/Technikon) was subsequently re-moisturized with either AO-clean water (AO-CW), AO-blackwater (AO-BW), or AO-underwater plasma blackwater (AO-UWAP-BW). The incremental mass loss data for Trial 1 of the re-moisturized sand is shown in Figure 3.2-6.

Many TGA experiments were conducted to derive these average incremental mass loss results for the four moisture conditions and to develop a sufficient population for statistical analysis. The average incremental mass losses for the CH (turns 1-6, tap) green sand contain all CH experiments from Trials 1 and 2. The differences from the figures have been tabulated in Table 3.2-5 with the percent change from the CH experiments and the statistical significance noted. The mass loss results for the CI (turns 1-24) AO and CI AO-BW treated sand for every temperature interval except 239-343°C are statistically different from the CH tap-treated sand. The results for the CI UWAP-BW treated green sand are only significantly different over the 511-650°C interval. The lower mass loss for the CI green sands over the 343-510°C interval should correspond to lower VOC

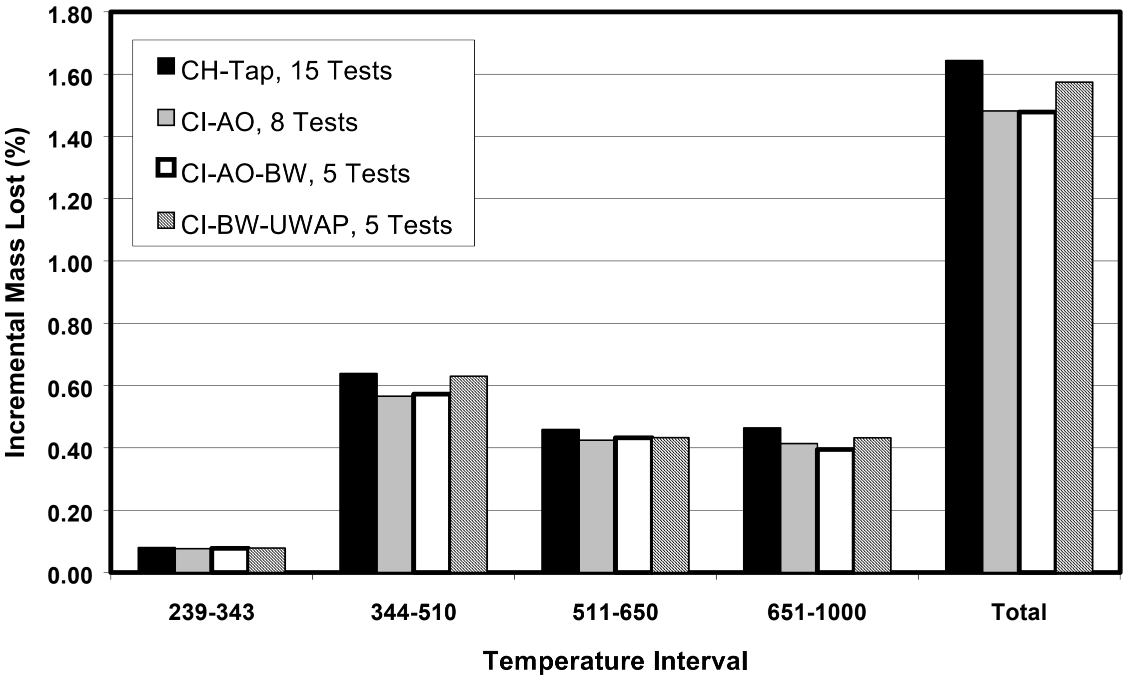


**Figure 3.2-6: Thermogravimetric analysis: incremental mass loss results from remoisturized CH (turns 1-6) TAP, CI (turns 1-24) AO, CI AO-BW and CI UWAP-BW green sand samples for Trial 1.**

**Table 3.2-5: Summary of incremental mass loss data (%) for Trial 1 with remoisturized green sand samples.**

| | CH TAP | CI AO | Diff. vs. CH % | CI AO BW | Diff. vs. CH % | CI UWAP BW | Diff. vs. CH % |
|---|---|---|---|---|---|---|---|
| **# of Tests** | 15 | 8 | | 5 | | 5 | |
| **Temperature Interval (°C):** | | | | | | | |
| **239-343** | 0.080 | 0.077 | -3.8 | 0.077 | -3.8 | 0.079 | -1.2 |
| **344-510** | 0.639 | 0.566 | -12.1** | 0.573 | -10.9** | 0.614 | -4.0 |
| **511-650** | 0.459 | 0.425 | -7.7** | 0.433 | -5.8** | 0.431 | -6.3** |
| **651-1000** | 0.465 | 0.414 | -11.6** | 0.395 | -16.3** | 0.434 | -6.9 |
| **Total:** | 1.643 | 1.482 | -10.3** | 1.479 | -10.5** | 1.558 | -5.3 |
| ** Significant to the 95% confidence level. | | | | | | | |

emissions. This was shown to be the case from the VOC $_{H-(C6-C16)}$ data discussed previously.

It is important to note that the percent change includes the initial difference in the "as-received" material. Therefore, the total change presented in the table represents both the change in the properties of the "as-received" green sand due to AO treatment at CERP-Technikon, plus the change achieved by subjecting the green sand to fresh moisture (AO or non-AO) at Penn State. For example, the incremental mass loss over the 343-510°C interval for CI AO-treated green sand versus CH TAP is 12.1%, however this contains the 7.4% difference in the initial "as-received" materials, as shown in Figure 3.2-5. Therefore, subsequent AO treatment at Penn State achieved an additional 4.7% reduction in mass loss.

The VOC emissions results comparing CH (turns 1-6) to CI (turns 1-24) were somewhat different. As discussed elsewhere, the emissions from the "as-received" green sand materials (CH turns 1-6 vs. CI turns 1-24) were the same, however subjecting the CH and CI sands to AO re-moisturization at Penn State reduced the VOC emissions of the CI sands by up to 23% compared to CH sands that were re-moisturized with tap water. The emissions reductions were greater than the incremental mass losses with additional AO treatment. It may be that the mass loss is more influenced by the evolution of other chemicals that are not classified as VOCs, such as CO, $CO_2$, $H_2O$, $CH_4$, or by emissions that were not captured, such as condensables. The generation of these compounds has not been reduced as much by the addition of AO-treated water, as determined in parallel research. Since the $VOC_{H-(C6-C16)}$ measurement does not include these compounds, the percent changes in the emissions are greater than the incremental mass loss.

A second trial was conducted to examine emissions and mass loss of CH and CI sands. The Trial 2 experiments were conducted using a different mixture of CI green sands, including only the last six turns (19-24) of the AO treatment pre-production sand from CERP/Technikon. This ensured that all the green sand that was tested at Penn State had experienced the AO effect at CERP/Technikon. Also, the loss on ignition (LOI) of this CI (turns 19-24) mixture was 5.29%, very close to the LOI of the CH (turns 1-6) mixture, which was 5.28%.

The corresponding mass loss data was very repeatable and was once again analyzed for differences in moisture conditions over various temperature intervals. Once again, the "as-received" CH (turns 1-6) tap water-treated and CI (turns 19-24) AO-treated average green sands were analyzed. An odd shift in the incremental mass loss was seen over the 651-1000°C interval, where the CI (turns 19-24) AO-treated "as-received" green sand lost significantly more mass than the CH (turns 1-6) tap-treated sand. This result could be due to the reactivation of clay. Figure 3.2-7 presents the incremental mass loss data for the "as-received" sands.

The difference in incremental mass loss over the range responsible for the most emissions (343-510°C) was relatively unchanged from Trials 1 to Trial 2. The "as-received" results show the CI (turns 19-24) green sand lost more mass over the 239-343°C and the 650-1000°C intervals. It may be that the AO reactions with the CI green sand during the pre-production trials at CERP/Technikon fundamentally changed the

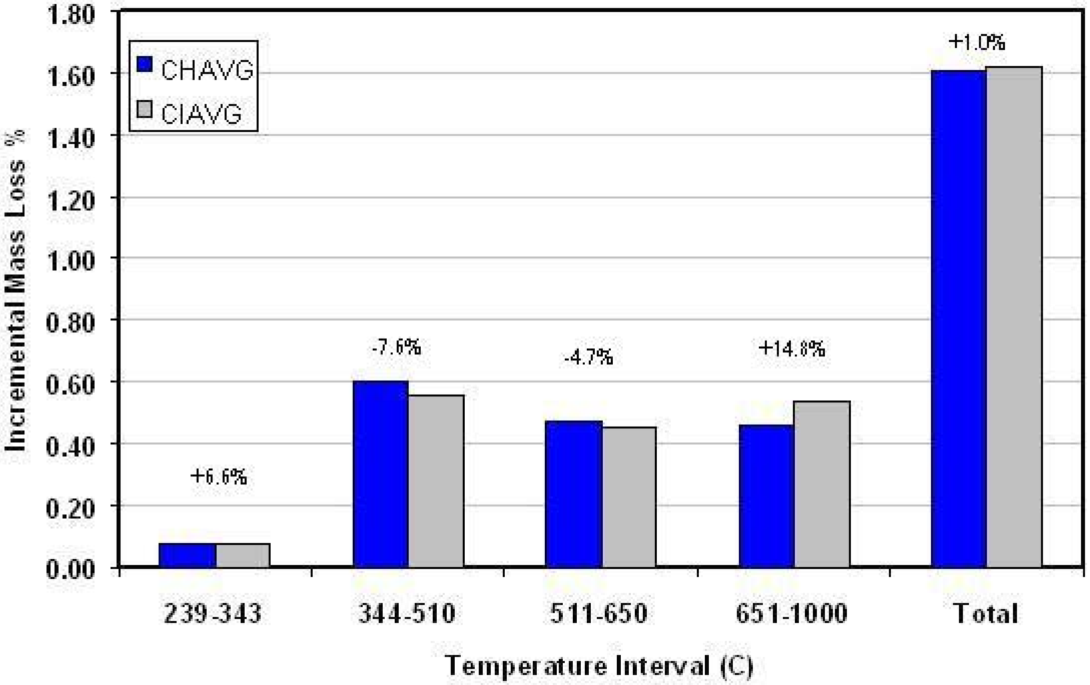


**Figure 3.2-7: Thermogravimetric analysis: incremental mass loss results for CH tap-treated (turns 1-6) and CI AO treated (turns 19-24) "as-received" green sand samples for Trial 2.**

green sand and its constituents. One explanation is that the coal surfaces in AO-treated green sands are radicalized. We hypothesize that in green sand molds, when AO radicals react with coal, they create a reactive surface that will form bonds with low molecular weight organic fragments, which may themselves be radicals. As a result of this bonding, the organic fragments remain attached to the solid coal matrix, rather than being released as VOCs, therefore retaining mass (Cannon, *et al*., 2000).

With the differences in the "as-received" samples quantified, an examination of the re-moisturized green sand samples could be conducted through TGA analysis. This would represent the mass loss changes that could be expected through one more treatment with AO water. Changes to the clay in the green sand could have an effect on high-temperature mass loss. Since the clays lose waters of hydration over the range of 650-1000°C, an increase in mass loss over that range would indicate a greater loss of waters of hydration. Therefore, the mass increase over 650-1000°C for AO-treated sands, as shown in Figure 3.2-7, seems to indicate that the AO facilitated a prior retention of these waters of hydration, and that these waters of hydration were thus available for release in the 650-1000$^{o}$C range during the TGA tests.

The incremental TGA mass loss data for the Trial 2 re-moisturized sands are displayed in Figure 3.2-8. The CI sands (turns 19-24) had been re-moisturized with either AO, AO-BW, or UWAP-BW water. The data were summarized in Table 3.2-6. For Trial 2 (CI sands from turns 19-24 only), significant differences between the tap

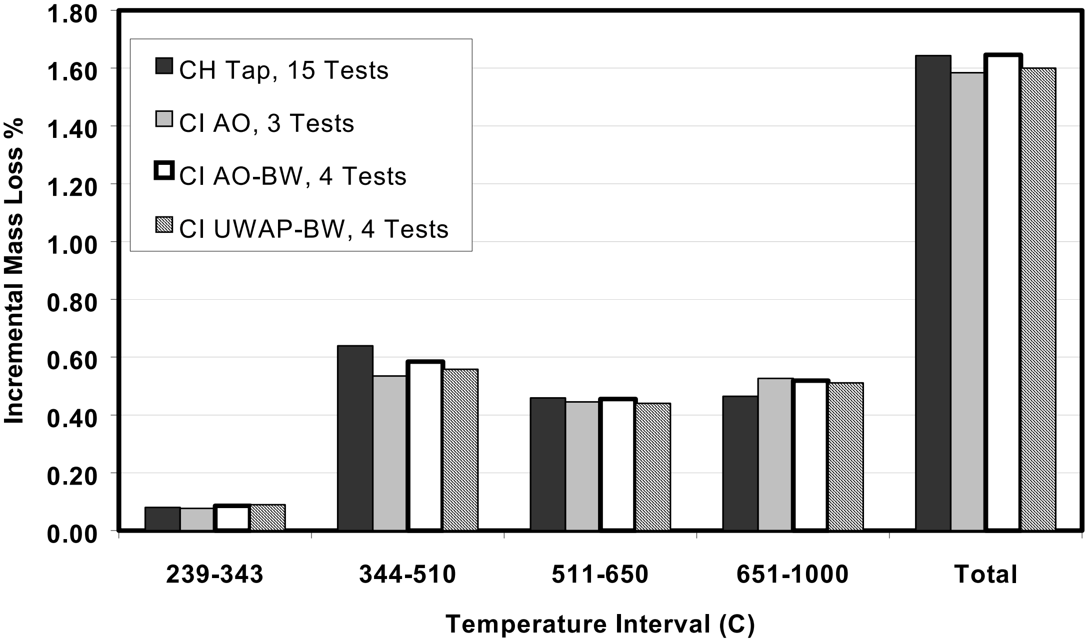


**Figure 3.2-8: Thermogravimetric analysis: incremental mass loss results from re-moisturized CH (turns 1-6) tap, CI (turns 19-24) AO, CI AO-BW and CI UWAP-BW green sand samples for Trial 2.**

**Table 3.2-6: Summary of incremental mass loss data (%) for Trial 2 with re-moisturized green sands.**

| | CH TAP | CI AO | Diff. vs. CH % | CI AO BW | Diff. vs. CH % | CI UWAP BW | Diff. vs. CH % |
|---|---|---|---|---|---|---|---|
| **# of Tests** | 15 | 3 | | 4 | | 4 | |
| **Temperature Interval:** | | | | | | | |
| **239-343** | 0.080 | 0.077 | -3.8 | 0.086 | +7.2 | 0.090 | +11.8 |
| **344-510** | 0.639 | 0.535 | -17.7** | 0.586 | -8.8 | 0.558 | -13.5 |
| **511-650** | 0.459 | 0.446 | -2.9 | 0.455 | -0.9 | 0.441 | -4.0 |
| **651-1000** | 0.465 | 0.526 | -12.3** | 0.520 | +11.2* | 0.511 | +9.4** |
| **Total** | 1.643 | 1.584 | -3.7 | 1.646 | +0.2 | 1.600 | -2.7 |
| ** Significant to the 95% confidence level.<br>* Significant to the 90% confidence level. | | | | | | | |

moisture condition and AO-treated moisture conditions are seen over the VOC emission-generating interval (343-510°C).

Once again, it should be noted that the overall changes in the mass losses for the re-moisturized green sand samples include the initial differences in the "as-received" materials. So from Table 3.2-6, it can be seen that the addition of fresh AO moisture (without blackwater) will decrease mass loss 17.7%. The as-received differences were 7.6% (from Figure 3.2-7), due to the fundamental changes in the green sand that had been treated with AO at CERP/Technikon about 1-2 years prior to the Penn State tests. This leaves 10.1% of the difference that could be attributed to the addition of fresh moisture to the green sand.

A statistical analysis of the materials showed no significant difference between the incremental mass losses of any of the CI re-moisturized sands (i.e. between CI AO, CI AO BW, or CI UWAP BW). Specifically, in the 343-510°C range, the mass loss for CI AO green sand (0.535%) was not statistically different from either the CI AO-BW (0.585%) or the CI UWAP-BW (0.558%) mass losses over that same interval. Also, the incremental mass loss for the CI AO-BW was not statistically different from that for CI UWAP-BW.

In summary, this TGA-GC-FID protocol was found to be capable of quantifying changes in emissions and mass losses between tap and AO moisture treatment; however the distinctions between AO versus non-AO green sands were smaller in one cycle of TGA runs than in 6-24 cycles of pre-production trials. Via TGA, green sand samples can be tested either in the "as-received" dry conditions or with fresh moisture applied. Even though the heating rate is slower than the green sand would experience in the mold, valuable information can still be obtained. The biggest advantage of the TGA-GC-FID experiments is that many samples can be run quickly and readily. This allows for testing of more AO variables and for larger sample populations to be generated for analysis. This helps to ensure that the changes are significant.

#### 3.2.3.2 TGA-FID Studies

The Flame Ionization Detector (FID) was coupled to the effluent of the thermogavimetric analyzer (TGA) to measure the amount of emissions generated during the TGA heating experiments. The TGA can measure the total organic emissions that are generated by the heated green sand during the TGA heating cycle, however the FID cannot speciate those emissions. The FID will not measure water, CO or $CO_2$. The emissions are burned in an atmosphere of 1:10 hydrogen/air and ions are generated. These ions are collected on an electrode and a voltage is recorded. This voltage can be standardized to a calibration gas to determine the mass of emissions of that calibration gas.

The Penn State experiments involved the TGA-FID testing of green sands that were collected from Neenah Foundry, Plant 2. This foundry installed an AO-dry dust-to-black water system on a vertical parting line molding line to produce gray iron castings in January 2000. In this system, green sand system baghouse fines are re-wetted ultrasonically, exposed to AO, and concentrated in a clarifier. The AO black water is recycled to the sand cooler and the muller. This foundry has a capacity of 10-20 tons of gray iron per hour, 100-150 tons of green sand per hour and 110-250 green sand molds per hour. Emissions analyses were conducted prior to and following AO system installation. These tests were conducted either with cores or without cores. Green sand samples were collected during these experiments and used by Penn State for TGA-FID experiments. Table 3.2-7 contains a summary of the samples used for the Penn State TGA-FID experiments.

**Table 3.2-7: Neenah Foundry Plant 2 green sand samples.**

| Sample | Date | AO | Core Loading (lb/ton of Iron) |
|---|---|---|---|
| A | 3/3/00 | Yes | 2058 |
| B | 7/15/99 | No | 1571 |

Two samples were used, both originating from heavily core-loaded green sands. The difference in core loading comes from slightly different castings being produced, with sample A having a higher amount of core/ton of metal.

The green sands were tested in the "as-received" condition, meaning no fresh tap or advanced oxidant moisture was added to the samples. The samples were heated in the TGA in a 1:1 nitrogen/helium atmosphere at 6°C/min. The effluent (120 mL/min) was passed through a heated transfer line (200°C) to the stand-alone FID. Figure 3.2-9 contains the results from the TGA-FID experiment for green sand A. The darker line represents the FID voltage response and is plotted on the left axis. The lighter line represents the TGA derivative mass loss, which is the percent mass lost per degree Celsius. The graph shows that emissions were not generated until 300°C with the largest portion of emissions coming over the 400-600°C temperature range, which is where coal pyrolyzes. The derivative mass loss profile also shows a significant mass loss over this pyrolyzing range of 400-600°C. Moreover, there is also a peak in mass loss between 600-700°C. This mass loss is thought to be due to the pyrolyzing of the residual core resin. Figure 3.2-10 shows the response for the heavily cored sand in the non-AO treated condition, sample B.

The derivative mass loss curves for both samples are similar; however the FID voltage response is higher for sample B. The voltage peaks at a higher value and the area under the voltage response curve is greater. With the large difference seen, it was necessary to duplicate the experiments, which are presented in Figures 3.2-11 and 3.2-12.

The duplicate experiments show a reversal in FID voltage responses with the non-AO-treated sand being lower. This led us to examine the FID and the experimental protocol for possible sources of contamination. One source identified was the heated transfer line. The transfer line was only heated to 200°C, which is lower than some of the larger molecular weight organics being formed. For example, naphthalene has a boiling point of 218°C. This means that the naphthalene could condense in the line and contaminate future experiments. Also, chemicals like phenol with a boiling point of

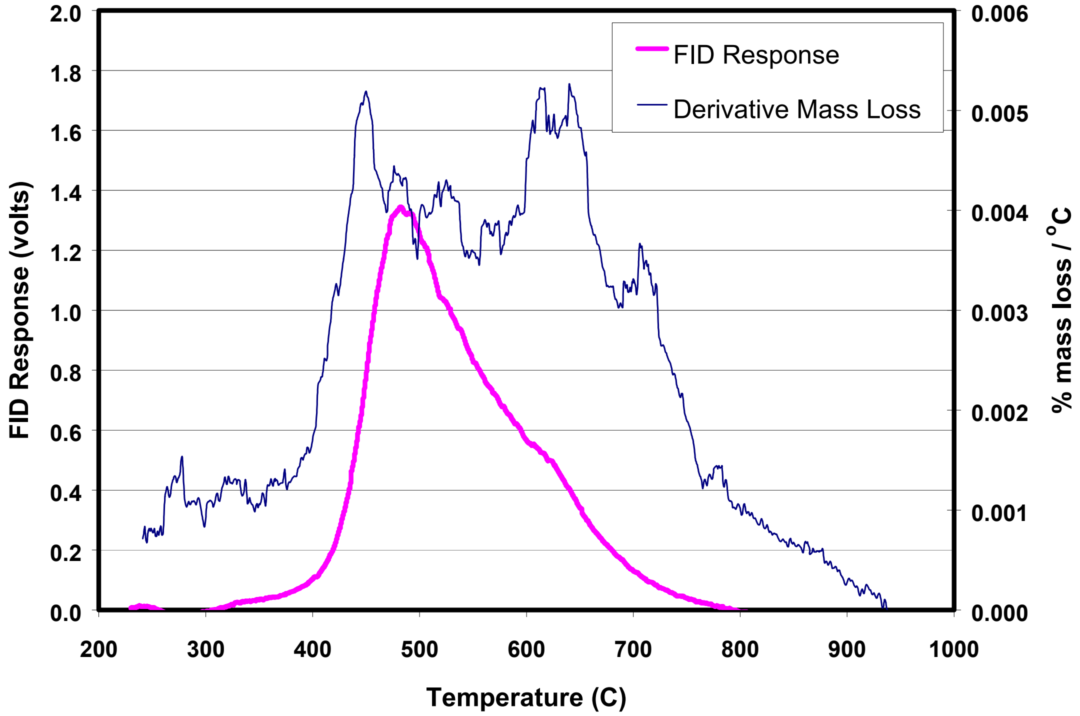


**Figure 3.2-9: Thermogravimetric analysis with flame ionization detection: results for green sand A (heavy core, AO-treated).**

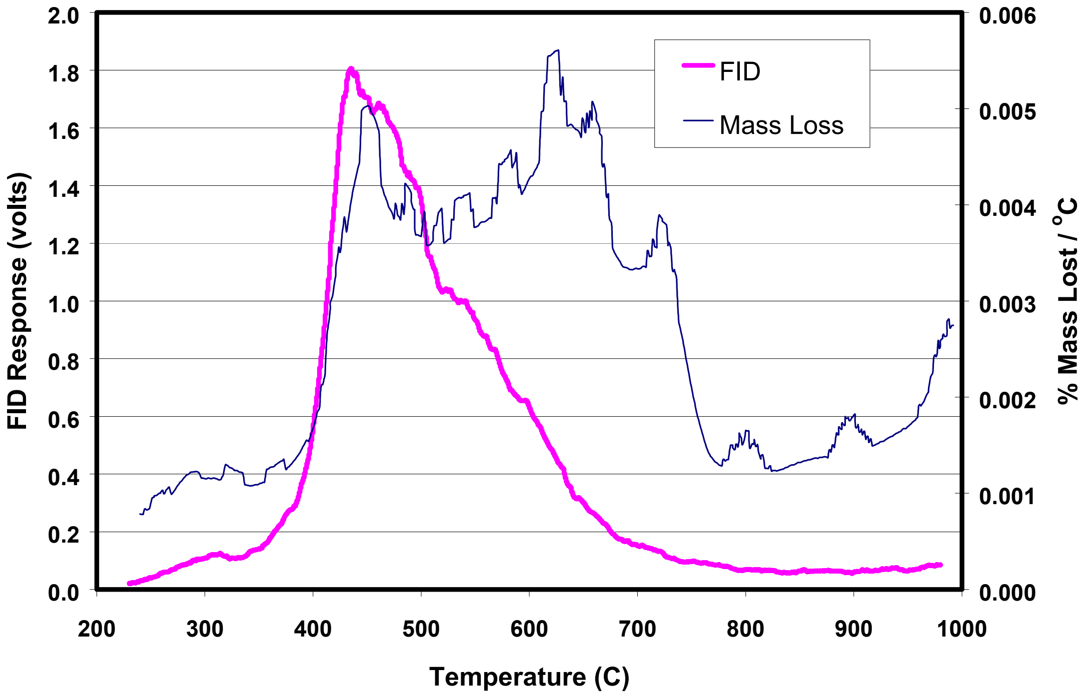


**Figure 3.2-10: Thermogravimetric analysis with flame ionization detection: results for green sand B (heavy core, non- AO-treated).**

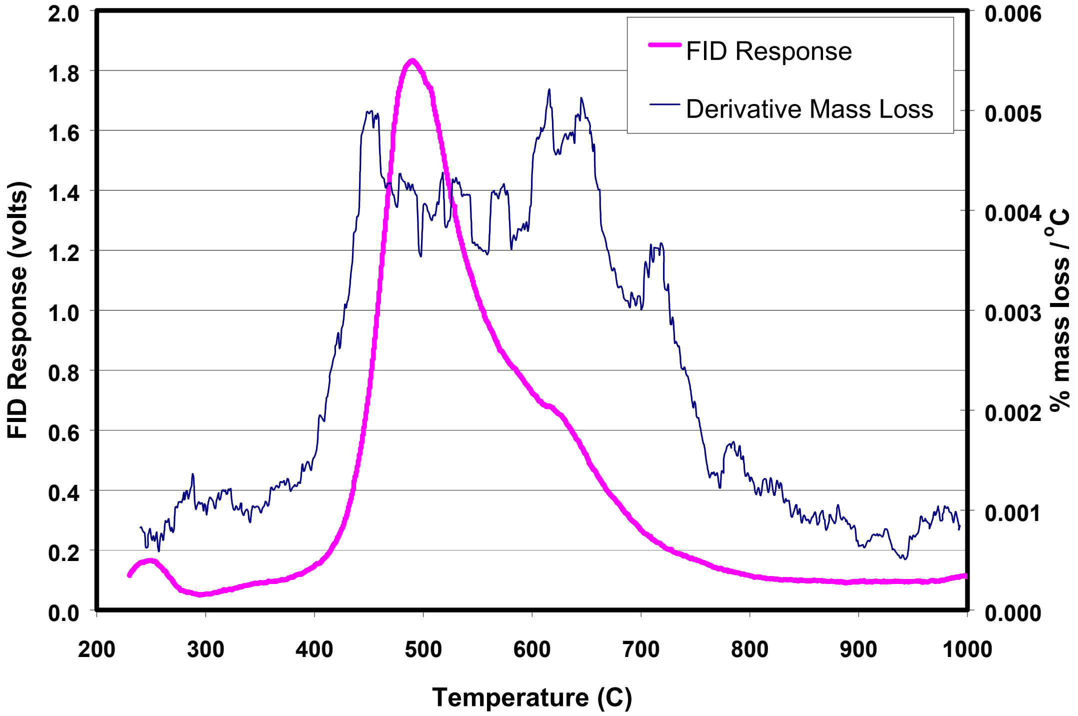


**Figure 3.2-11: TGA with FID: results for green sand A (heavy core, AO treated) duplicate experiment.**

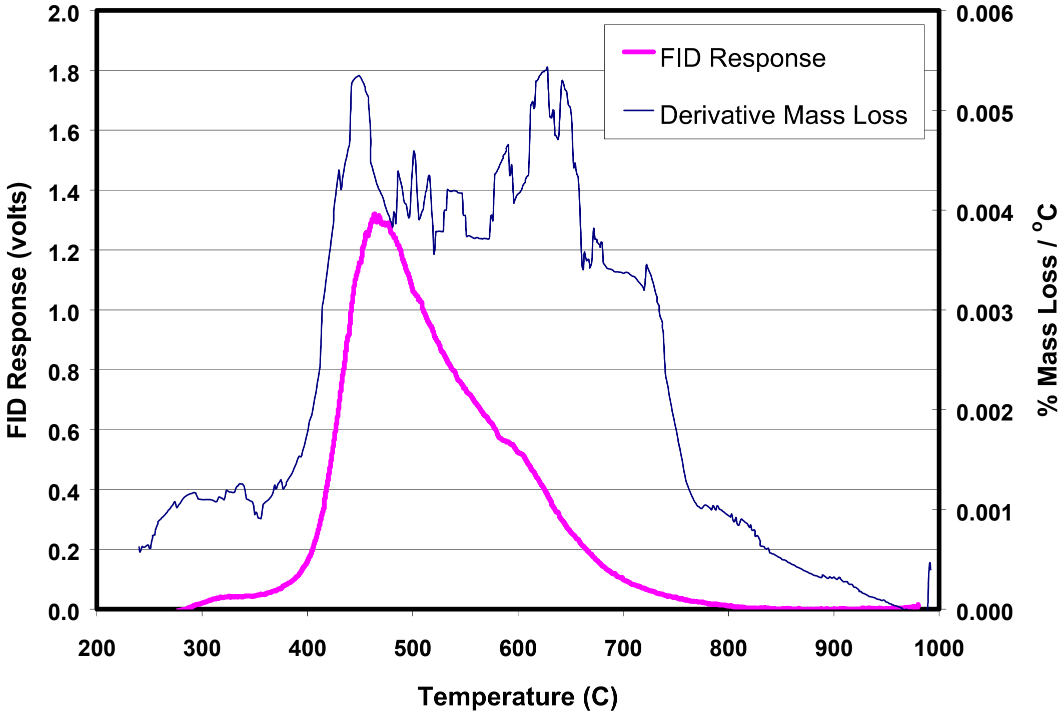


**Figure 3.2-12: TGA with FID: results for green sand B (heavy core, non- AO-treated) duplicate experiment.**

182°C could condense in the line when the heated transfer line was cool. This possible contamination could account for the differences in the duplicate experiments. The researcher tried several methods of remediation, such as cleaning the transfer line and heating the transfer line for 30 minutes prior to and following an experiment; however repeatable results could not be achieved. Currently other members of the Penn State team are modifying the TGA-FID for future experiments. The TGA-FID can only be used for qualitative analysis for this thesis by identifying at what temperatures emissions can be expected. These results were employed in the experiments discussed previously.

#### 3.2.3.3 TGA-GAC Studies

Thermogravimetric analysis and emissions monitoring were conducted on non-AO-treated versus AO-treated green sands that had undergone multiple turns of mulling, molding, metal pouring, cooling, and shakeout at CERP/Technikon. CERP had conducted a series of pre-production pours of sodium silicate cored molds that were treated with tap water versus AO water. Emissions were compared to observe the effect of AO treatment on foundry green sand emissions. CERP labeled the green sand treated with tap water "CH" and the greensand treated with AO water "CI." The "CH" green sands had undergone six cycles ("turns") of mulling, molding, pouring, cooling, shake-out, and re-moisturizing, while the "CI" green sands had undergone 24 turns. Since the tap water-treated and AO water-treated green sand was carefully characterized at CERP, it was fruitful to evaluate these green sands further at Penn State as a means of developing a bench-scale protocol that characterizes foundry green sand in a manner that would discern between AO treatment and non-AO treatment. Once this protocol was developed and correlated to full-scale behavior, it was anticipated that the bench-scale tests could be used to predict the effectiveness of various combinations of AO treatment. Since the bench-scale tests could be conducted more readily than full-scale tests, this was promoted as a means of more readily arriving at the more efficient means of applying advanced oxidants in the foundry. The first of these bench-scale protocols that Penn State developed was one that employed thermogavimetric analysis (TGA), granular activated carbon (GAC), and gas chromatography-flame ionization detection (GC-FID).

The TGA-GAC-GC-FID tests characterized the green sand from two different perspectives. First, the CH and CI sands were characterized by mass loss during a TGA run (as discussed in sections 3.2.3.1 and 2). Second, the two green sands were characterized by emissions generation, and this will be discussed as follows.

While the TGA experiments were being conducted on the CERP/Technikon green sands, the authors also collected emissions from the off-gas into granular activated carbon tubes. The analytes were extracted from the GAC tubes with a $CS_2$-methanol solvent, and the extract was monitored for VOCs via GC-FID analysis. Emissions were collected from CH (non-AO) and CI (AO) sands as they were received, i.e. before they experienced any re-moisturization at Penn State, and from CH and CI sands that were re-moisturized with tap water or various combinations of advanced oxidation-treated water. Two series of tests were conducted on the re-moisturized green sands. The first (Trial 1) compared CH green sands that were a mixture of sand from turns 1-6 versus CI green sands that were a mixture of turns 1-24. The GAC extracts for Trial 1 were analyzed with a manual injection GC-FID technique. The second round of trials (Trial 2) compared CH greensands that were a mixture of sand from turns 1-6 versus CI green sands that were a mixture of turns 19-24, i.e. after the electrical wiring had been corrected in the CERP building, and the AO process could properly operate (as previously discussed). The GAC extracts for Trial 2 were analyzed using automatic injections for GC-FID analysis.

As indicated in the following discussion, no differences were observed in TGA-GAC-GC-FID emissions for as-received samples of CH versus CI, however there were statistically significant differences in the GC-FID emissions when these samples were re-moisturized with AO versus tap water.

- Results of TGA-GAC Tests on As-Received CH and CI Green Sands Prior to Moisture Addition:

Figure 3.2-13 shows the total $VOC_{(C6\text{-}C16)\ \text{as Hexane}}$ collected by TGA-GAC-GC-FID tests of two turns from the CH green sands and two turns of the CI green sands as they were received from CERP (i.e., before re-moisturization at Penn State). Similar toluene data for the as-received CH and CI sands is laid out Figure 3.2-14. The tests were conducted at Penn State more than a year after CERP poured the CH and CI series of molds.

$VOC_{(C6\text{-}C16)\ \text{as Hexane}}$ includes all analytes with elution times between hexane ($C_6$) and hexadecane ($C_{16}$). As shown in Figure 3.2-13, there was no noticeable difference between the as-received CH versus CI results for TGA-GAC-GC-FID (see statistical discussion below). Comparing the total $VOC_{(C6\text{-}C16)\ \text{as Hexane}}$ and toluene values collected from green sands over the entire TGA-GAC run showed that the toluene fraction of total $VOC_{(C6\text{-}C16)\ \text{as Hexane}}$ was approximately 16% of the total $VOC_{(C6\text{-}C16)\ \text{as Hexane}}$ collected from 20 to 1000°C (Figure 3.2-14).

Figure 3.2-13 reveals a general trend in total $VOC_{(C6\text{-}C16)\ \text{as Hexane}}$ generation. The green sand emitted very little $VOC_{(C6\text{-}C16)\ \text{as Hexane}}$ at temperatures lower than 343°C. The majority of the total VOC emissions, about 63%, were released between 343 and 510°C. At temperatures greater than 510°C, the green sand emitted less $VOC_{(C6\text{-}C16)\ \text{as Hexane}}$ with approximately 23% of the total $VOC_{(C6\text{-}C16)\ \text{as Hexane}}$ collected from 510-1000°C.

Figure 3.2-14 shows that the temperature dependence of toluene emissions generally corresponded with total VOCs: essentially no toluene was generated at temperatures below 343°C. Approximately 60% of the total toluene emissions were captured by GAC between 343 and 510°C. The green sands emitted the remaining 40% at temperatures greater than 510°C.

The within-sample error for the CH and CI as-received green sands was calculated as standard deviations from the mean. Dividing the standard deviation by the mean provided a percent error for each condition. The within-sample error with respect to total $VOC_{(C6\text{-}C16)\ \text{as Hexane}}$ varied from 5.5 to 16.1%. The within-sample error with respect to toluene emissions was below 5% in each case except for CI turn 22, which had a within-sample error of 15%.

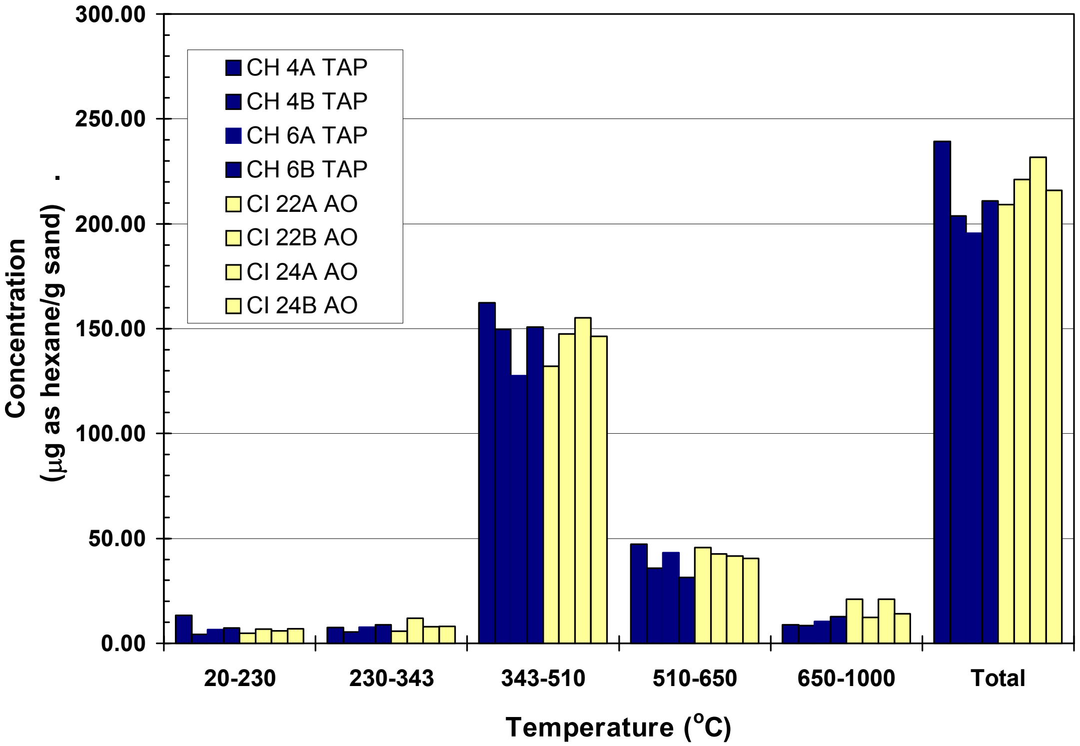


**Figure 3.2-13: Total VOC ($C_6$-$C_{16}$) as hexane mass per gram of green sand for as-received CH (tap) and CI (AO) samples.**

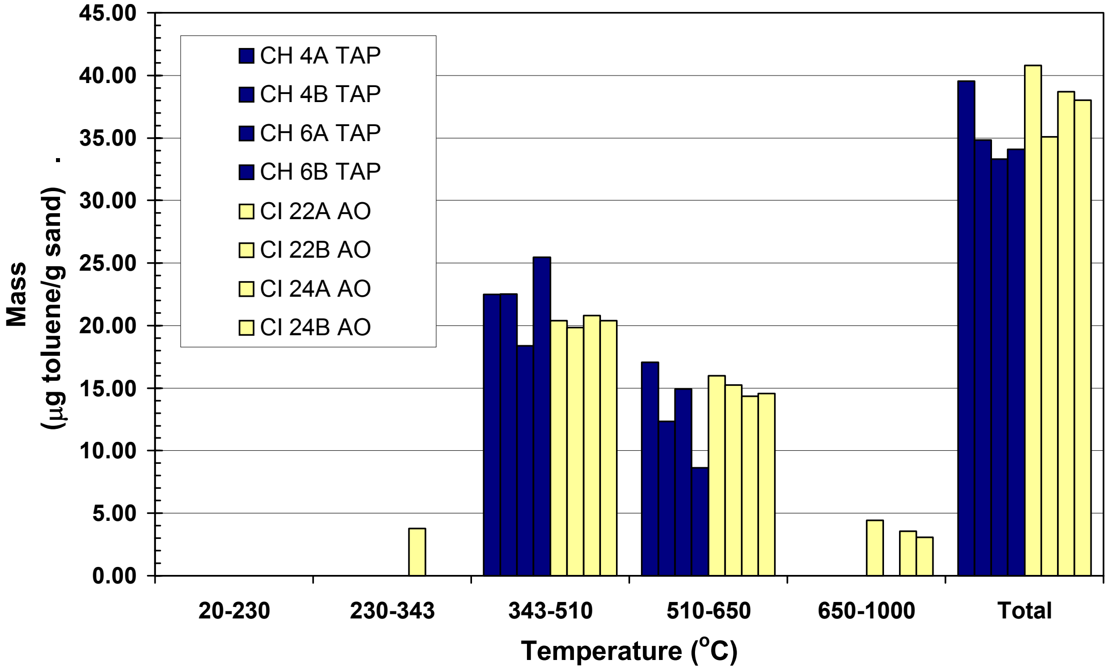


**Figure 3.2-14: Toluene mass per gram of green sand for as-received CH (tap) and CI (AO) samples.**

Figures 3.2-13 and 3.2-14 indicate that the residual effects of the AO treatment that occurred more than a year earlier no longer affected the level of emissions from the AO-treated versus the non-AO-treated green sands. The as-received conditions of CH and CI sands were compared by the t-test assuming unequal variances. This statistical tool is most appropriate to compare two differently sized sets of data with one variable changed. CH and CI total VOC and toluene emissions were not significantly different even at an alpha value of 0.5 (the 50th percentile).

At CERP, during pre-production trials, total VOC $_{\text{(C6-C16) as undecane}}$ emissions were reduced by 55% with AO treatment. When Penn State performed TGA tests one year after the AO treatment of the green sand, there was no significant reduction in total VOC emissions on the as-received CI (AO) versus CH (tap) samples. Likewise, the 52% reduction in toluene emissions from CH to CI that was observed at CERP was not observed when Penn State performed the TGA tests on as-received samples. The results of this experiment indicate that there was no lingering effect of the AO on emissions for the green sands that had experienced AO treatment more than a year prior to TGA testing: any radical scavengers and consequent electron imbalances had long since dissipated.

Table 3.2-8 displays the comprehensive data collected from TGA tests of CH and CI green sand samples as they were received (before moisture addition) and after re-moisturization. Table 3.2-8 also lists the results of statistical analyses by the t-test for all the TGA experiments.

### 3.2.3.4 TGA-GAC Studies of Re-Moisturized Green Sands

Tests next appraised the effects of recent AO treatment incurred by re-moisturizing the green sand samples with AO-treated water immediately before the green sand underwent TGA heating. This second series of tests compared the CH green sand (turns 1-6) that had been re-moisturized with tap water (designated as CH-TAP) versus CI green sand (turns 19-24) that had been re-moisturized with: (a) clean water AO (designated CI AO 19-24), (b) blackwater AO (CI AO BW 19-24), and (c) blackwater AO-underwater plasma (CI AO UWAP BW 19-24). In these tests, the air-dried green sands, which contained 0.5 to 1.0% moisture, were re-moisturized with water to the extent that the total amount of moisture equaled 4.0%. When monitored by a moisture-measuring instrument, this registered as 3.4 – 3.6% moisture.

The results of this comparison are in Table 3.2-8 and Figure 3.2-15. It is noted that turns 19-24 of the CI green sand had a similar average loss on ignition (LOI) to the CH average LOI of turns 1-6. GC-FID analysis of Series 2 of TGA tests used the auto-sampler for injections.

Figure 3.2-15 displays the amount of total VOC $_{\text{(C6-C-16) as Hexane}}$ collected on GAC tubes over the three temperature ranges of the TGA tests. The data reveals a perceptual difference between the non-AO and the AO conditions. The statistical significance of these differences is discussed below. As for the as-received green sands, the re-moisturized green sands emitted the most VOC$_{\text{(C6-C-16) as hexane}}$ between 343 and 510°C,

**Table 3.2-8: Comprehensive emissions and differences from CH to CI green sand samples before and after re-moisturization with tap and various AO treatments.**

| TGA Trial Condition | Total Emissions (µg/g greensand) ± standard dev. | | | | Differences, % [Percent Significance] | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **As-Received<br>CH 4, 6 vs. CI 22, 24<br>Manual Sampler** | CH | | CI | | CH vs. CI | | | | |
| Total $\mathrm{VOC}_{\mathrm{Hex.-(C6-C16)}}$ | 212 ± 19 | | 220 ± 10 | | -3.3 [< 85] | | | | |
| Toluene | 35.4 ± 2.8 | | 38.2 ± 2.4 | | -7.4 [< 85] | | | | |
| **Re-moisturized Ser. 2<br>(CH 1-6 vs. CI 19-24)<br>Autosampler** | CH TAP | CI AO | CI AO-BW | CI AO-UWAP-BW | CH vs. CI AO | CH vs. CI AO-BW | CH vs. CI AO-UWAP-BW | CI AO vs. CI AO-BW | CI AO BW vs. AO UW-AP BW |
| Total $\mathrm{VOC}_{\mathrm{Hex.-(C6-C16)}}$ | 224 ± 0.7 | 187 ± 35 | 180 ± 28 | 189 ± 14 | 17.8 [91] | 21.8 [94] | 17.3 [98] | 4.0 [< 85] | 4.5 [< 85] |
| Benzene | 14.7 ± 0.6 | 13.4 ± 1.2 | 14.4 ± 1.4 | 14.1 ± 0.4 | 9.4 [90] | 1.5 [< 85] | 4.1 [< 85] | -7.9 [< 85] | 2.7 [< 85] |
| Toluene | 30.5 ± 0.9 | 26.7 ± 3.2 | 27.6 ± 2.9 | 26.8 ± 1.6 | 13.3 [94] | 10.0 [86] | 12.9 [99] | -3.3 [< 85] | 3.0 [< 85] |
| $\mathrm{VOC}_{\mathrm{Hex.-(C6-C16)}}$ in 343-510°C range | 171 ± 7 | 154 ± 28 | 139 ± 23 | 145 ± 9 | 10.5 [< 85] | 20.9 [94] | 16.3 [99] | 10.4 [< 85] | 4.6 [< 85] |
| **Re-moisturized Ser. 1<br>(CH 1-6 vs. CI 1-24)<br>Manual sampler** | CH TAP | CI AO | CI AO-BW | CI AO-UWAP-BW | CH vs. CI AO | CH vs. CI AO-BW | CH vs. CI AO-UWAP-BW | CI AO vs. CI AO-BW | CI AO BW vs. AO UW-AP BW |
| Total $\mathrm{VOC}_{\mathrm{Hex.-(C6-C16)}}$ | 302 ± 9 | 233 ± 13 | 239 ± 8 | 266 ± 8 | 26.0 [97] | 23.4 [98] | 12.7 [94] | -13.4 [91] | -10.8 [92] |
| Benzene | 17.5 ± 0.0 | 17.1 ± 0.5 | 16.6 ± 0.6 | 17.7 ± 0.0 | 2.6 [< 85] | 5.1 [< 85] | -0.9 [< 85] | -6.0 [< 85] | -3.5 [< 85] |
| $\mathrm{VOC}_{\mathrm{Hex.-(C6-C16)}}$ in 343-510°C range | 233 ± 12 | 174 ± 7 | 183 ± 3 | 210 ± 9 | 29.1 [97] | 24.1 [89] | 10.3 [84] | -13.9 [95] | -18.9 [85] |

and this amounted to approximately 70% of the total VOC emissions. A very small amount of VOCs were generated at temperatures below 343°C, while approximately 30% of the total VOC emissions were generated from 510 to 1000°C.

The CH green sands that were re-moisturized with tap water produced approximately 224 µg of total $\mathrm{VOC}_{\mathrm{(C6\text{-}C\text{-}16)\ as\ hexane}}$ per gram of green sand over the entire temperature range of the TGA tests. As shown in Table 3.2-8, lower amounts of VOCs, which ranged from 180 to 189 µg per gram of green sand, were found for the sands re-moisturized with AO. Similarly, the data in Table 3.2-8 show a decrease in VOC emissions for AO-remoisturized sands over the main VOC generation temperature range (343 to 510°C). From the total VOC $_{\mathrm{(C6\text{-}C\text{-}16)\ as\ Hexane}}$ data, one can surmise that advanced

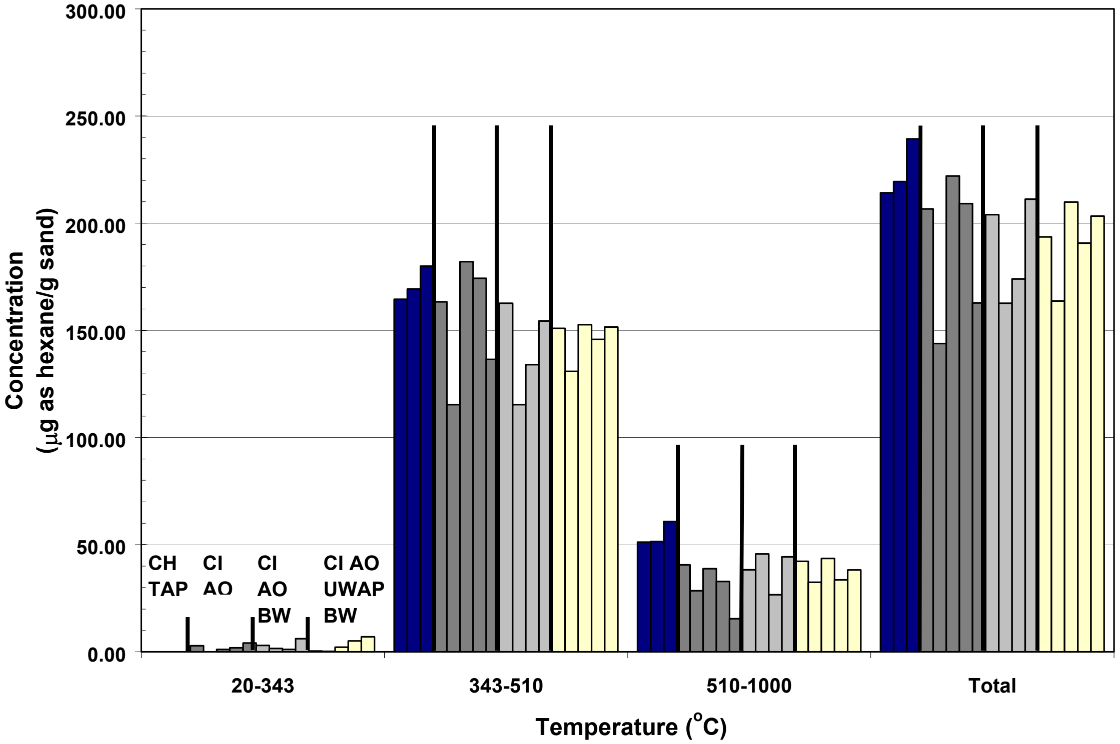


**Figure 3.2-15: Total VOC $_{\text{(C6-C-16) as Hexane}}$ mass per gram of green sand, CH versus CI (turns 19-24) green sands re-moisturized with tap water or a variety of advanced oxidation water conditions.**

oxidation treatment reduced the amount of VOCs generated by the CI green sands which were re-moisturized with various AO water conditions, and that this distinction was statistically significant to the 91-98% confidence level.

Figure 3.2-16, Figure 3.2-17, and Table 3.2-8 show the mass of benzene and toluene per gram of green sand collected on GAC tubes during TGA tests of CH and CI (19-24) green sands. The green sands produced the majority of benzene at the 510-1000°C temperature range, and this amounted to approximately 57% of total benzene generated. Between 20-343°C only about 10% and between 343-510°C about 33% of the total benzene mass was emitted. CH green sands that were re-moisturized with tap water generated around 15 µg benzene per gram green sand over the entire TGA run. CI AO (19-24) produced approximately 13 µg/g, CI AO BW (19-24) produced approximately 14 µg/g, and CI AO UWAP BW (19-24) produced approximately 14 µg/g. Thus, AO treatment only slightly decreased the benzene emissions, if at all. These benzene distinctions were generally not statistically significant, as identified in Table 3.2-8.

The toluene trend shown in Figure 3.2-17 mimicked that seen for total VOC $_{\text{(C6-C16) as Hexane}}$. About 55% of the total toluene emissions were collected between 343 and 510°C. Approximately 10% of the total toluene emissions were collected between 20 and 343°C, and approximately 30% of the total toluene emissions were collected between 510 and 1000°C. CH green sands re-moisturized with tap water produced 31 µg toluene

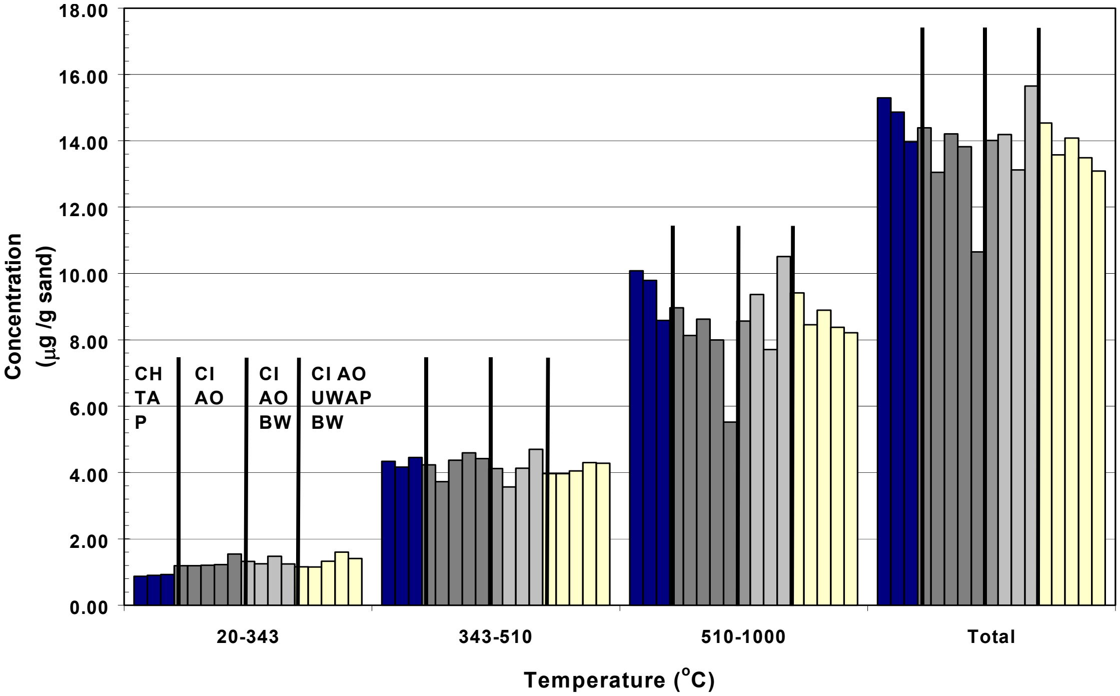


Figure 3.2-16: Benzene mass per gram of green sand, CH and CI (19-24) green sands re-moisturized with tap water or a variety of AO-treated waters (Series 2 emissions capture tests).

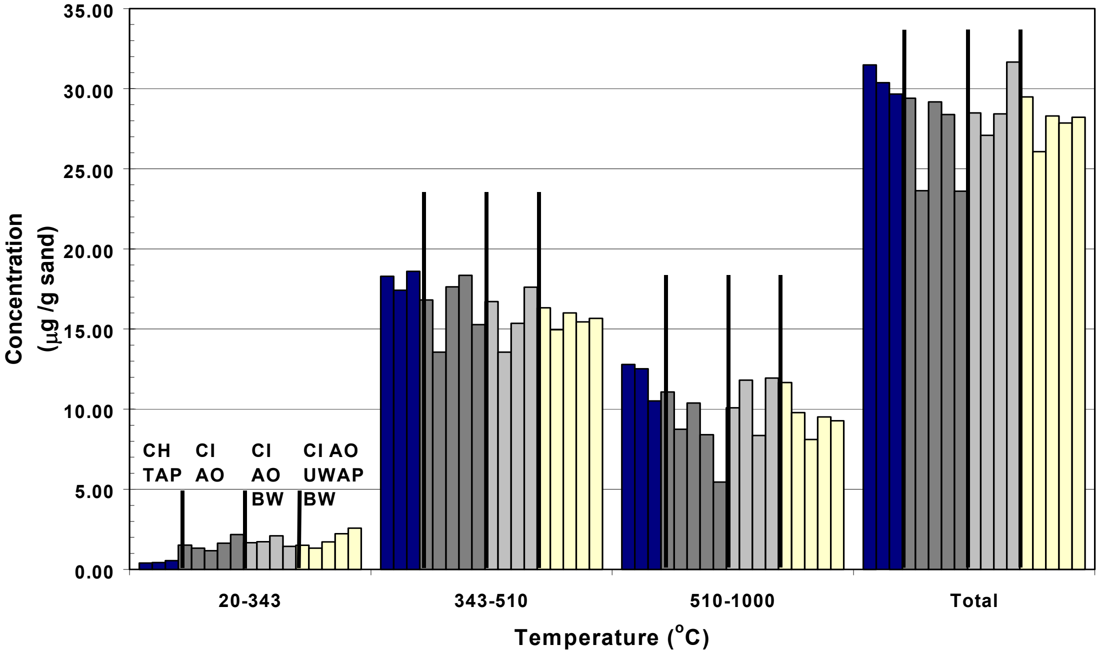


Figure 3.2-17: Toluene mass per gram of green sand, CH and CI (19-24) green sands re-moisturized with tap water or a variety of AO-treated waters (Series 2 emissions capture tests).

per gram of green sand between 20 and 1000°C. In comparison, CI AO (19-24) produced approximately 27 μg/g, CI AO BW (19-24) produced approximately 28 μg/g, and CI AO UWAP BW (19-24) produced 27 μg/g. Thus, advanced oxidation treatment reduced the toluene emissions of CI green sands. These differences were statistically significant to the 86-99% confidence interval.

Total VOC $_{\text{(C6-C-16) as Hexane}}$ included all analytes with elution times between hexane and hexadecane. Benzene and toluene were two analytes that were included in the total VOC $_{\text{(C6-C-16) as Hexane}}$ value. By comparing the total mass of VOC, benzene, and toluene, the fractions of VOCs consisting of benzene and toluene were determined as 7% and 14%, respectively.

To determine statistical differences between CH that was re-moisturized with tap water versus CI (19-24) treated with AO, AO-BW and AO UWAP-BW, within-condition errors as well as between-condition differences were calculated. The within-condition errors for all the emissions collected during the TGA tests of CH and CI (19-24) were calculated as standard deviations from the mean, and these have been listed in Table 3.2-8. Dividing the standard deviation by the mean for each condition (CH, CI AO, CI AO BW, and CI AO UWAP BW) provided a within-condition error as coefficient of variance. The majority of conditions had within-condition coefficients of variance of less than 10%. Several coefficients for total VOC $_{\text{(C6-C-16) as Hexane}}$ and VOCs collected between 343 and 510°C deviated above 10% due to the compounding error of individual analytes. However, no coefficient of variance exceeded 19%. The within-condition error was higher for the second series of tests than for the first series because the auto-sampler caused greater injection error than did manual injection under the conditions that were employed. The low within-condition error suggests that the TGA-GAC emissions capture test was a repeatable bench-scale test in assessing the emissions.

Between-condition differences were calculated for total VOCs, benzene, toluene, and VOCs emitted between 343 and 510°C. The following equation calculated the percent difference between the CH and CI conditions:

$$\%\ \text{Difference} = \left(\text{Average}_2 - \text{Average}_1\right) \Big/ \left(\text{Average}_2 + \text{Average}_1\right)/2$$

Several of the CI conditions were compared to determine whether TGA heating could distinguish the various AO treatments from each other. Table 3.2-8 includes the differences between CI AO (19-24) versus CI AO BW (19-24). Calculations showed the differences between CI AO (19-24) versus CI AO BW (19-24) were minimal for VOCs, benzene, and toluene. Similarly, the differences between CI AO BW (19-24) versus CI AO UWAP BW (19-24) were minimal for all emissions. Thus, there was no consistent statistical difference between any of the advanced oxidation protocols relative to TGA-monitored emissions.

As previously mentioned, mass loss was also recorded while GAC tubes collected emissions during the TGA tests of CH and CI green sands. Illustrating the parallel nature of green sand mass loss and emissions, Figure 3.2-18 displays the mass loss for CH and CI (19-24) green sands that were re-moisturized with tap water or a variety of advanced oxidation water conditions. Figure 3.2-18 reveals that in the 343-510°C temperature range, true differences in mass loss were manifest between CH versus CI AO (19-24), CI AO BW (19-24), and CI AO UWAP BW (19-24). This is the temperature range in which the majority of VOCs were emitted by the green sand. Observing the mass loss between 343 and 510°C, one can see that CH TAP lost significantly more mass than CI AO (19-24), CI AO BW (19-24), and CI AO UWAP BW (19-24). CI AO (19-24) lost the least amount of mass of all the CI (19-24) conditions. This concurs with our findings that that CI AO (19-24) would generate the least emissions because it showed the least mass loss (although mass loss could also reflect the release of water, CO, $CO_2$, organic compounds less than $C_6$ or greater than $C_{16}$, and condensables).

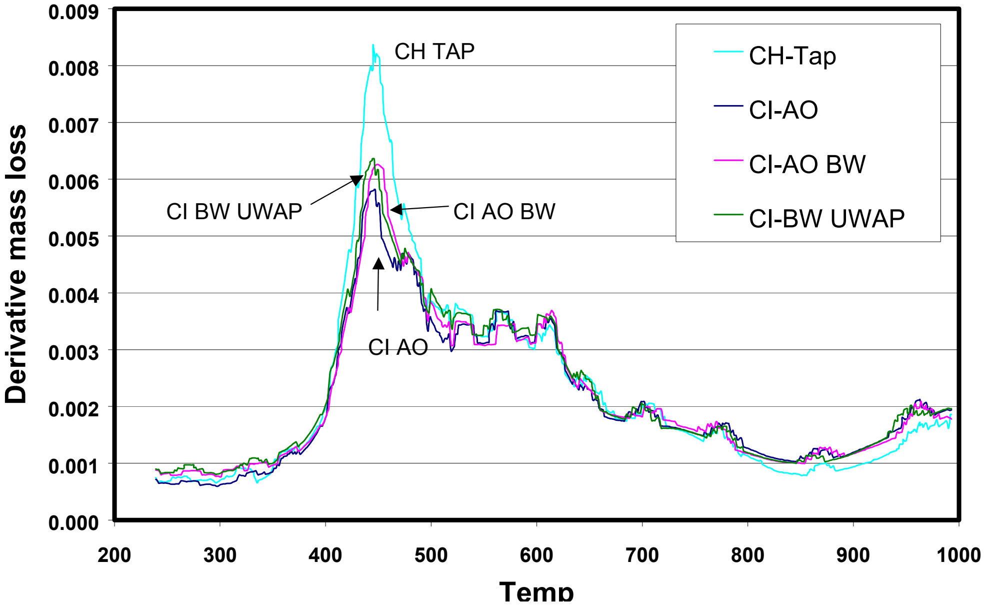


**Figure 3.2-18: Derivative of the mass loss per degree Celsius for the TGA mass loss tests of CH (turns 1-6) and CI (19-24) green sands that were re-moisturized with tap water or a variety of AO-water conditions, Series 2. Each line is an average.**

- Results of the First Series of TGA tests on CH and CI Green Sands Re-moisturized with Tap Water or a Variety of Advanced Oxidation Water Conditions:

The first series of the TGA tests on re-moisturized sands assessed the CH green sand that had been re-moisturized with tap water (as a control) versus all the turns (1-24) of CI green sand that had been re-moisturized with: (a) clean water AO (CI AO 1-24), (b) blackwater AO (CI AO BW 1-24), and (c) blackwater AO-underwater plasma (CI AO UWAP BW 1-24). It is again noted that the Series 1 GC-FID analysis employed manual injections.

Figure 3.2-19 displays the total VOC $_{(C6\text{-}C16)\ \text{as Hexane}}$ mass emitted by CH TAP, CI AO (1-24), CI AO BW (1-24), and CI AO UWAP BW (1-24) green sands that underwent

TGA heating. The differences between AO and non-AO treatments are quite apparent visually, and the statistical significance of these differences is discussed below. As in the second series (where CH turns 1-6 were compared to CI turns 19-24), the majority of total VOC $_{\text{(C6-C16) as Hexane}}$ emissions, approximately 70%, were produced between 343 and 510°C. About 5% of the total VOC $_{\text{(C6-C16) as Hexane}}$ emissions were produced at temperatures lower than 343°C, and about 25% of the total VOC $_{\text{(C6-C16) as Hexane}}$ emissions were produced at temperatures greater than 510°C.

Over the full temperature range of 20-1000°C, the CH green sands that were re-moisturized with tap water produced 302 μg of total VOC $_{\text{(C6-C-16) as Hexane}}$ per gram of green sand. In contrast, CI AO (1-24) produced 233 μg/g, CI AO BW (1-24) produced 239 μg/g, and CI AO UWAP BW produced 266 μg/g. The differences between non-AO versus AO treatments were significant to the 94-98% confidence interval. In the 343-510°C range alone, the CH green sands that were re-moisturized with tap water produced approximately 233 μg/g, whereas CI AO (1-24) produced 174 μg/g, CI AO BW (1-24) produced 183 μg/g, and CI AO UWAP BW (1-24) produced 210 μg/g. Thus, for these TGA experiments, the variety of advanced oxidation treatments significantly reduced total VOC$_{\text{(C6-C-16) as Hexane}}$ (94-98% confidence interval) and the VOCs generated between 343-510°C (84-97% confidence interval). However, no advanced oxidation treatment significantly reduced benzene within the 85% confidence interval.

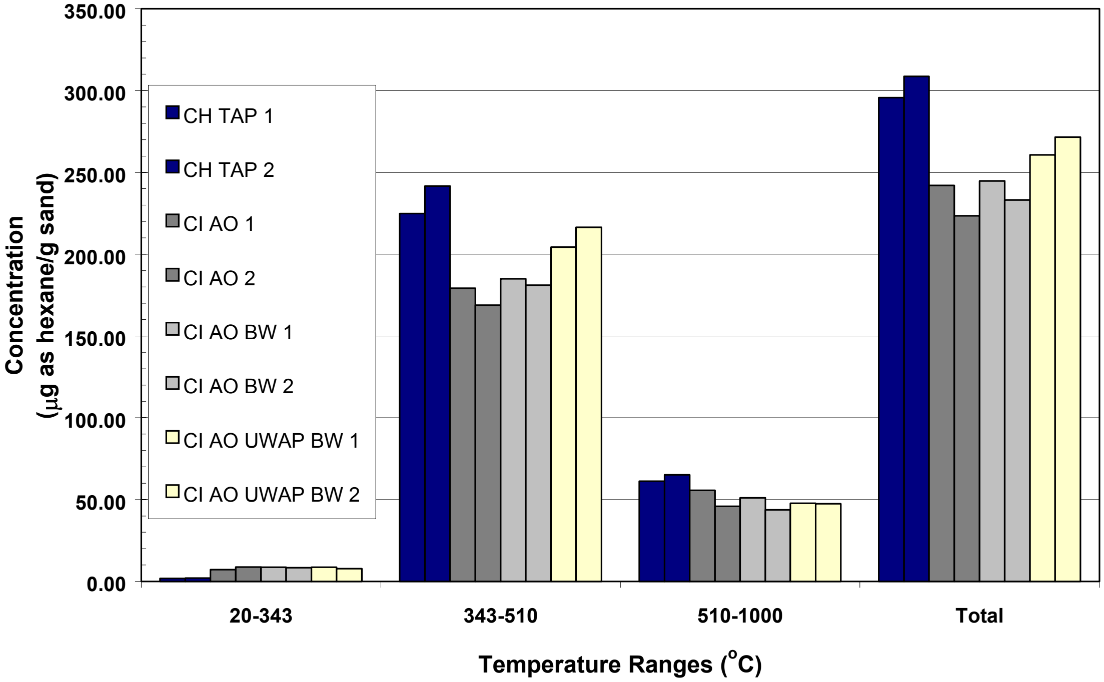


**Figure 3.2-19: Total VOC$_{\text{(C6-C16) as hexane}}$ mass per gram of green sand, CH (turns 1-6) and CI (1-24) green sands that were re-moisturized with tap water or a variety of advanced oxidation-treated water conditions (Series 1 emissions capture tests).**

The methods of manual versus auto-injection produced different concentrations of analytes detected by the GC-FID. With manual sampling, one microliter of sample followed by one microliter of solvent was injected into the GC column. With auto-injections, only the one microliter of sample was injected into the column. Results have shown the manual injection generated higher values than auto-injection cross-check. It was observed that auto-injection of two microliter samples generated similar values to manual injection of one microliter samples (plus one microliter of solvent). However, Penn State has conducted only a limited number of two microliter auto sample tests thus far; and thus the values in Table 3.2-8 were left as they are. The difference in injection methods is a topic that requires further study, and it highlights the difficulty of monitoring and analyzing volatile organic compounds.

Figure 3.2-20 shows the mass of benzene per gram of green sand collected on GAC tubes during the Series 1 TGA tests of CH and CI (1-24) green sands that had been re-moisturized. Table 3.2-8 lists the mass of benzene recovered from GAC tubes from 20-1000°C. As shown by the Figure 3.2-20 and Table 3.2-8 data, there was no statistically significant difference relative to benzene emissions between non-AO versus AO conditions for these re-moisturized conditions.

Unlike total VOC emissions, green sands produced the majority of the total benzene emissions, approximately 66%, at the 510-1000°C temperature range. Approximately 5% of the benzene was emitted at temperatures lower than 343°C, with about 29% of the total benzene emitted between 343 and 510°C.

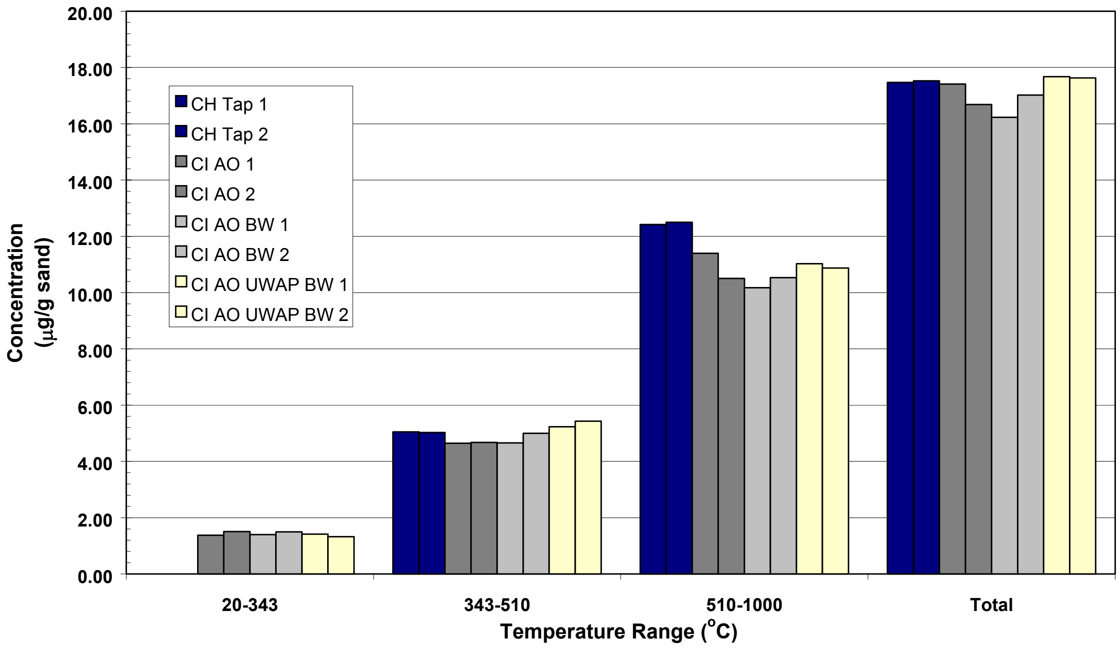


**Figure 3.2-20: Benzene mass per gram of green sand, CH (turns 1-6) and CI (1-24) green sands that were re-moisturized with tap water or a variety of advanced oxidation-treated water conditions (Series 1 emissions capture tests).**

Since total VOC $_{\text{(C6-C-16) as Hexane}}$ included all analytes with elution times between hexane and hexadecane, benzene ($C_6H_6$) was a subset of the total VOC $_{\text{(C6-C-16) as Hexane}}$ analysis. By comparing the total mass of VOC to the total mass of benzene, the fraction of VOC consisting of benzene was determined as approximately 7%.

The within-condition errors for all the emissions collected during the TGA tests of CH (turns 1-6) and CI (1-24) were calculated as standard deviations from the mean, and these are listed in Table 3.2-8. Dividing the standard deviation by the mean for each condition (CH, CI AO, CI AO BW, and CI AO UWAP BW) provided a coefficient of variance within each condition. The majority of conditions had coefficients of variance of less than 5%, suggesting that the results of the TGA-GAC emissions capture tests were repeatable.

Table 3.2-8 also includes the percent differences between CI AO (1-24) versus CI AO UWAP BW (1-24) and CI AO BW (1-24) versus CI AO UWAP BW (1-24). The VOC differences between CI AO (1-24) and CI AO UWAP BW (1-24) were approximately 15%, and the benzene difference was minimal. Similarly, the VOC differences between CI AO BW (1-24) and CI AO UWAP BW (1-24) were between 10 and 20%, and the benzene difference was minimal.

As an overall summary relative to the series 1 (CI turns 19-24) and 2 (CI turns 1-24) tests of the CH versus CI greensands, the TGA tests at Penn State showed statistically significant differences between green sands that were re-moisturized with tap or advanced oxidation treated waters. However, the magnitudes of these differences were not as great as the emissions reductions seen in the preproduction pours at CERP/Technikon. These distinctions are highlighted in Table 3.2-9. CERP/Technikon calculated a total VOC $_{\text{(C6-C16) as Undecane}}$ reduction of 53-55% from the CH (system using tap water) to the CI (system using AO clean water) green sands. In contrast, TGA tests at Penn State showed a reduction in total VOC $_{\text{(C6-C16) as Hexane}}$ emissions from CH tap re-moisturized to CI AO re-moisturized green sands on the order of 18-26%. Similarly, CERP/Technikon experienced decreases of 44-46% in benzene and 18-26% in toluene emissions from CH to CI green sand molds. Penn State TGA analyses resulted in decreases of 1-9% in benzene and 10-13% in toluene emissions from CH tap water re-moisturized green sand to CI AO water re-moisturized green sands.

There are several features that distinguish TGA conditions (at Penn State) from the conditions that occur during the casting process (at CERP/Technikon). First, in the TGA tests, the green sand experienced one cycle of advanced oxidation and thermal exposure, whereas in the preproduction foundry pours at CERP/Technikon, the green sand experienced multiple turns of advanced oxidation and thermal exposure. Second, in a TGA run, all the green sand experienced elevated temperatures up to 1000°C, whereas during the casting process only the green sand that is closest to the molten metal experiences the highest temperatures. This distinction is highlighted by the results shown in Table 3.2-9, which show that for the TGA experiments total VOC $_{\text{(C6-C16) as Hexane}}$ losses were 180-300 μg/g of green sand, whereas in a preproduction mold, they were 10-20 μg/g of green sand, only 4-8% as much.

In addition, during the TGA heating the temperature was slowly raised at 6°C/minute. The slow temperature ramping drove out the loosely bound water in the

**Table 3.2-9: Emissions results of CERP/Technikon pre-production pours of CH and CI green sands and Penn State TGA-GAC tests of CH green sand re-moisturized with tap water and CI green sand re-moisturized with AO clean water.**

| Preproduction pours at CERP<br>lbs emissions/ton of metal poured | CH | CI<br>(7-12)&(19-24) | %<br>Difference |
|---|---|---|---|
| Total VOC(C6-C16) as undecane | 0.206 | 0.117 | 55 |
| Total Benzene | 0.0572 | 0.0358 | 46 |
| Total Toluene | 0.0375 | 0.0221 | 52 |
| µg emissions/g green sand | | | |
| Total VOC(C6-C16) as undecane | 18.1 | 10.5 | 53 |
| Total Benzene | 5 | 3.2 | 44 |
| Total Toluene | 3.3 | 2 | 49 |
| TGA-GAC at Penn State<br>µg emissions /g green sand | CH | CI<br>(7-12)&(19-24) | %<br>Difference |
| Total VOC(C6-C16) as hexane | 224 | 187 | 17.8 |
| VOC(C6-C16) (343-510°C) | 171 | 154 | 10.5 |
| Total Benzene | 14.7 | 13.4 | 9.4 |
| Total Toluene | 30.5 | 26.7 | 13.3 |
| TGA-GAC at Penn State<br>µ emissions /g green sand | CH | CI (1-24) | %<br>Difference |
| Total VOC(C6-C16) as hexane | 302 | 233 | 26 |
| VOC(C6-C16) (343-510°C) | 233 | 174 | 29.1 |
| Total Benzene | 17.5 | 17.1 | 2.6 |

green sand, rendering the water (and perhaps some of the radicals that it contained) unavailable for reactions at higher temperatures where coal is pyrolyzed and VOCs are emitted. In contrast, during a casting pour, the green sand that is adjacent to the molten metal heats up to over 1000°C instantaneously. Green sand that is farther away from the casting probably experiences elevated temperatures while water still exists in the green sand mix. Thus, during the casting, water treated with advanced oxidation may still be present at higher temperatures to react with the emissions during the casting process.

Another distinguishing feature of the TGA tests is that they employed only one gram of green sand, thus emissions could not re-adsorb in the green sand. In contrast, in full-scale conditions many pounds of green sand are pressed tightly together, and volatiles that are emitted from the hot interior of the mold can be re-adsorbed by cooler green sand away from the casting surface.

Despite these distinctions between the TGA tests and the casting conditions, the trends of the TGA data reflect the same trends as for the casting emissions, with the VOC reductions from tap to advanced oxidation treated green sands about half as pronounced in the TGA tests as in the pre-production pour tests. Thus, the TGA procedure can be usefully employed as a surrogate for some of the important features of full-scale foundry operation for predicting relative trends of emissions that would occur from various advanced oxidation scenarios.

The results from the TGA tests of the re-moisturized sands depicted some basic findings about AO treatment. Specifically, the TGA tests showed that advanced oxidation treatment effectively reduced green sand emissions. Further, the statistical analysis of the second series CI turns 1-24) of TGA tests indicated that all three varieties of AO treatment had about the same effectiveness. The analysis of the first series (CI turns 19-24) of TGA tests indicated that AO UWAP BW was not quite as effective at reducing VOC emissions as AO or AO BW, but the distinctions were not significant to the 85% confidence level. From this analysis, TGA tests can serve as a useful screening test to assist foundry personnel in selecting the AO treatment that would most effectively reduce foundry green sand emissions.

The hypothesized explanations for the effect of advanced oxidation on foundry emissions include the changing characteristics of green sand constituents and chemical reactions within the green sand mold due to the sudden temperature increase. One proposed mechanism of the effect of AO on green sand emissions is that the coal in the mold is converted to activated carbon. If generated, the cooler activated carbon within the outside portions of the mold could adsorb the VOCs that are released by the hotter interior of the mold, and this would reduce the emissions released out of the mold. Continuing research at Penn State is suggesting that the AO process does indeed create activated carbon in the portion of the green sand mold that is closest to the mold surface.

Another explanation for the reduction of emissions of AO-treated green sand molds is that clay platelets remain further spaced from one another when the clays are exposed to advanced oxidants. X-ray diffraction can measure the distance between clay platelets, and the exploratory results to date show that clay platelets of green sand that have been treated with advanced oxidation remain further apart than those treated with tap water. Thus, the clay platelets of AO-treated green sand could retain more water than tap-treated platelets. This maintained spacing also translates to retaining the green sand strength and methylene blue clay levels. The TGA mass loss data of CH and CI (1-24), (19-24) green sands support this notion as well. The CI AO sands that were treated with AO water lost slightly more mass at 625°C where waters of hydration are driven out of the clay. This indicates that the AO-treated sand retained more clay hydration water (before being driven out at temperatures greater than 625°C). Along with improved activation of the clay, AO processes may clean the organic coat around the clays and sand grains, allowing them to more fully reactivate over several turns in the foundry and adsorb more HAPs.

Another hypothesis as to how AO reduces foundry emissions involves radical scavengers, such as carbonate, carbon, or metal oxides. These scavengers release electrons to the hydroxyl radicals at ambient temperatures, and then become highly reactive in search of electrons when the mold reaches the high casting temperatures. The scavengers could thus serve to meld VOCs to the coal matrix via the same mechanism that is used to form rubber with advanced oxidation.

While we are continuing to explore the reasons why advanced oxidation is so effective in the foundry, bench-scale tests are helping find answers. Future pilot-scale foundry pours should shed new light on the effects of AO on foundry emissions, since a repeatable emissions capture protocol has been developed. Despite the questions that remain regarding the AO mechanism, the emissions reduction effects of AO are indisputable.

### 3.2.4 Summary of Section 3.2

1. The Penn State team conducted tests that coupled thermogravimetric analysis (TGA), emissions capture onto granulated activated carbon (GAC) tubes with carbon disulfide ($CS_2$) and methanol extraction, and VOC monitoring by gas chromatography-flame ionization detection (GC-FID).

2. The tests compared two different green sands that had been processed in pre-production foundry tests at CERP/Technikon. The first composite (labeled "CH") represented green sand that had experienced multiple turns without AO treatment. The second ("CI") had experienced multiple turns with an advanced oxidation-clean water system (Sonoperoxone$^{TM}$). Both of these greens sands included sodium silicate cores.

3. The Penn State research team compared the response of these two green sands to TGA, GAC, and GC-FID testing. These tests were conducted with the "as-received" green sands (no further modification at Penn State) more than 2 years after the CERP trials. The tests were also conducted with these green sands after they had been re-moisturized at Penn State: the CH (non-AO) green sand, was re-moisturized with tap water at Penn State, whereas the CI (AO) green sand was re-moisturized with either advanced oxidation clean water with the Sonoperoxone$^{TM}$ system (designated as CI AO), or with AO-blackwater (CI AO BW), or with AO-underwater plasma blackwater (CI AO UWAP BW).

4. When CERP/Technikon processed these sodium silicate-cored green sands, the AO-treated sands released 45-55% less emissions than the non-AO-treated green sand.

5. In comparison, during TGA-GC-FID tests at Penn State, the AO green sands (CI) that were re-moisturized with AO, AO-BW, or AO-UWAP-BW released 13-26% fewer TGA-VOCs then did the non-AO green sands (CH) that were re-moisturized with tap water. These differences were statistically significant to the 91-98% confidence interval. Thus, AO reduced VOC emissions, and the TGA protocol mimicked some, but not all, of the pour-in-mold conditions.

6. Using TGA, the VOC emissions distinctions among the three methods of AO re-mositurization (i.e. AO versus AO-BW versus AO-UWAP-BW) were not statistically significant. Therefore one AO method could not be considered better or worse than another from the tests performed.

7. The TGA emissions from the "as-received" non-AO green sand (CH) and AO green sand (CI) were about the same as one another. This indicated that the favorable emissions effects of AO treatment did not carry over more than two years after initial treatment. These results could be attributed to the disappearance of active radicals that remained a short time within the green sand, rather than to any potential physical changes that might have remained within the green sand for more than a year.

## 3.3 EMISSIONS PERFORMACE – PLANT TRIALS

The emissions performance of AO systems was evaluated at operating foundries from historical emissions data as well as carefully conducted plant stack testing. This included data on the operating performance of AO-CW systems, an AO-BW system and a comprehensive study of an AO-DBW system. For the AO-DBW system, baseline data was collected prior to AO regarding emissions and sand system performance. Such data was also collected during phased start-up and near-steady-state operation over a two year period of time.

### 3.3.1 AO-CW Emissions Performance – Grede-Reedsburg

Grede-Reedsburg (WI) has operated an AO-CW system since 1995 on a high production vertical parting molding line that produces ductile iron castings while using phenolic urethane cold box cores. AO additions are made at the sand cooler, at the blender and at the muller. Since 1995, they have performed comprehensive stack tests on a bi-weekly basis for specific casting part numbers. All stack tests of combined pouring, cooling and shakeout have been performed in the middle of long production runs for a specific cored and no-core casting after the sand system has been “turned over” and the emissions profile of the molding line has stabilized. One-hour stack tests using slip stream capture methods (U.S. EPA Method 18) have been conducted by foundry personnel. All emissions tube samples were sent to a single commercial laboratory for analysis. Figures 3.3-1 through 3.3-4 summarize benzene and total VOC emissions results over a three year period of time for both a no-core casting and a heavily cored casting. A small number of initial baseline results before AO system installation (and a single early test with the AO system intentionally turned off) are indicated in these figures.

This exhaustive set of stack test results shows emissions changes from AO additions, from AO-driven sand system optimization and from other property-driven sand system additive adjustments over this four year period of time. Table 3.3-1 summarizes key sand system characteristics before AO installation in 1995 and in 1999. Some of the major sand system changes to the AO system over this emissions testing time period are also shown in Table 3.3-1. The effects of these sand system control actions are confounded with the influence of AO and AO-driven sand system optimization on emissions. However these data can be summarized and the overall effect of AO clean water processing can be assessed by looking at the starting and ending points on the time plots.

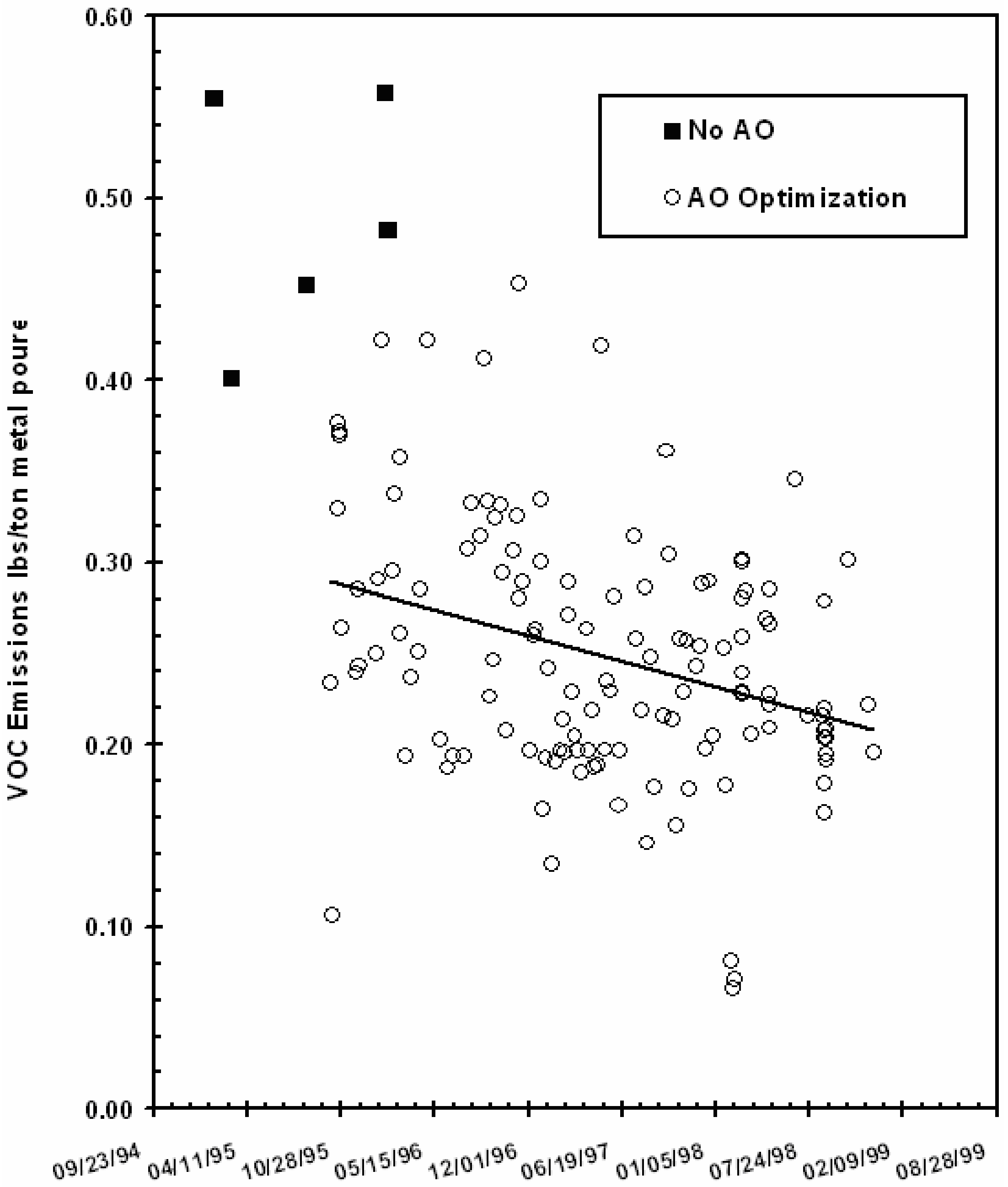


**Figure 3.3-1: Total VOC emissions collected by stack tests of phenolic urethane cored jobs before and after AO installation at Grede-Reedsburg.**

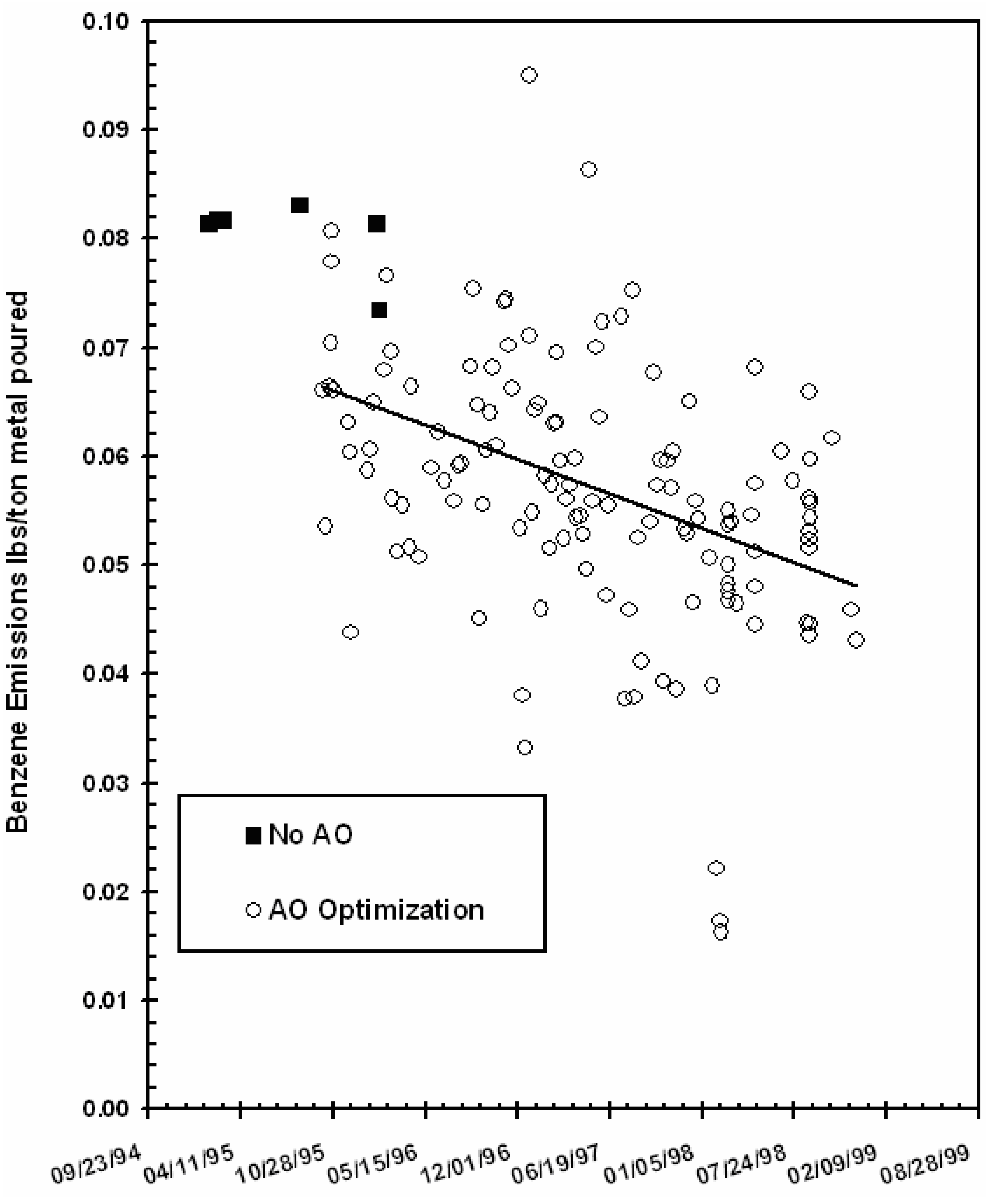


**Figure 3.3-2: Benzene emissions collected by stack tests of phenolic urethane cored jobs before and after AO installation at Grede-Reedsburg.**

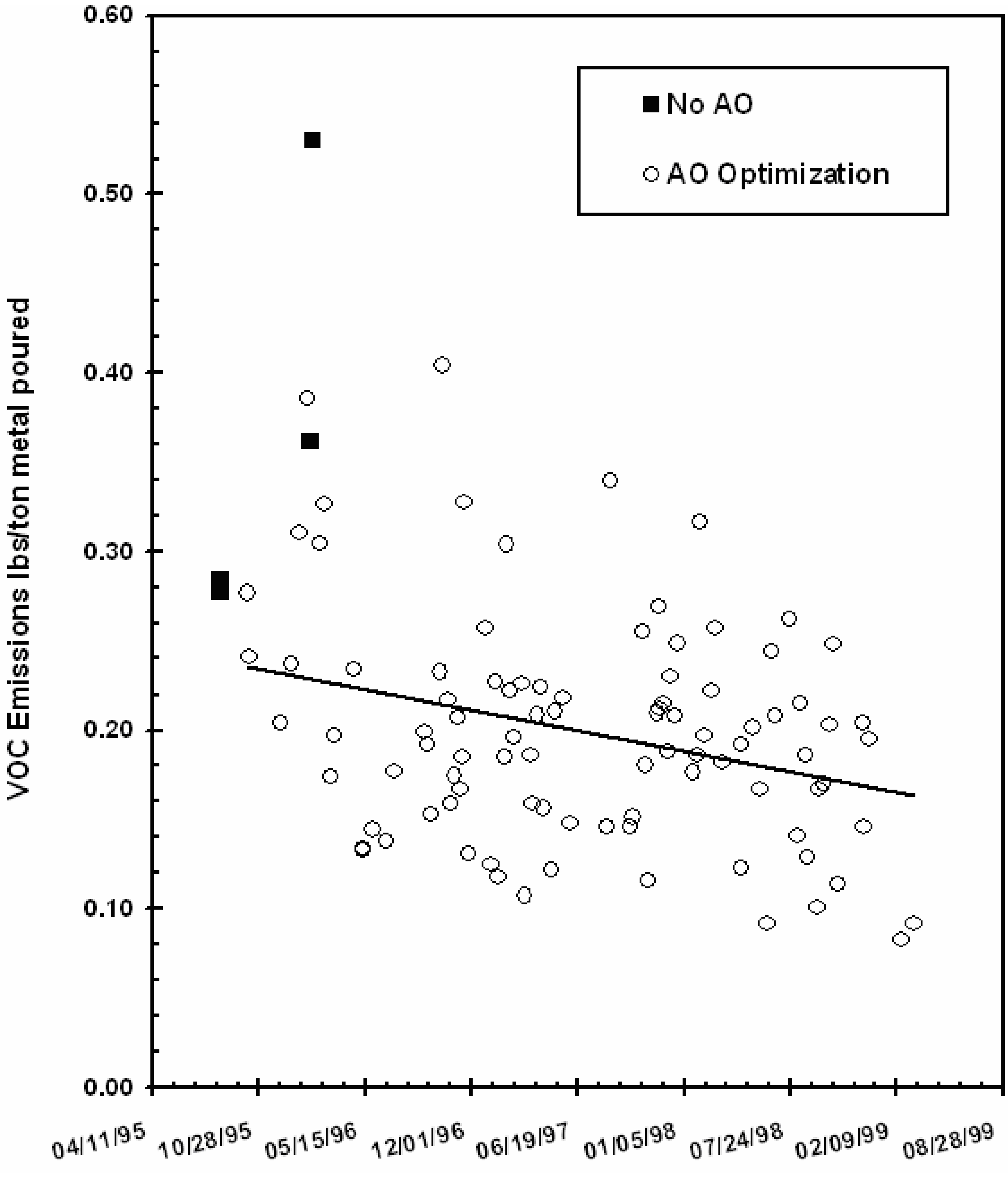


**Figure 3.3-3: Total VOC emissions collected by stack tests of no-core jobs before and after AO installation at Grede-Reedsburg.**

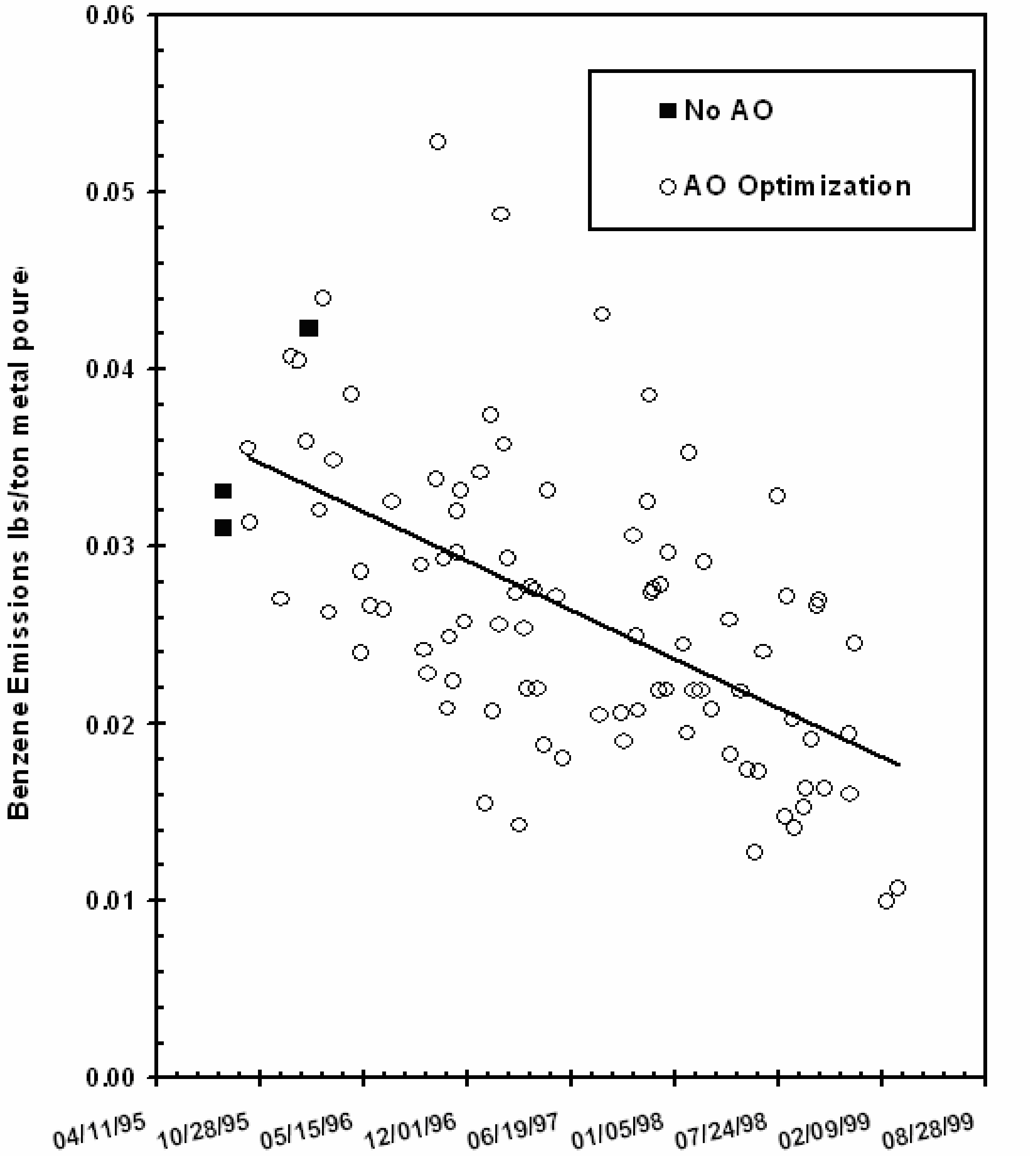


Figure 3.3-4: Benzene emissions collected by stack tests of no-core jobs before and after AO installation at Grede-Reedsburg.

**Table 3.3-1: AO clean water (AO-CW) green sand system operating conditions at Grede-Reedsburg during the emissions testing period.**

| | Baseline Oct. 1995 | AO Sand System Oct. 1998 |
|---|---|---|
| Loss on ignition (LOI, 1800°F), % | 3.0 | 3.4 |
| Volatiles (VCM, 1200°F), % | 1.5 | 1.5 |
| Methylene blue clay (MB clay), % | 11.0 | 10.2 |
| Green compressive strength (GCS), psi | 27 | 27 |
| Compactibility set point, % | 39 | 39 |
| Moisture, % | 3.4 | 3.4 |
| Mulling efficiency (AMB/MB), % | 60 | 61 |
| Water-to-MB Clay Ratio, % | 31 | 33 |

Other Significant Green Sand System Changes/Observations During the Reporting Period:

| | |
|---|---|
| 1/96 | Excessive coal fines observed |
| 5/96 | High $H_2O$ trial |
| 7/96 | Coarser coal blend trials |
| After 1/97 | Continued monitoring and adjustment of coal coarseness as needed |

From 1995 to 1999, total VOC emissions for this heavily cored casting dropped from an initial average of 0.5 lbs/ton of iron poured to the 1999 average of 0.23 lbs/Ton of iron poured while benzene emissions dropped from 0.08 lbs/Ton of iron poured to 0.05 lbs/ton (Figures 3.3-1 and 3.3-2). Similar results are seen for the non-cored casting (Figures 3.3-3 and 3.3-4). Initial 1995 VOC levels estimated to be less than 0.4 lbs/ton and benzene levels of less than 0.036 lbs/ton dropped to 0.18 lbs/ton for VOCs and less than 0.02 lbs/ton for benzene in 1999. Thus, with AO, VOC emissions dropped 50-60%, and benzene dropped 30-50%.

Comparisons between cored and un-cored casting show the influence of core binder emissions on overall green sand system emissions, as shown in Figure 3.3-5. Not only are overall emissions higher (by about 25%) from cored castings, but the ratio of benzene to total VOCs increases for cored castings. Clearly, organic cores (and core binder residuals in green sand systems) are a major source of emissions including benzene.

### 3.3.2 AO-CW Emissions Performance – Navistar International

Navistar International Transportation Corporation (Waukesha, WI) is a medium production jobbing foundry that produces ductile iron castings ranging from 2-75 lbs while using horizontal parting line molding with phenolic urethane cold box cores. This foundry started up an AO-CW system for emissions reduction in 1998. AO water is added to both the sand cooler and the muller. Baseline emissions testing were performed in 1997 before AO system installation and again in 1999 after AO system installation. Sand system changes from 1997 to 1999 include only an AO-driven reduction in bond addition levels to maintain constant sand system green compressive strength. Combined pouring, cooling and shakeout emissions results are shown in Figures 3.3-6, 3.3-7, and 3.3-8 for "total VOC", benzene, and carbon monoxide, respectively. In each case, an

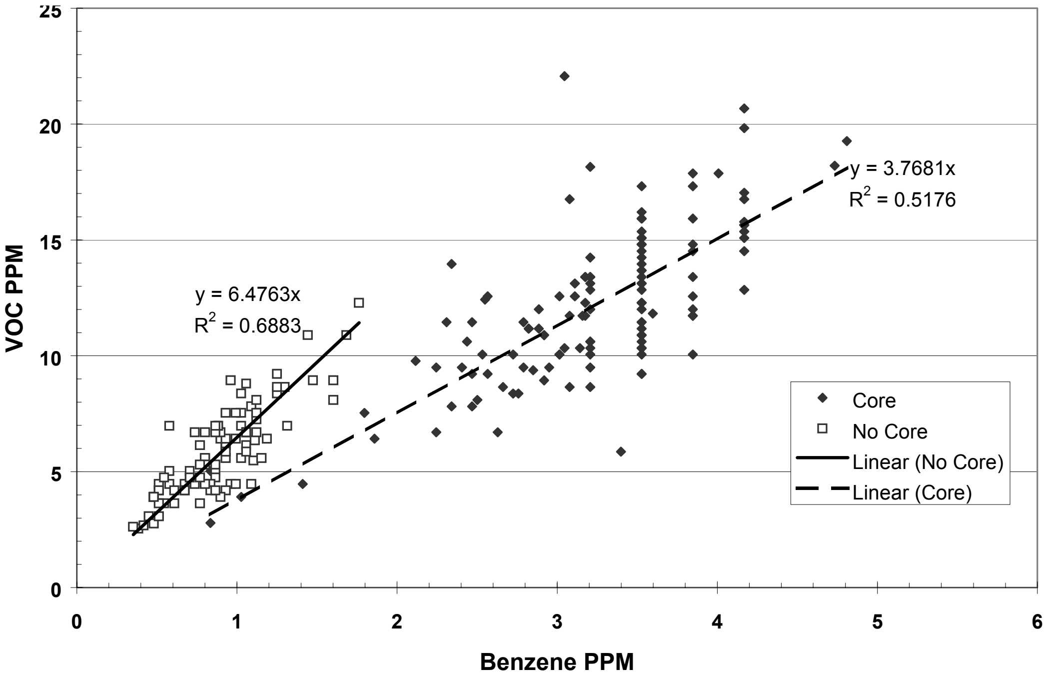


**Figure 3.3-5: Benzene-to-VOC emission relationship for cored and un-cored castings from Grede Foundry.**

independent testing laboratory conducted and analyzed three consecutive one-hour stack tests while using slip stream capture on an activated carbon tube, as per U.S. EPA Method 18. Total VOC values reported for Navistar represent VOCs captured on activated carbon, extracted with carbon disulfide, monitored by gas chromatography, and reported "as hexane." Only one baseline and one AO test were performed for carbon monoxide. Emissions trials in 1997 and 1999 were performed under typical production conditions with a typical casting mix. However, it was not possible to ensure that the identical casting part numbers were in production during each set of trials. Three consecutive trials were performed to ensure that representative emissions data for a range of casting part numbers were collected during each test sequence in 1997 and 1999.

The stack tests show an average 74% reduction in VOC emissions and a corresponding 65% average reduction in benzene emissions. CO emissions were reduced by 10%. Foundry personnel have reported that AO processing has also significantly reduced the amount of visual smoke and observable odor inside the plant; and it has reduced stack odor outside of the plant. However, these reductions in smoke and odor have not been quantified. Sand system cost/performance improvements have also been observed with the AO-clean water system. The AO system has been operated continually since 1999.

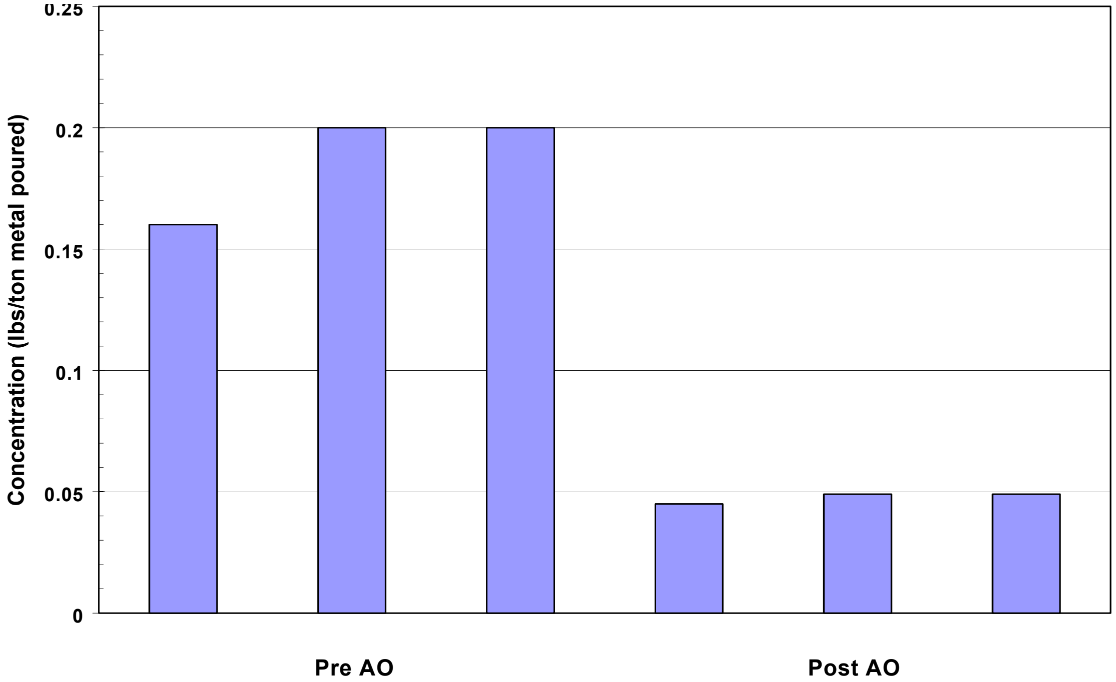


**Figure 3.3-6: Pounds of total VOC per ton of iron poured generated by phenolic urethane cored castings, before AO installation and after AO system optimization at Navistar International.**

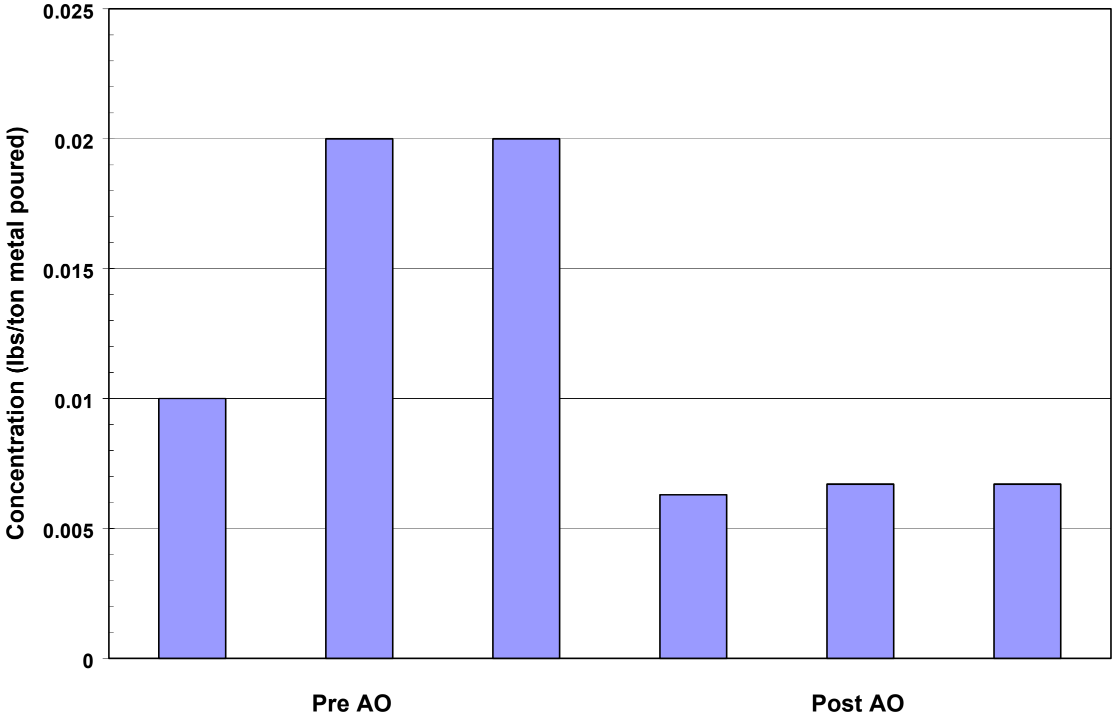


**Figure 3.3-7: Pounds of benzene per ton of iron poured generated by phenolic urethane cored castings, before AO installation and after AO system optimization at Navistar International.**

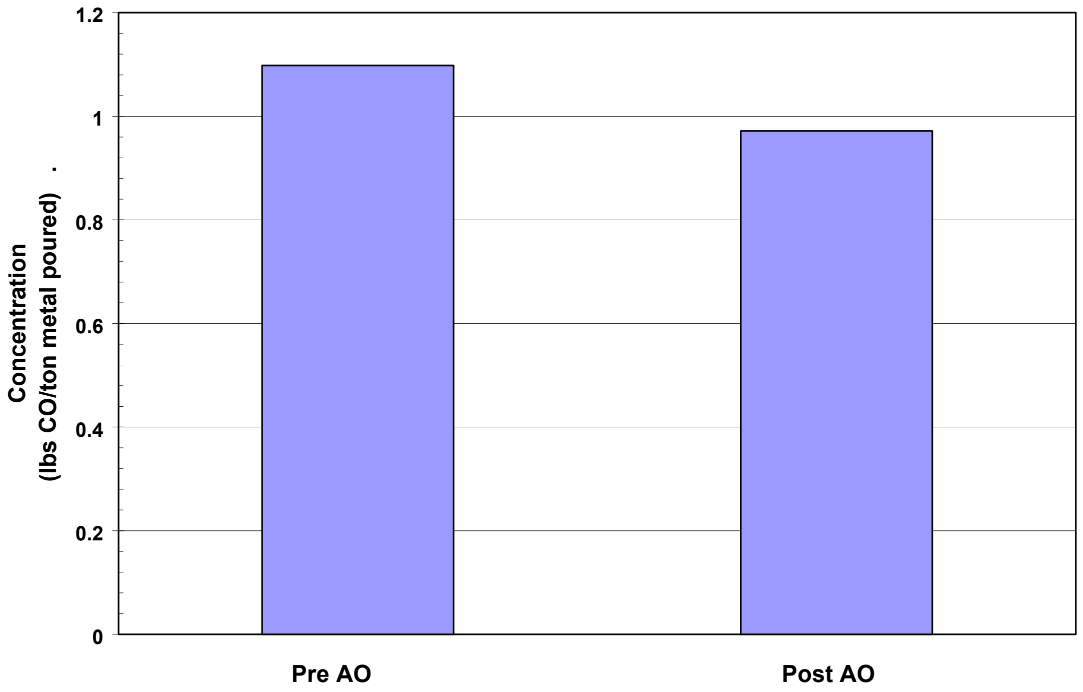


**Figure 3.3-8: Pounds of CO per ton of iron poured from phenolic urethane cored jobs, sampled from a non-AO treated molding line and an AO-treated molding line at Navistar International.**

### 3.3.3 AO-DBW Emissions Performance: Neenah Plant 2

*Neenah Foundry Company has conducted the most careful and comprehensive study of the influence of AO on foundry stack emissions. This includes characterization of base-line emissions from their Plant 3 molding line prior to AO system start-up, as well as emissions during and after a phased start-up of an AO-DBW system. Reported herein is an emissions performance summary adapted from the text of a presentation made by Jeff Goudzwaard, Senior Environmental Engineer, Neenah Foundry during the spring of 2002.*

Neenah Foundry began its evaluation of Hazardous Air Pollutant (HAP) formation mechanisms as a result of Wisconsin's Hazardous Air Pollution Rule, NR445, which affects facilities built or modified after 1988. Benzene and formaldehyde are two of the main HAPs emitted by foundries. Benzene is a "group A" compound and requires application of "Lowest Achievable Emissions Rate" (LAER) if greater than 300 pounds per year are emitted. Formaldehyde is a "group B" compound and requires application of Best Available Control Technology (BACT) if greater than 250 pounds per year are emitted. Emissions in excess of these levels were anticipated at Neenah Foundry. Incineration was originally thought to be the control technology to achieve LAER, however incineration of foundry emissions is expensive. Foundries move vast quantities of air from their processes to maintain indoor air quality standards for their employees. The actual concentration of pollutants in the stack gases was low, on the order of a few ppms. This means that unlike most existing stack incineration installations, the organic pollutants in the collected air stream provide virtually no fuel to help support and reduce the cost of combustion. Incineration fuel costs for only one of Neenah's several production lines were estimated at $3.5 million per year!

Neenah Foundry cooperated with several participating Wisconsin Cast Metals Association (WCMA) foundries to develop a sound response to the staggering costs of applying incineration. The joint WCMA efforts can be categorized as a two pronged approach. The first was to quantify emissions from Wisconsin foundries. To quantify these emissions, a series of round robin emission tests was performed in late 1995. Several foundries participated and quantified benzene, formaldehyde and total hydrocarbon emissions from their pouring, cooling, and shakeout operations. Neenah was one of these foundries and contributed emissions data from mold cooling operations. The second effort from WCMA was to argue for a reduction in emissions by reducing the emitting potential of foundry sands. Furthermore, two new sand tests were proposed to quantify the emissions potential of molding sands: the Volatile Carbon Matter (VCM) and Maximum Potential to Emit (MPTE) tests.

Having quantified mold-cooling emissions through the WCMA round robin tests, an emissions baseline for Plant 3's 2070 and 2013 Disa line was established to measure future emission reductions against. Neenah Foundry then set out to optimize and reduce the HAP emitting potential of its sand systems. Neenah began slow reductions in bond additions and a search for bond inefficiencies. The term Sand System Optimization was given to these processes. Optimization is defined as a process of reducing methylene blue clay targets or coal levels, measured as loss on ignition (LOI), in the molding sand without an increase in scrap rates. Numerous areas were found in the sand system where, unknowingly, bond was removed from the sand system. Air ducts were reconfigured to minimize bond losses, and clay and coal levels were reduced to minimum levels that made acceptable castings. At the practical conclusion of the sand optimization stage a process called Sonoperoxone® was introduced.

The Sonoperoxone® process was developed by Furness-Newburge, Inc. This process consists of the formation of highly reactive advanced oxidants in the makeup water within the green sand system. Advanced oxidation processes are widely utilized in municipal water treatment systems and in wastewater treatment systems. Furness-Newburge, Inc. was the first to apply this technology to foundry sand systems. The process employs high-intensity sound waves to generate free radicals in water. Hydrogen peroxide is also added to the water to facilitate decomposition of ozone, which is also bubbled into the water to generate more free radical oxidants. Baghouse dust may also be mixed with makeup water to create black water Sonoperoxone®.

The first advanced oxidation system used at Neenah Foundry was initially a black water Sonoperoxone® system. However, the initial dust handling system was too small, so the process was operated without baghouse dust and became a clear water system. The AO water was introduced to sand coolers and pre-blenders at Plant 3. Increases in green strength were observed as well as visible reductions in smoke and fumes from the mold cooling and shake out processes. This system has been successfully supplying clear water Sonoperoxone® to Plant 3's sand cooler and pre-blender for several years.

A similar series of events was also carried out at plant 2's 2070 Disa line. Sand optimization was carried out, then a series of air emission tests was performed. A more robust black water Sonoperoxone® system was then installed. The Sonoperoxone® system was phased in beginning with a month of clear water operation. Gradual increases of bag house dust were introduced. The initial dust addition was 5% by volume, which was later increased to 8%, 10%, and 12%. The baghouse dust was found to be a rich source of clay and coal. MB clay tests for one of Neenah's dust sources average 34%. LOI tests average 19.5%. Emissions tests were performed at several stages along the development of the system.

Figure 3.3-9 illustrates the black water Sonoperoxone® system. The system is essentially an open system with five material inputs (water, bag house dust, ozone, oxygen and hydrogen peroxide) and two discharges (enriched water via a blackwater pump and a sludge from a drag chain). By introducing baghouse dust to water just upstream of the ultrasonic transducers, a secondary benefit is achieved from ultrasonics. Similar to a standard foundry clay wash test, ultrasonic energy facilitates the removal of adhered clay and coal from fine sand grains in the baghouse dust. After the water has been enriched with clay and coal from the baghouse dust and exposed to additional advanced oxidants, it is pumped into a sand cooler or into one of three 4000-pound sand mullers.

A series of graphs are presented in Figures 3.3-10 to 3.3-18 that illustrate emission rates of several pollutants tested at Neenah Foundry. Emission rates for most pollutants were observed to increase proportionately with the amount of core utilized in the mold package. A phenolic urethane cold box system was utilized, and the core resin source used throughout these emission tests was constant at 1.1-1.2% by weight. Equations for each emission factor regression line have been provided on the graphs. The average core loading was 316 pounds per ton iron poured. An emission reduction estimate has been made at the average core value and the results are indicated on the graph. The organic content of the green sand (represented by LOI) has also been recorded adjacent to each regression equation. The LOI temperatures were 1800 and 1200°F.

Figure 3.3-10 shows the emission results for the group of pollutants defined as volatile organic compounds (VOCs). Separate graphs are presented for the mold cooling process and the combined mold cooling and shake out processes. It was found that approximately 60% of the VOCs are emitted during shakeout. A direct relationship of emitted VOCs to the amount of core is observed in both graphs. VOC emissions from the mold cooling process were reduced 84% from the original levels measured in 1995. A 68% reduction was achieved by sand optimization. Another 49% reduction was achieved by use of black-water Sonoperoxone®. The combined mold cooling and shakeout emissions were reduced 48% by implementation of the black water Sonoperoxone® system. This value is very similar to the 49% value reported in mold cooling. It appears as if the AO effect is very similar between mold cooling and shakeout processes.

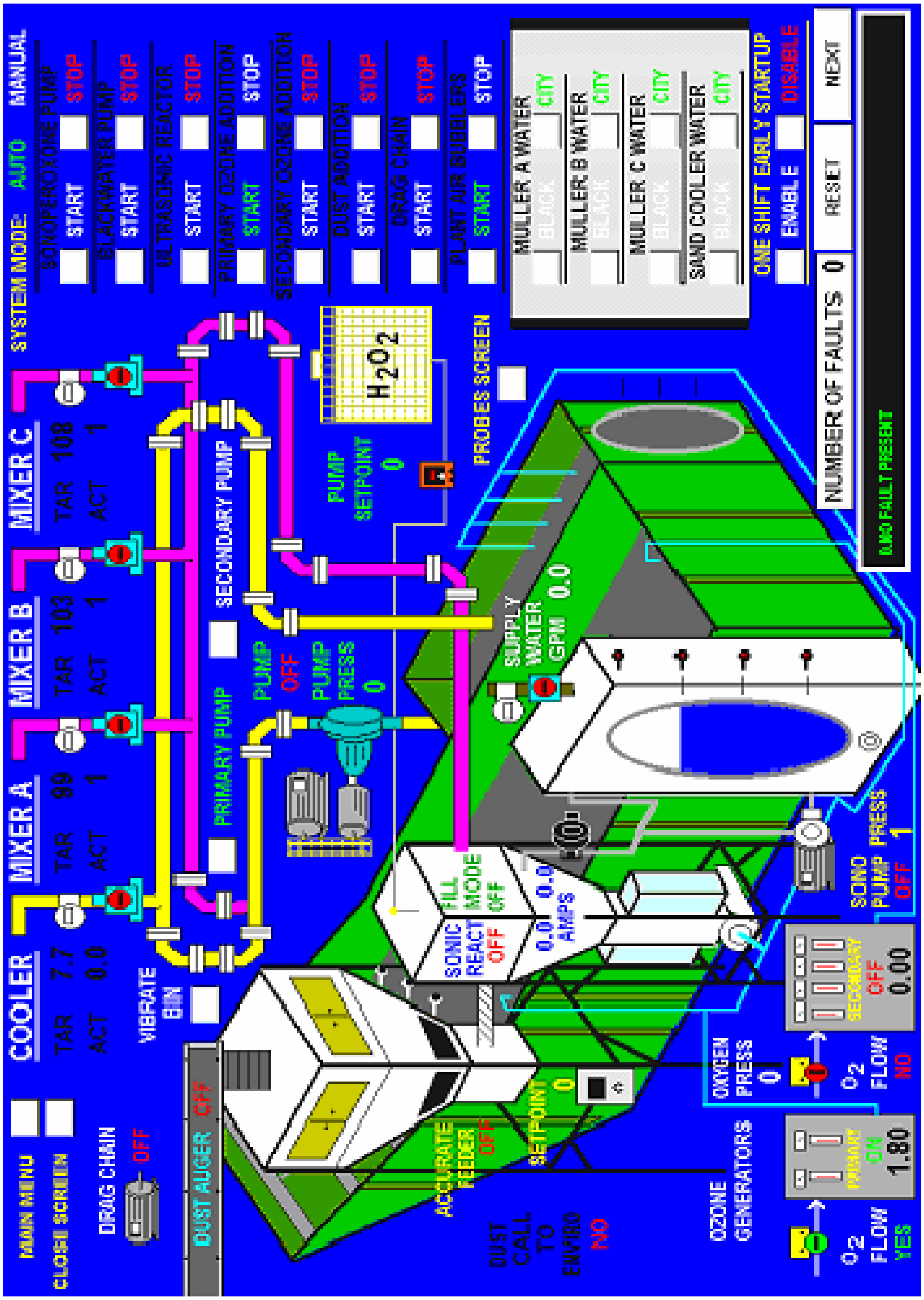


Figure 3.3-9: Schematic of Neenah's AO-DBW Sonoperoxone® system.

Figure 3.3-11 shows the emission results for benzene. Benzene emissions were reduced by 53% during mold cooling from initial 1995 values. A 25% reduction occurred from optimizing the sand system. Another 37% reduction was achieved after employing black water Sonoperoxone®. The combined mold cooling and shakeout emissions behave differently from the previous VOC graph in that the amount of emission reduction from Sonoperoxone® decreased with increasing core load. A 19% reduction in benzene between the optimized sand system and black water Sonoperoxone® emissions is observed at average core loads. At high core loads no reduction is predicted. Again most of the emissions, 55%, occur from shakeout. If the same 37% reduction measured during mold cooling is applied to the 45% of the total emissions occurring at mold cooling, one can predict that at least a 17% reduction should occur. The combined graph shows a 19% reduction. It appears as if advanced oxidants have little effect on benzene shakeout emissions where the core fume is exposed to ambient air. Advanced oxidants have a larger effect on mold cooling process emissions where fumes from the cores, at least partially, pass through the treated green sand mold.

The combined process emission results for formaldehyde are shown in Figure 3.3-12. A similar emission pattern is observed between combined process emissions for benzene and formaldehyde. An apparent emission reduction is observed for black water Sonoperoxone® at average core loads, but at higher core loads this difference disappears. Some caution is necessary in use of the formaldehyde emission graph, as large scatter is observed in formaldehyde measurements. This is particularly true for the optimized sand data where an $R^2$ value of only 0.39 is observed.

Carbon monoxide emissions are illustrated in Figure 3.3-13. Similar emission rates of carbon monoxide are observed between the optimized sand and Sonoperoxone® conditions. Carbon dioxide emissions are also illustrated in Figure 3.3-14. Carbon dioxide emissions do not appear to be significantly affected by Sonoperoxone®. Methane plus ethane emissions are illustrated in Figure 3.3-15. A 34% emissions reduction was measured between the optimized sand and black water Sonoperoxone® conditions at average core loading. Propane was also measured and is shown in Fig 3.3-16. AO processing apparently decreased propane emissions at low core loadings, but increased propane emissions at high core loading conditions.

In addition to air emissions tests, surrogate sand tests were also performed during emissions testing. Figure 3.3-17 illustrates the progression of the 950°F weight loss parameter from the stepped VCM test. This particular component of the stepped VCM test is thought to best correlate to the HAP emissions of interest. The weight loss parameter is generally seen to decrease across the time frame listed. An increase, however, was observed when black water was first introduced. Emissions tests performed at that time (not reported here) confirm that an increase in emissions resulted. Operational controls to the black water Sonoperoxone® system were made after these measurements and emissions, as measured by the stepped VCM parameter and air emissions tests, have subsequently been reduced. This observation strongly suggests that an AO system must be operated properly. Left on its own, recycling of bag house dust can cause an increase in emissions. The VCM weight loss parameter reported has not been sorted for core loading. Some of the scatter associated with different data groups is certainly associated with a core loading effect. The MPTE sand test illustrated in Figure 3.3-18 shows the same trends with but with more data scatter than for the VCM test.

In summary, Neenah Foundry has implemented sand optimization and Sonoperoxone® technology in its sand systems. Air pollution emissions and sand properties associated with implementation of these processes have been studied. Mold cooling and shake out emissions have been estimated. Total reductions of 80% for VOCs and 25% for benzene have been estimated. During these changes, the molding sand has also beneficially changed (see section 3.5.2). Bond costs have been significantly reduced. These changes are all favorable. Both technologies are favorable to the foundry industry. It is hoped that these concepts, and additional concepts expected in the near future, reduce hazardous air pollutants and prevent mandated implementation of wasteful, costly end-of-pipe control technologies.

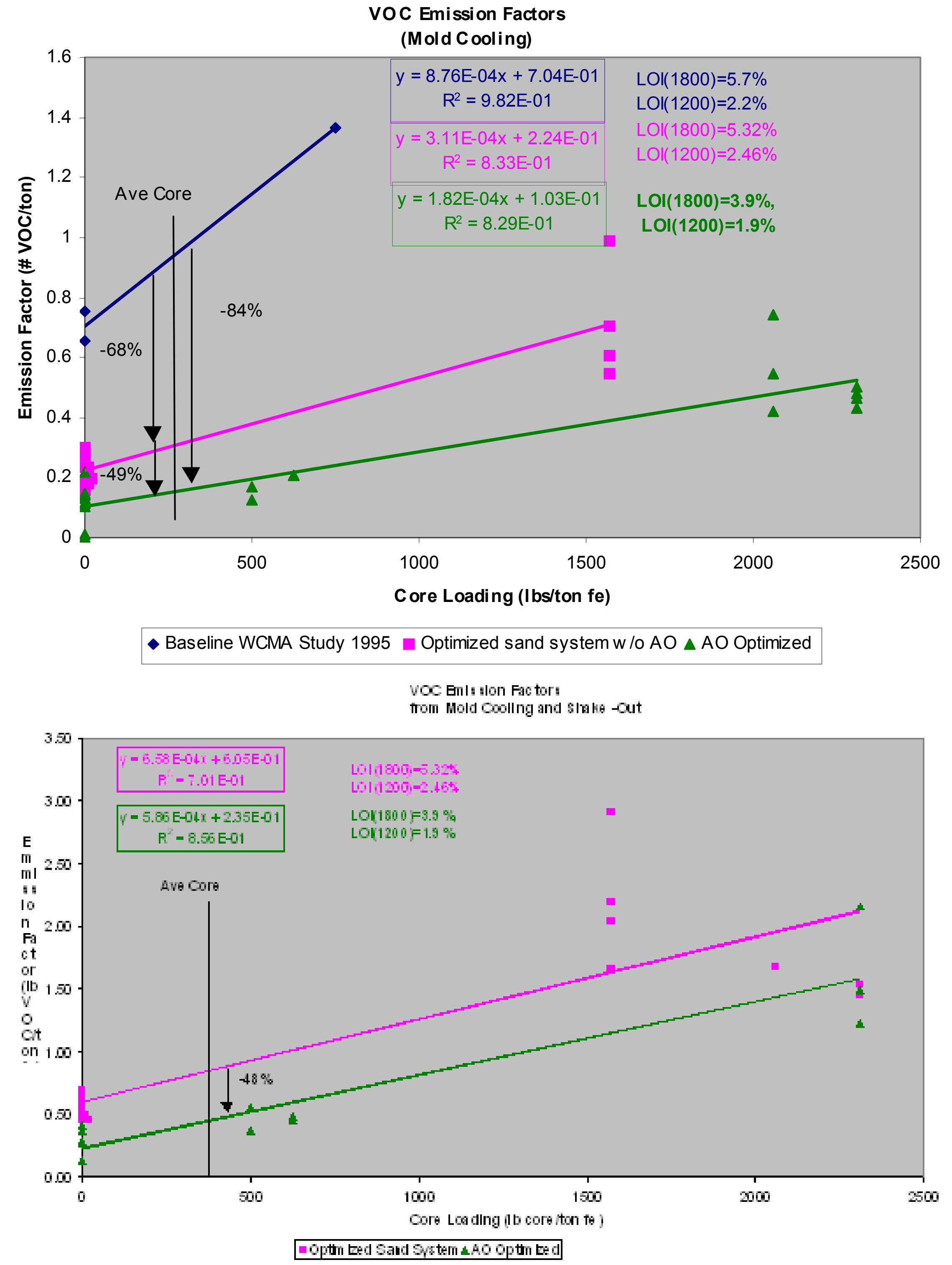
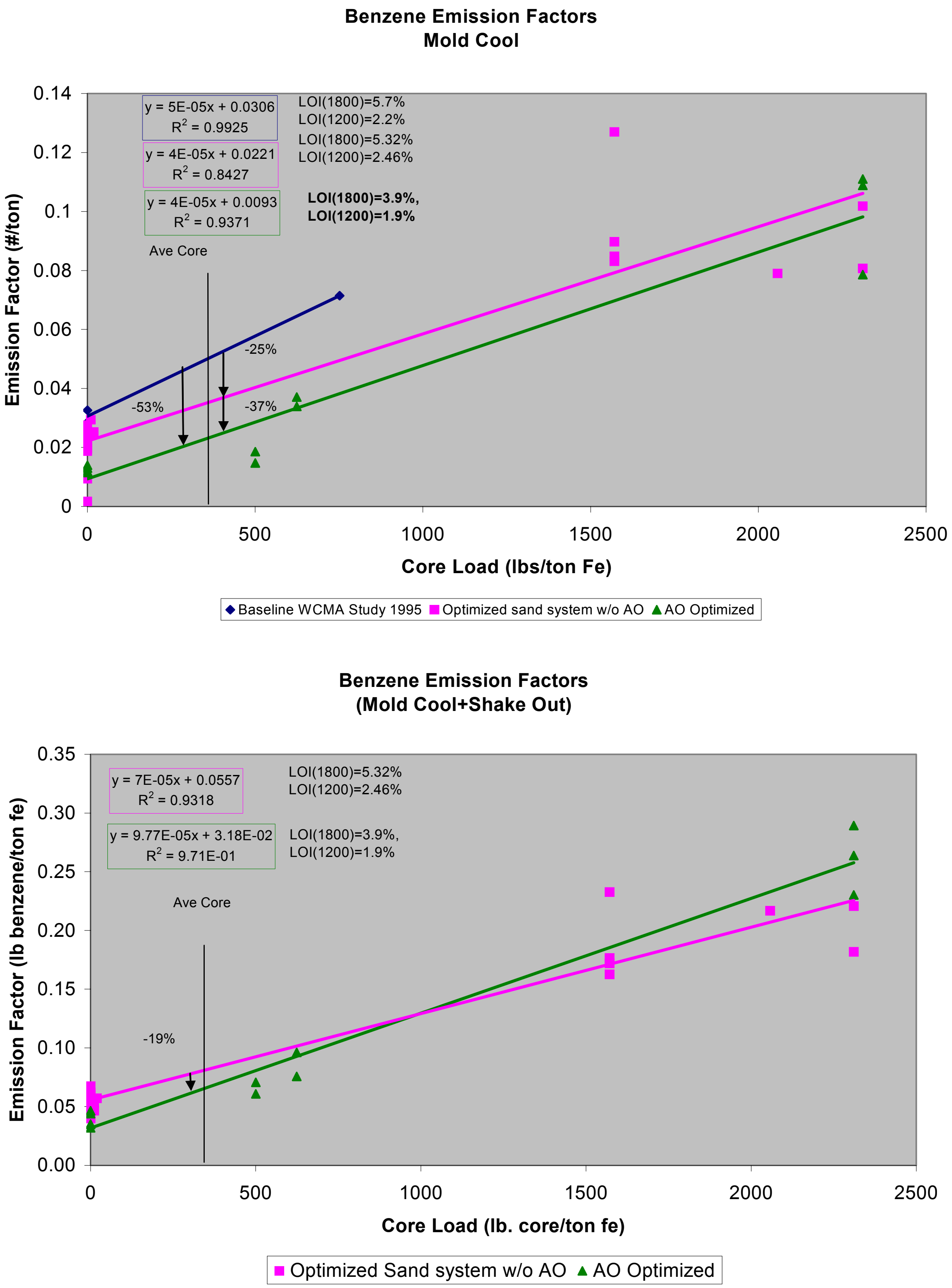


**Figure 3.3-10: VOC emission factors (lbs. VOCs / ton iron poured) for mold cooling and mold cooling plus mold shakeout.**



**Figures 3.3-11: Benzene emission factors for mold cooling and mold cooling plus mold shakeout.**

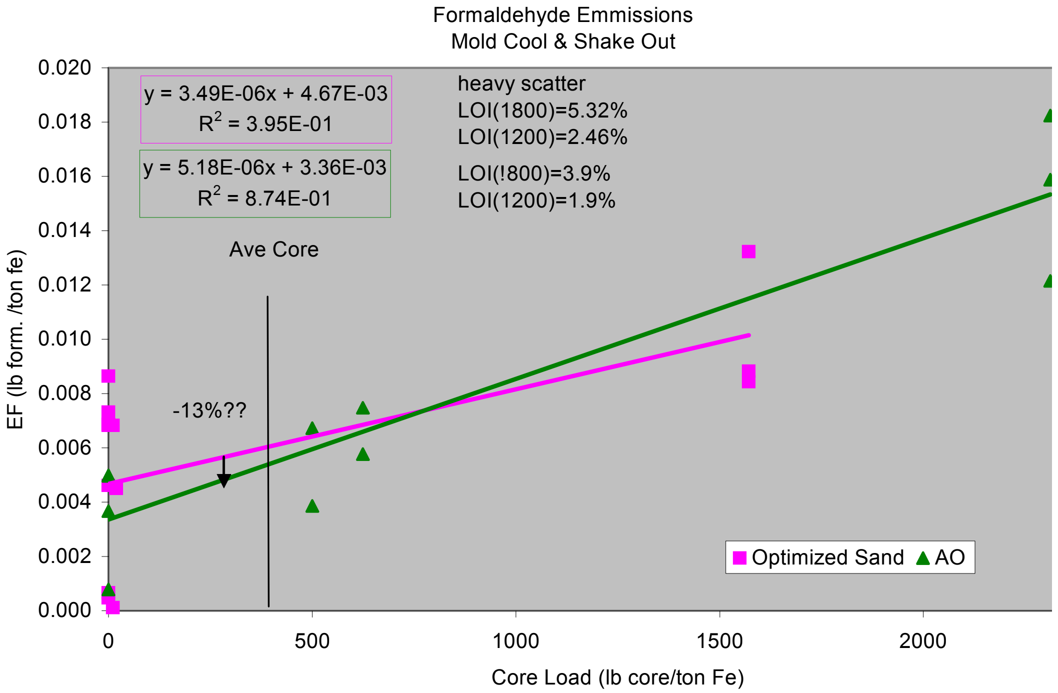


Figure 3.3-12: Formaldehyde emission factors for mold cooling plus shakeout.

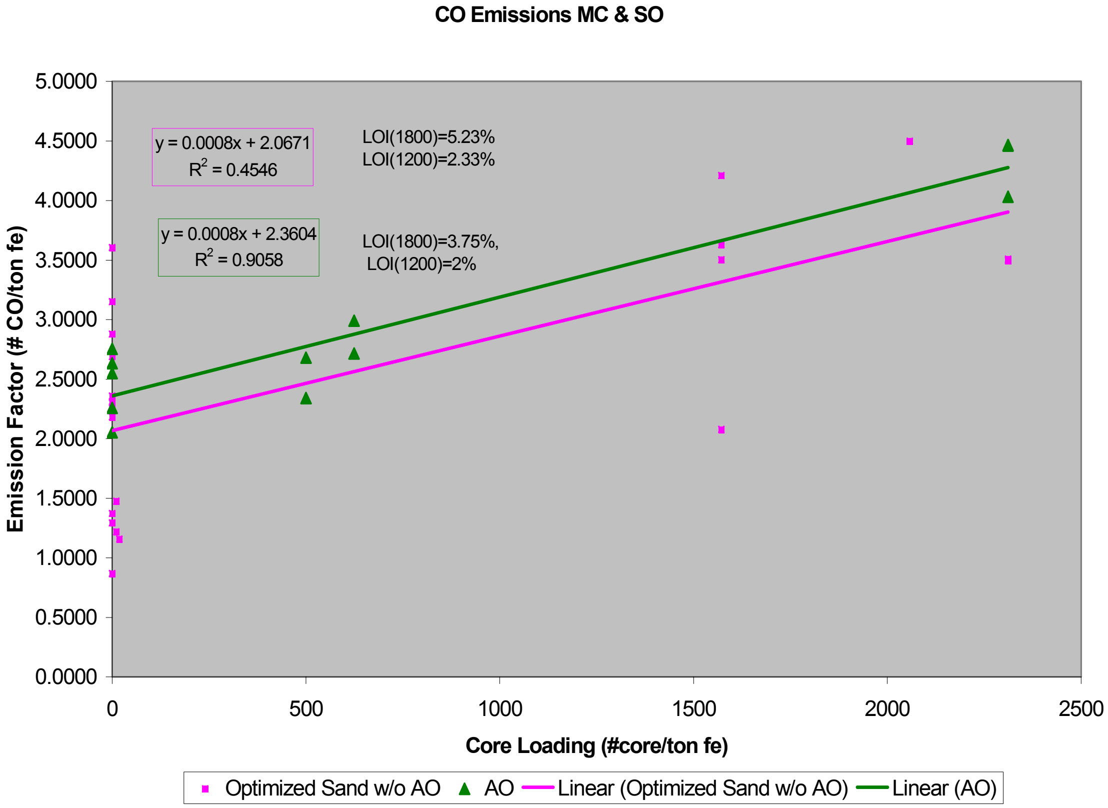


Figure 3.3-13: CO emission factors for mold cooling plus shakeout.

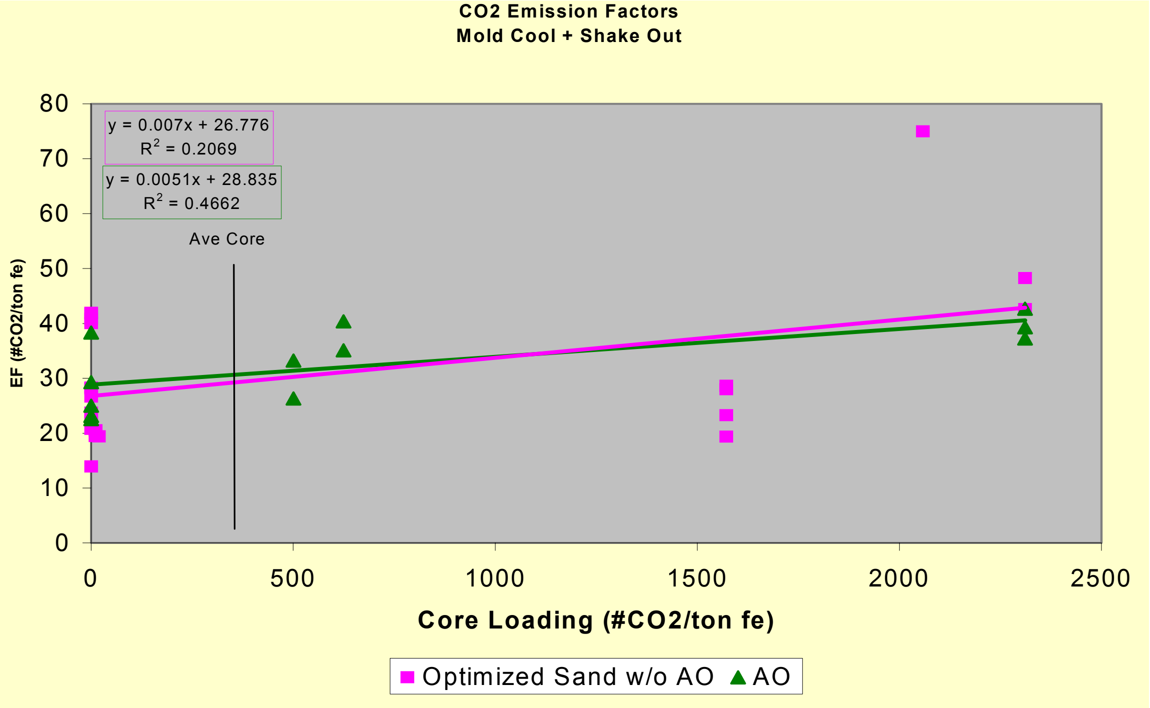


Figure 3.3-14: $CO_2$ emission factors for mold cooling plus shakeout.

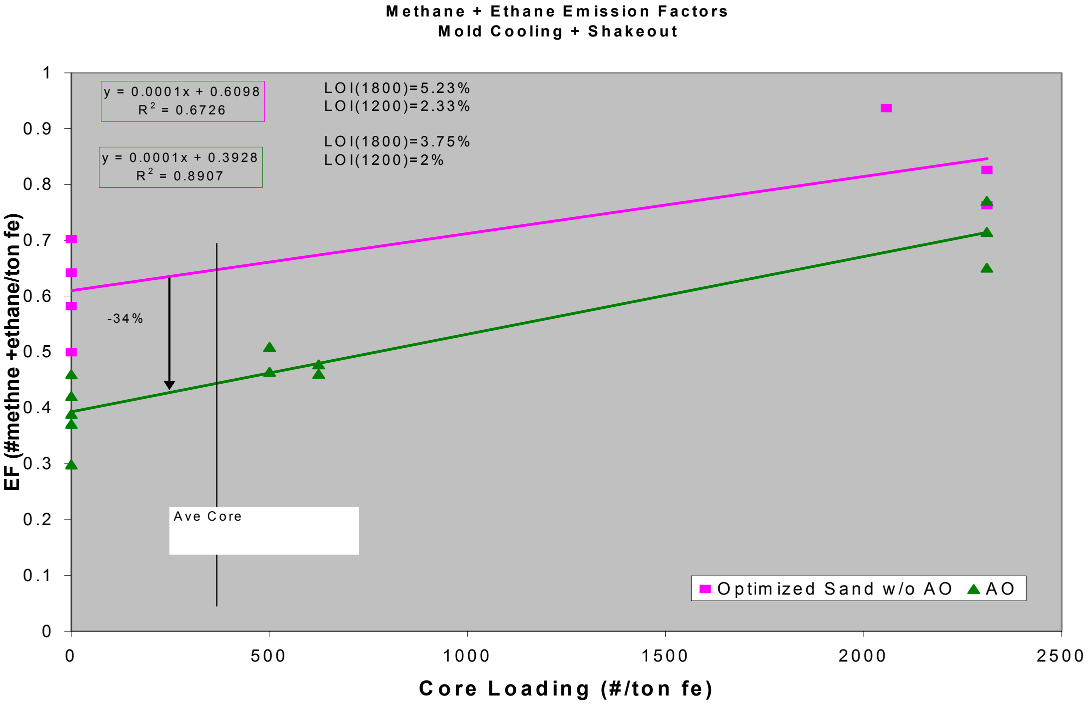


Figure 3.3-15: Methane plus ethane emission factors for mold cooling plus shakeout.

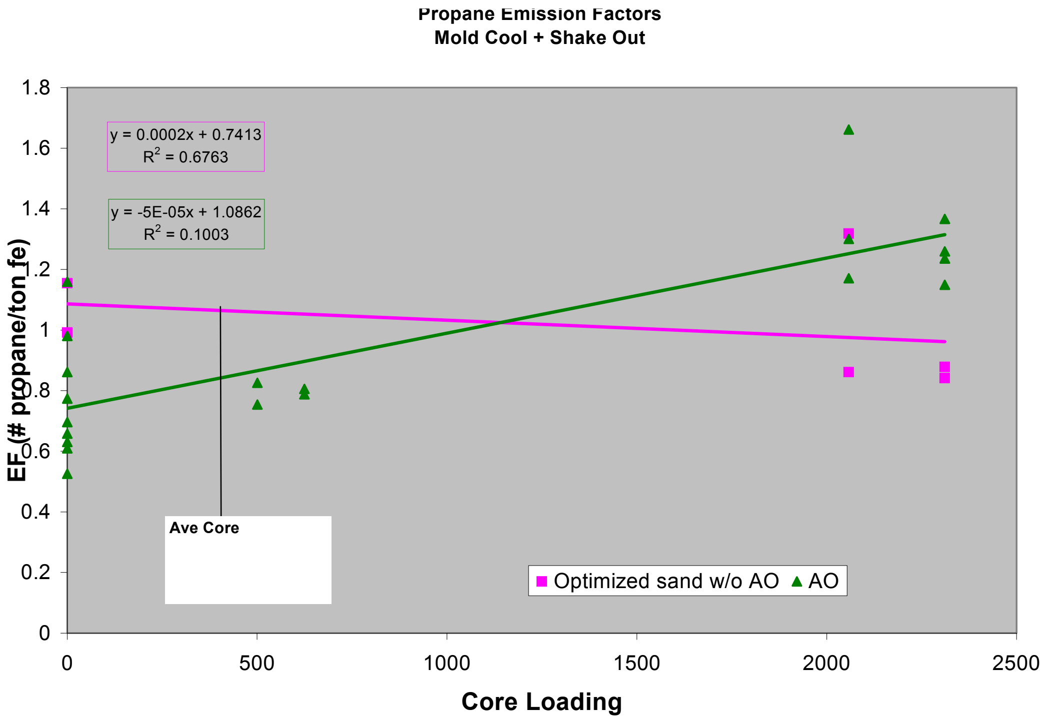


Figure 3.3-16: Propane emission factors for mold cooling plus shakeout.

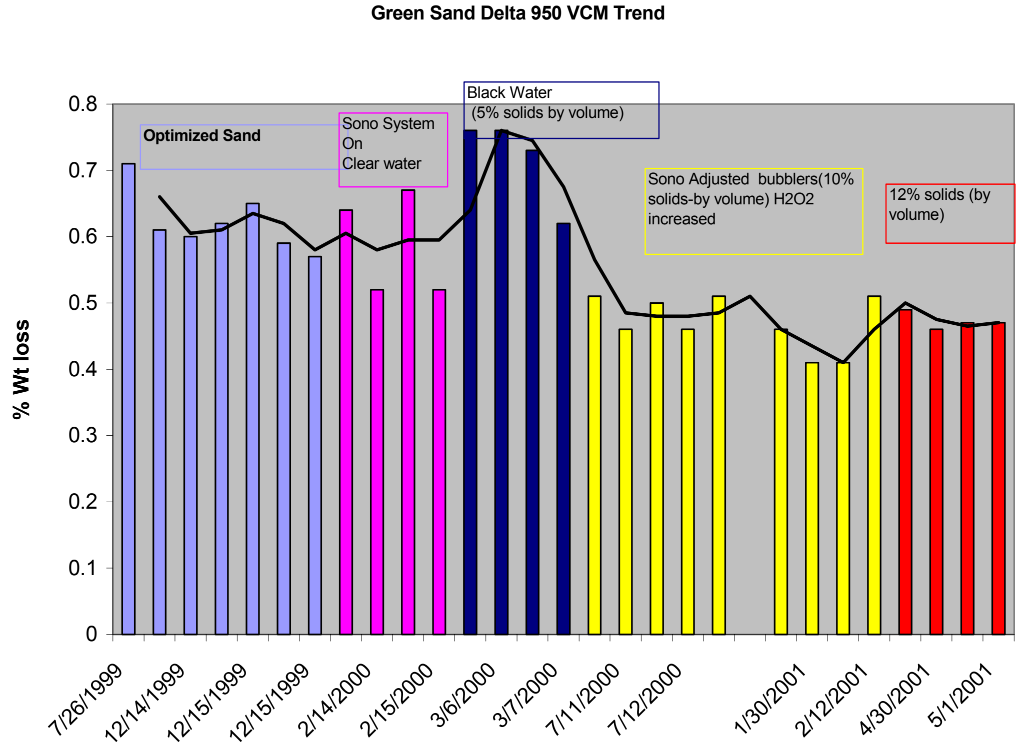


Figure 3.3-17: Surrogate sand test – 950°F VCM weight loss results over time.

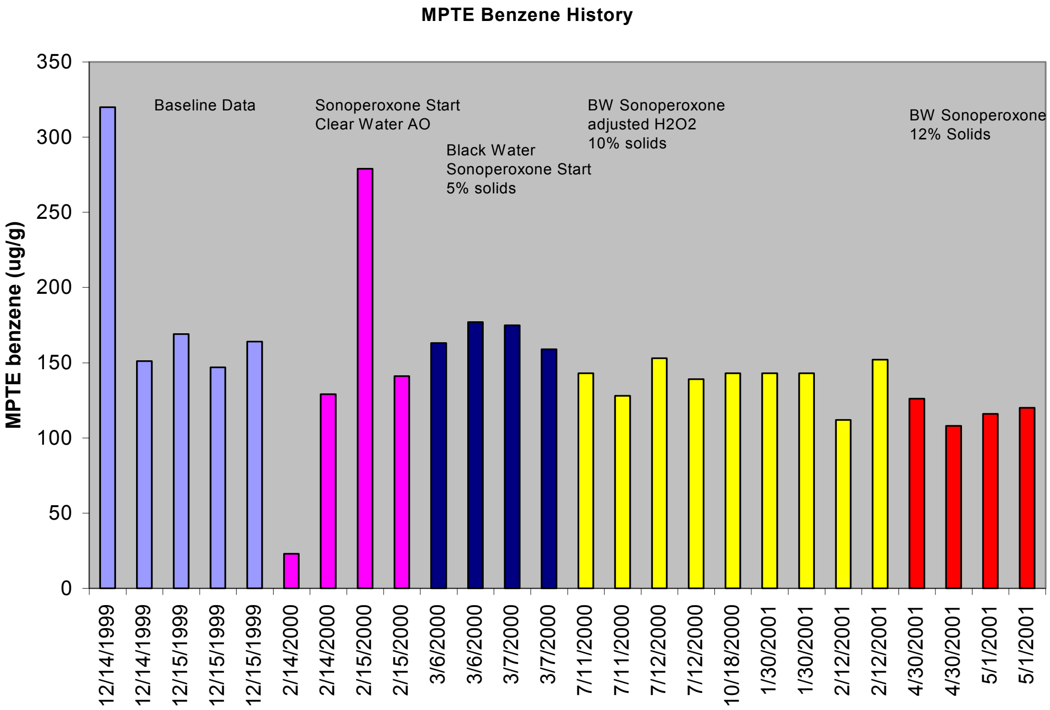


**Figure 3.3-18: Surrogate sand test – MPTE results over time.**

## 3.3.4 AO-CW Emissions Performance – Cooperative CERP/Technikon

Technikon Environmental Development Center™, formerly the Casting Emissions Reduction Program (CERP), was established to evaluate materials, equipment and processes used in the production of metal castings (Technikon, 2001). The goal of this research is a reduction in air emissions including Hazardous Air Pollutants (HAPs), Volatile Organic Compounds (VOCs) and Polycylic Organic Matter (POMs). The facility has undertaken a number of product tests including core binders and pre-blends. Recently, Technikon tested the advanced oxidation (AO) system, Sonoperoxone™, to determine its effect on emissions. Much of the information contained in this summary is found in the Technikon Pre-Production Air Emission Test Reports. These reports contain the experimental design, testing procedures and the full suite of tests done. To keep this summary brief, only the most important results are described in this section. The reports are listed as follows:

- Production Foundry Airborne Emission Test Report: Emissions from Greensand Prepared with Tap Water and Advanced Oxidant Enriched Water," Aug. 1, 2001.
- Pre-production Air Emission Test Report: The Effect of Advanced Oxidant Enriched Water on Organic Emissions from Cored Greensand Molds, Part 1 -- Phenolic Urethane Core Emissions," Jan. 5, 2001.

- Pre-production Air Emission Test Report: The Effect of Advanced Oxidant Enriched Water on Organic Emissions from Cored Greensand Molds, Part 2 -- Penn State University Greensand Formulation," Jan. 5, 2001.
- Pre-production Air Emission Test Report: The Effect of Advanced Oxidant Enriched Water on Organic Emissions from Cored Greensand Molds, Part 3 – Bentonite Clay Ratios," Jan. 5, 2001.
- Pre-production Air Emission Test Report: 20/80 Western/Southern Bentonite Clay Ratios" (non-AO), Apr. 25, 2001.
- Pre-production Air Emission Test Report: 20/80 Western/Southern Bentonite Clay Ratios" (AO), June 12, 2001.
- Pre-production Air Emission Test Report: 50/50 Western/Southern Bentonite Clay Ratios" (non-AO), May 15, 2001.
- Pre-production Air Emission Test Report: 50/50 Western/Southern Bentonite Clay Ratios" (AO), Apr. 26, 2001.
- Pre-production Air Emission Test Report: 80/20 Western/Southern Bentonite Clay Ratios" (non-AO), May 10, 2001.
- Pre-production Air Emission Test Report: 80/20 Western/Southern Bentonite Clay Ratios" (AO), May 17, 2001.

The AO process known as Sonoperoxone™ combines ozone, hydrogen peroxide and ultrasonics to facilitate the generation of highly reactive radicals that can engage in both oxidation and reduction reactions. These radicals react relatively slowly at ambient temperatures, however are very reactive at the extreme temperatures experienced in the foundry greensand mold. It is theorized that the radicals combine with pollutants such as benzene, toluene and phenol through addition and abstraction reactions (Kao, 1994). These reactions can degrade the pollutants to less harmful intermediates.

The aim of the Technikon testing was to identify both the level of emission reduction and the location of these reductions in the greensand mold by using the Sonoperoxone™ system AO water. Tests that were conducted with tap water served as baselines for comparison. To simulate the foundry operation in the pilot-scale mode, Technikon "turned" the sand through several repetitions to allow for emission and greensand properties to stabilize and approach steady state. Casting molds included both cored and "non-cored" molds (cores made of sodium silicate that did not release emissions). The make up of individual molds is found in the Technikon report. Technikon personnel made molds of roughly 1400 lbs. An emissions capture device allowed for collection during pouring, cooling and shakeout of the molds. Capture time totaled 75 minutes: 45 minutes during cooling, 15 minutes during shakeout and 15 minutes after shakeout. Emissions testing performed by Technikon followed the EPA methods 1, 2, 3a, 4, 18, 25, TO11, and NIOSH 2002 (U.S. EPA, 2000).

The full suite of chemicals tested included many of the BTX (benzene, toluene, and xylene) compounds, phenols, naphthalenes, aldehydes, aniline, cresol, methane and several other alkanes. Samples were tested by an outside laboratory and in some cases by several labs in a round robin test that involved Penn State University. The Technikon tests that are discussed in the most detail within this report are introduced in Table 3.3-2.

**Table 3.3-2: Tests conducted by Technikon (CERP) to evaluate the effect of AO water on cored greensand mold emissions.**

| CERP Designation | Greensand Composition | Turn #'s | Core Composition |
|---|---|---|---|
| CH Tap | CERP system greensand 80/20 western/southern bentonite clays, Tap water | 1-6 | Sodium silicate |
| CI AO | CERP system greensand 80/20 western/southern bentonite clays, AO water | 1-24 | Sodium silicate |
| CE Tap | CERP system greensand with seacoal 80/20 western/southern bentonite clays,<br>Tap water | 1-9 | Phenolic urethane cold box |
| CF AO | CERP system greensand with seacoal 80/20 western/southern bentonite clays, AO water | 1-17 | Phenolic urethane cold box |
| CV Tap | Penn State greensand formulation*<br>80/20 western/southern bentonite clays<br>80/20 seacoal/lignite,<br>Tap water | 1-9 | Phenolic urethane cold box |
| CV AO | Penn State greensand formulation*<br>80/20 western/southern bentonite clays<br>80/20 seacoal/lignite,<br>AO water | 10-27 | Phenolic urethane cold box |
| CX Tap | Penn State greensand formulation*<br>80/20 western/southern bentonite clays<br>80/20 seacoal/lignite,<br>Tap water (just after completing AO water turns) | 1-11 | Phenolic urethane cold box |
| * The water-to-MB Clay ratio was considerably lower than what was prescribed by Penn State. | | | |

Technikon turned the green sand molds (put them through a complete cycle) using AO water more times than those using tap water in hopes to stabilize the system to a pseudo-steady state condition. It was determined during these runs that when AO was employed, the emissions continued to decline each turn during at least the first six turns. Thus, it was perceived that the first several turns "conditioned" the greensand with AO water and therefore were not included in the emissions analysis. Full-scale data has shown that emissions continue to decrease and sand properties continue to change even up to three months after advanced oxidation start-up, which would entail hundreds of turn of the sand system; however this was not practical for testing at CERP/Technikon. One must remember that as the greensand is turned, the cores are burned out and unless removed become part of the greensand matrix. These cores can contain residual binder levels that may increase emissions. Core mass per mold during the Technikon greensand tests was between 4 and 4.5% each turn, and the core sand was either 1.1 or 1.74% resin. This was an important factor with the phenolic urethane cold box cores.

### 3.3.4.1 Pre-Production Trials

The CERP/Technikon team conducted several comparisons of AO versus non-AO conditions, using sodium silicate cores (i.e., no organic binder), or cores using organic binder at either a moderate or high level.

In the first of the pre-production trials, Technikon compared AO versus non-AO conditions while employing sodium silicate binders. These tests were designated by Technikon as "CH" and "CI". These are the same greensands that the Penn State team conducted bench-scale experiments on, as discussed in section 3.2.3. Since sodium silicate binders contain no organics, they do not represent a source of volatile organic emissions. As shown in Table 3.3-3, the greensand molds contained a 5-5.3% loss-on-ignition (LOI), 6.7–7.2% methylene blue clay (MB clay), and a moisture-to-clay ratio of 30-38%. During these tests, 161 ppm of hydrogen peroxide was included in the AO water. The green sand had been previously conditioned through multiple turns at a full-scale foundry and at Technikon. For the CH (non-AO) trials, the green sand experienced six turns, and the emission data from all six of these turns was compiled and averaged. For the CI (AO) trials, the greensand experienced 24 turns, and the emissions data from turns 7-12 and 19-24 were compiled and averaged. Prior to turn 7, the data showed a continuing decline in emissions as the system progressed to pseudo-steady state (data not reported herein). The data from turns 12-18 was not reported due to electrical problems affecting the circulation of the AO water.

The reductions in emissions that could be attributed to the advanced oxidation system (Table 3.3-3, CI vs. CH) amounted to 46% for the total hydrocarbons ($C_6$-$C_{14}$) as undecane, 43% for the sum of all specifically monitored volatile organic compounds (VOCs), 44% for the sum of volatile compounds that have been specifically identified as hazardous air pollutants (HAPs), and 65% for the sum of polycyclic organic material (POMs). Likewise, AO incurred a 37% reduction in benzene, 41% reduction in toluene, a 44% reduction in the xylenes (m, p + o), and a 79% reduction in phenol. With AO, emissions of $CO_2$ and methane went down slightly (but not statistically significantly),

## Table 3.3-3: CERP/Technikon pre-production-scale operation parameters and emissions for AO or non-AO water conditions and with sodium silicate cores or organic cores.

| **Parameters**: | CH: Non Core (No A0) | CI Non Core (AO) | *%Δ* CH vs. CI* | CV-Tap: Core, 4% LOI (No AO) | CV-AO: Core, 4% LOI (AO) | *%Δ* CVT vs. CVA* | CX: Tap, after CVA (AO) | *%Δ* CVT vs. CX* | CE: Core, 5% LOI (No AO) | CF: Core, 5% LOI (AO) | *%Δ* CE vs. CF* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Organic Core, % of core sand | 0 | 0 | *0* | 1.1 | 1.1 | *0* | 1.1 | *0* | 1.74 | 1.74 | *0* |
| Mold Loss on Ignition % | 5.28 | 5.02 | *-4.9* | 3.85 | 3.69 | *-4* | 3.69 | *-4* | 5.39 | 5.0 | *-7* |
| Mold MB Clay % | 7.18 | 6.75 | *-6* | 8.39 | 8.12 | *-3.2* | 8.29 | -- | 6.97 | 6.96 | *-0* |
| Moisture % | 2.13 | 2.35 | -- | 1.64 | 1.84 | -- | 1.71 | -- | 1.92 | 1.91 | -- |
| Moisture / Clay (%) ** | 29.7 | 34.5 | -- | 19.8 | 22.3 | -- | 20.0 | -- | 28.0 | 27.9 | -- |
| Lb org. binder/ ton metal | 0 | 0 | -- | 5.26 | 5.27 | -- | 5.28 | -- | 8.2 | 8.2 | -- |
| Lb. Org. binder/ ton green sand | 0 | 0 | -- | 0.89 | 0.93 | -- | 0.93 | -- | 1.49 | 1.41 | -- |
| $H_2O_2$ dose mg/L | 0 | 160 | -- | 0 | 495 | -- | 0 | -- | 0 | 160 | |
| Soda Ash lb / lb coal + clay | yes | yes | -- | 0.005 | 0.005 | -- | 0.005 | -- | 0 | 0 | |
| Compactibility, % | 46 | 47 | -- | 47 | 47 | -- | 47 | -- | 45 | 49 | *8.8* |
| **Emissions: (lb/ton metal poured)** | | | | | | | | | | | |
| Hydrocarbons | 0.309 | 0.167 | *-46* | 0.830 | 0.630 | *-24* | 0.773 | *-7* | 0.926 | 0.831 | *-10* |
| Sum VOC | 0.206 | 0.117 | *-43* | 0.722 | 0.530 | *-27* | 0.528 | *-27* | 0.742 | 0.696 | *-6* |
| Sum HAPs | 0.157 | 0.089 | *-44* | 0.578 | 0.439 | *-24* | 0.434 | *-25* | 0.634 | 0.600 | *-5* |
| Sum POMs | 0.017 | 0.006 | *-65* | 0.077 | 0.061 | *-21* | 0.055 | *-29* | 0.117 | 0.109 | *-6* |
| Benzene | 0.057 | 0.036 | *-37* | 0.138 | 0.106 | *-21* | 0.112 | *-19* | 0.150 | 0.153 | *+2* |
| Toluene | 0.038 | 0.022 | *-41* | 0.065 | 0.051 | *-21* | 0.045 | *-31* | 0.057 | 0.052 | *-8* |
| Xylenes | 0.023 | 0.013 | *-44* | 0.040 | 0.029 | *-28* | 0.024 | *-40* | 0.031 | 0.026 | *-15* |
| Phenol | 0.006 | 0.001 | *-79* | 0.109 | 0.090 | *-18* | 0.086 | *-21* | 0.134 | 0.120 | *-11* |
| Naphthalene | 0.007 | 0.003 | *-58* | 0.023 | 0.017 | *-24* | 0.018 | *-23* | 0.029 | 0.023 | *-19* |
| CO lb/ton | 4.66 | 4.99 | *+7* | 4.45 | 4.54 | *+2* | 4.05 | *-7* | 4.08 | 4.73 | *+16* |
| $CO_2$ lb/ton | 29.78 | 27.5 | *-7* | 26.9 | 27.7 | *+3* | 27.4 | *+2* | 28.6 | 29.4 | *+3* |
| Methane | 0.647 | 0.589 | *-9* | 0.816 | 0.551 | *-32* | 0.465 | *-43* | 0.615 | 0.655 | *+7* |
| Condensibles lb/ton | 0.185 | 0.106 | *-43* | 0.25 | 0.27 | *+10* | 0.20 | *-20* | na | na | *na* |

* % Change (Δ) equals (1st number - 2nd number) / 1st number

** The water-to-MB clay ratio (in %) that the Sonoperoxone$^{TM}$ manufacturer recommends and designs around is 30-42 %. When the water-to-MB clay ratio was lower than this, the level of advanced oxidants that was present was lower than was designed for.

while CO emissions went up slightly (and also not statistically significantly). These reductions in emissions accomplished with advanced oxidation are quite significant. Moreover, the percent reductions correlate with the range of percent reductions that full-scale foundries have observed for non-cored conditions (as discussed in section 3.3.4.2).

The second set of pre-production trials compared emissions using AO versus non-AO for green sand including a phenolic urethane core binder. The organic core represented 1.1% of the core sand, amounting to 0.89-0.93 lb core binder per ton of green sand.

These trials employed green sand materials that were all initially virgin. For the first nine turns, the green sand was tested without AO (designated as "CV-Tap"). During turns 10-18, the system was conditioned to AO, but emissions were not taken for these turns. During turns 19-27, AO treatment continued, and emissions were compiled and averaged as "pseudo-steady state" values (designated as "CV-AO"). This same green sand was then cycled through eleven more turns without the AO system. Emissions data was also compiled and averaged during this cycle (designated as "CX"). The final eleven turns were conducted to discern whether the favorable effects of AO treatment would linger in subsequent molds that were made from this green sand, even if the AO system was no longer used.

During these tests, the average MB clay was 8.1-8.4%, the average LOI was 3.69-3.85%, the average moisture was 1.64-1.84%, and the average water-to-MB clay ratio was 19.8-22.3%. Soda ash additions amounted to 0.005 lb $Na_2CO_3$ / lb coal and clay, to attempt to maintain the green sand slurry pH at 10.0-10.5 (although the actual slurry pH was closer to 9.5). The hydrogen peroxide dose was maintained at 495 ppm.

The AO (CV-AO) versus non-AO (CV-Tap) comparison for the 1.1% core trials shows that hydrocarbon emissions dropped from 0.83 lb/ton metal without AO to 0.63 lb/ton with AO - a 24% reduction (Table 3.3-3). Similarly, VOCs dropped from 0.72 to 0.53 lb/ton (27% reduction), HAPs dropped from 0.53 to 0.44 lb/ton (24% reduction), benzene dropped from 0.14 to 0.11 lb/ton (24% reduction), and phenol dropped from 0.109 to 0.09 lb/ton (18% reduction).

It should be noted that these results occurred with less than prescribed levels of advanced oxidants, because of a lower-than-prescribed level of moisture in the molds. The CERP/Technikon test plan for the CV and CX series called for "8 ± 0.5% MB clay" and to "make every attempt to achieve a moisture range of 2.8-3.6%." This would translate to a water-to-MB clay ratio of 33-45%. The actual moisture levels were lower (1.64-1.73%) and thus the actual water-to-MB clay ratio was only 19.8-22.3%. The reason for the low moisture levels was that the CERP/Technikon test plan also called for a target "compactibility in the range of 45-51%", while the actual compactibility was near 47% at 1.64-1.73% moisture. Therefore, the operators at Technikon perceived that they could not add the prescribed amount of moisture without exceeding the compactibility target for these near-virgin green sand materials.

In contrast, the Neenah foundry that uses AO has operated with a water-to-MB clay ratio of 30-34%, while the compactibility set-point has been 38%. Grede-Reedsburg has maintained a water-to-MB clay ratio of 31-33% while maintaining a compactibility of 39%. Likewise, the Wheland foundry that also uses AO has operated with a water-to-MB clay ratio of 34-43%, while the compactibility remained in the 39-40% target range.

Likewise, for the CH and CI trials at CERP that employed non-virgin green sands, Technikon maintained a 30-38% water-to-MB Clay ratio, while maintaining compactibility at 46-47%.

The Technikon CV and CX sands required less moisture than typical foundries because in the CERP/Technikon mulling procedure, the operators added some moisture to greensand, mulled the sand, tested compactibility, then added more water and re-mulled until the desired compactibility was reached. Thus, by the nature of this protocol, the Technikon green sand often received 10 minutes or more of mulling, whereas in a full-scale foundry, green sand would commonly receive 1-1.5 minutes of mulling. Since compactibility increases with increasing mulling time, the net effect of this protocol was that a number of the Technikon greensand molds contained less water for a given compactibility level then has occurred in a full-scale foundry. This translated to less AO water used in the AO trials, and a presumed lesser AO effect than originally prescribed.

An additional note is that the CERP/Technikon staff noticed that when they used virgin or near-virgin green sand materials, they could not work the water into the green sand as well as they could when they used green sands that had been re-circulated multiple times through a foundry. The natural progression of this notion is that the near-virgin green sand materials had not reached a true steady–state condition relative to the time that they were tested for green sand properties and emissions.

Regardless of why more water was not worked into the CERP green sand, the bottom line is that these green sands contained two-thirds as much water, and therefore two-thirds as much ozone or sonication levels as was prescribed or as would be used in full scale conditions.

Table 3.3-3 shows a quantitative decline in phenol of 0.0192 lb/ton metal when comparing the CV-AO versus the CV-Tap 1.1% cored green sands. This decline was considerably greater than the 0.0047 lb/ton difference that occurred for the sodium silicate cored green sands (CI versus CH). Since most of the phenol originates from the phenolic urethane core binder, this comparison indicates that the advanced oxidation process eliminated some of the phenol emissions (12-16%) that originated from the smoldering core binders. We hypothesized that this occurred because the AO-treated green sand served as a better adsorbent and/or reactive sink for these phenol emissions than did the non-AO treated green sand. Ongoing tests at Penn State further verify this notion.

Similarly, for many of the other emissions parameters, the quantitative decline that was achieved by AO for the 1.1% cored green sands (CV-AO versus CV-Tap) was greater than for the sodium silicate cored green sands (CI AO versus CH tap). Specifically, when comparing CV-AO to CV-Tap, hydrocarbons dropped 0.20 lb/ton, whereas when comparing CI to CH, hydrocarbons dropped 0.142 lb/ton. Likewise, VOCs dropped 0.192 lb/ton for organic-cored green sands, but only 0.089 lb/ton for sodium silicate cored green sands. These trends indicate that the AO-treated green sand could adsorb and/or capture core-generated emissions more significantly than could the non AO-treated green sand.

As a further commentary that relates to the influence of water-to-MB clay ratio, we note that a 43% reduction in the sum of VOCs occurred when comparing the sodium silicate cored trials (CI versus CH); whereas a 27% VOC reduction occurred when comparing the sum of VOCs for the 1.1% cored trial (CV-AO versus CV-Tap). The ratio of these two differences (43/27) equals 1.6:1. Similarly, the water-to-MB clay ratio for the sodium silicate cored AO trial (CI) was 34.5%, whereas this ratio for the 1.1% cored AO trial (CVA) was 22.3%. The ratio between these two values (34.5/22.3) equals 1.55:1. In light of this similarity, one could surmise that the lower emission reductions found for the 1.1% cored test (CV) could have either occurred because (a) the 1.1% cored tests employed a lower level of AO water, or (b) the emissions that potentially departed from the smoldering cores were not influenced by the AO treatment as much as the emissions that potentially departed from the non-core green sand materials, or (c) both. This data set alone does not distinguish between these possibilities.

After the 1.1% core AO trials (CV-AO) were culminated, the Technikon team continued to process this green sand material through eleven more cycles of mulling, molding, pouring, and shakeout. However, advanced oxidants were excluded from the last eleven turns, and moisture was made up solely with tap water. The objective of these trials was to discern whether the emission-diminishing effects of the advanced oxidation would linger on. If so, this would mean that advanced oxidation had physically or chemically altered the green sand in a manner that rendered it more able to adsorb or capture emissions.

As shown in Table 3.3-3, the emissions for the post-AO 1.1% core trials (CX), were lower than during the CV-Tap trials. Hydrocarbons were reduced by 7%, the sum of VOCs dropped 27%, the sum of the HAPs dropped 25%, and the phenol emissions dropped 21%. Intriguingly, in fact, the emission levels for nearly all of the species were about the same after AO had ceased (during the CX trials) as when AO was employed (during the CV-AO trials). The emissions that increased somewhat as these post-AO trials progressed were total hydrocarbons (reference to undecane), phenol, and condensables (see Technikon reports, Jan. 5, 2001).

Another noteworthy result observed from the 1.1% cored trials (CV-Tap, CV-AO, and CX) is that AO did not significantly affect CO or $CO_2$ emissions. However, the CV-AO and post-AO (CX) trials exhibited considerably lower methane levels (32 or 43% drop) than did the non-AO trials (CV-Tap).

The results from the post-AO trials confirm that the AO treatment physically or chemically altered the green sand grains in such a manner as to render them more capable of capturing emissions.

The third experiment from Technikon compared AO versus non-AO conditions for heavily cored molds. These have been designated by Technikon as “CE” and “CF” (see Table 3.3-3). These green sands had 1.74% core (compared to 1.1% core for CV-AO, CV-Tap, and CX green sands), 5-5.4% LOI, 6.9-7.0% MB clay, and a 27.9-28% moisture-to-methylene blue clay ratio. This core binder condition corresponded to 1.41–1.49 lb organic binder per ton of green sand. The CE (non-AO) sands were run through nine turns with tap water, while the CF (AO) sands were run through 17 turns with AO water. The AO-treated green sand (CF) emitted 10% less hydrocarbons, 6% less VOCs, and 5% less HAPs than the non AO-treated green sand (CE), but these differences were not statistically significant. It would appear that the advanced oxidation at the given moisture levels did not greatly affect emissions when the core loading was high.

In a fourth experiment, CERP/Technikon also monitored the effects of AO when employing near-virgin green sand that contained no coal but did contain phenolic urethane cores. This core sand represented 1.74% of the green sand material, and the core binders amounted to 8.2 lb core binder / ton of metal poured. The tap water treated green sands were put through 12 turns, while the AO-treated sands were put through 25 turns. There were no statistical differences in emissions when AO was employed (see Technikon reports, Jan. 5, 2001). This result is telling, but not surprising. The authors herein perceive that the AO-treated coal provides the major enhancement for emission removal, and when the coal is not present, it cannot facilitate this improvement.

In a fifth series of pre-production tests, CERP/Technikon appraised the influence of clay origin on AO benefits. These trials used virgin materials and compared AO versus non-AO conditions when using (a) 80% western (sodium) bentonite / 20% southern (calcium) bentonite ("DT" non-AO and "DU" AO), (b) 50% western / 50% southern ("DR" non-AO and "DS" AO), and (c) 20% western / 80% southern ("DQ" non-AO and "DA" AO). The results are summarized in Table 3.3-4. These trials employed 6.4-7.3% MB clay, 4.8-5.0% LOI, and a 22.8-24.6% water-to-MB clay ratio. The AO system employed 161 or 495 ppm hydrogen peroxide, as per the manufacturer's guidance (see Table 3.3-4).

Emission levels were about the same regardless of which clay mixture was used and regardless of whether AO was employed or not. The one exception to this is that the emissions for the AO-treated 50w/50s trials (DS) were lower than their non-AO counterpart (DR) in all categories of emissions. For all of these trials, hydrocarbons (as hexane) ranged from 0.48 to 0.64 lb/ton metal, sum of VOCs ranged from 0.21 to 0.25 lb/ton, benzene ranged from 0.081 to 0.099 lb/ton, and phenol ranged from 0.010 to 0.013 lb/ton.

The emission results are considerably different from the CH versus CI test and full-scale operating foundry results which show a 40-60% emissions reduction when AO is applied to molds that have no organic binder. When observing such wide disparity, one could discern either that (a) 22.8-24.7% water-to-MB clay ratio was too low to achieve a favorable emissions effect, (b) the AO induces more favorable effects on green sands that have undergone multiple cycles of reuse then it does on virgin green sand materials, (c) the AO system was not operated properly during the DA and DQ-DU trials whereas it was operating properly during the CH and CI trials, or (d) some combination of the previous. The AO system is presumed to have worked properly, so (c) can probably be ruled out. It should be noted that full-scale foundries do not operate with virgin materials.

### 3.3.4.2 Production Scale Trials

The CERP/Technikon team also conducted production scale testing of the advanced oxidation system. These tests employed Technikon's horizontal parting line system that totally encloses all sources of emissions. During these tests, green sand was continuously fed through the production foundry.

**Table 3.3-4: CERP/Technikon pre-production-scale operation parameters and emissions for AO and non-AO conditions with various proportions of western and southern bentonite clay.**

| **Parameters**: | DT: 80W/ 20S No AO | DU: 80W/ 20S AO | *% Δ DT vs. DU*$^{**}$ | DR: 50W/ 50S No AO | DS: 50W/ 50S AO | *% Δ DR vs. DS*$^{**}$ | DQ: 20W/ 80S No AO | DA: 20W/ 80S AO | *% Δ DQ vs. DS*$^{**}$ |
|---|---|---|---|---|---|---|---|---|---|
| Turns included in average* | 5,6,8-11 | 7-12 | -- | 4-9 | 7-12 | -- | 4-9 | 16-18 | -- |
| Mold LOI, % | 4.94 | 4.9 | *-1* | 5.0 | 4.77 | *-4.6* | 4.97 | 4.77 | *-4.0* |
| Mold MB Clay, % | 7.24 | 7.16 | -- | 6.89 | 7.08 | -- | 6.43 | 7.01 | -- |
| Mold Moisture, % | 1.66 | 1.76 | -- | 1.61 | 1.75 | -- | 1.54 | 1.68 | -- |
| Moisture / Clay, % | 23.1 | 24.5 | -- | 22.8 | 24.7 | -- | 24.0 | 24.0 | -- |
| Compactibility, % | 48 | 45 | -- | 47 | 47 | -- | 42 | 47 | -- |
| $H_2O_2$ dose, ppm | | 160 | | | 495 | | | 495 | |
| **Emissions:** **(lb/ton metal poured)** | | | | | | | | | |
| Hydrocarbons (as hexane) | 0.639 | 0.590 | *-7.7* | 0.620 | 0.479 | *-23* | 0.607 | 0.544 | *-4* |
| Sum VOCs | 0.212 | 0.249 | *+17* | 0.232 | 0.207 | *-11* | 0.209 | 0.223 | *+7* |
| Sum HAPs | 0.196 | 0.230 | *+17* | 0.211 | 0.189 | *-10* | 0.188 | 0.212 | *+13* |
| Sum POMs | ND | 0.024 | -- | ND | ND | -- | ND | ND | -- |
| Benzene | 0.087 | 0.090 | *+3* | 0.092 | 0.081 | *-12* | 0.089 | 0.099 | *-11* |
| Phenol | 0.0102 | 0.0108 | *+6* | 0.013 | 0.0097 | *-25* | NA | 0.011 | -- |

* Last six turns included in average; except for trial DA, where data from only last three turns was published.

** % difference = 100 x (1st – 2nd) / 1st

The Technikon team monitored emissions from several combinations of conditions: (i) from the 8th through 11th turns, they monitored engine blocks with phenolic urethane cores while using tap (non-AO) water, (ii) during turns 23-26, they monitored star patterns with no cores while using non-AO water, (iii) during turns 37-38, they monitored star patterns with no cores while using AO water, and (iv) during turns 46-50, they monitored engine blocks with phenolic urethane cores while using AO water. The test results that appraised phenolic urethane cores have not yet been released to the public (or to the Penn State research team). The test results that appraised star patterns without core are discussed as follows.

The non-AO non-cored star pattern tests (herein after to as "TAP-STAR") used a green sand with a 5.01% LOI, 7.8% MB Clay, 2.58% moisture, and 32.8% water-to-MB clay ratio. The AO non-cored star pattern test ("AO-STAR") used a green sand with a

3.53% LOI, 8.03% MB clay, 2.54% moisture, and 31.6% water-to-MB clay ratio. The rationale for employing a lower LOI level for the AO tests than for the non-AO tests is that many of the full scale foundries who use the AO process find that they can maintain proper metal finish quality with less LOI and less MB clay when they use the AO process then when they do not use it. For example, the Neenah data enclosed in this report show that non-AO system sand required a 5.44% LOI, while the AO system sand established proper control with a 3.65% LOI.

The emissions that were released during these two trials appear in Table 3.3-5. The total hydrocarbons dropped 49% from 1.88 to 0.95 lb/ton of metal poured. The sum of VOCs dropped 64% from 0.519 to 0.187 lb/ton, the sum of HAPs dropped 64%, benzene dropped 57%, and naphthalene dropped to non-detectable concentrations. The CERP/Technikon report states that "based on the CERP research paper, PROCESS VARIABLE EVALUATION, a reduction of 1.5% in the mold LOI would result in approximately 32% reduction in organic VOC emissions". Thus, half of the VOC emission reductions could be attributed to the AO process.

**Table 3.3-5: CERP/Technikon production-scale operation parameters and emissions for advanced oxidation versus non-AO, for STAR pattern (non-cored) trials.**

| **Parameter** | **Non-AO** | **AO** | **% Δ** |
|---|---|---|---|
| Cycle # | 654-744 | 1031-1109 | -- |
| Mold LOI, % | 5.0 | 3.6 | -28 |
| Mold MB Clay, % | 7.86 | 8.02 | -- |
| Mold Moisture, % | 2.58 | 2.54 | -- |
| Water/MB Clay, % | 32.8 | 31.6 | -- |
| $H_2O_2$ dose, ppm | 0 | 400 | |
| **Emissions (lb/ton metal)** | | | |
| TGOG (THC) as Propane | 4.36 | 2.04 | -53.2 |
| HC as Hexane | 1.88 | 0.949 | -49.4 |
| Sum of VOC's | 0.519 | 0.187 | -64.0 |
| Sum of HAP's | 0.519 | 0.187 | -64.0 |
| Sum of POM's | 0.008 | ND | -100 |
| Benzene | 0.159 | 0.069 | -56.9 |
| Toluene | 0.161 | 0.071 | -55.9 |
| Ethylbenzene | 0.032 | ND | -100 |
| O,m,p-Xylene | 0.135 | 0.052 | -61.5 |
| Naphthalene | 0.010 | ND | -100 |
| Phenol | ND | ND | N/A |
| Aniline | 0.025 | 0.002 | -91.9 |
| Condensables | 1.88 | 1.34 | -28.7 |
| Carbon Monoxide | ND | ND | N/A |
| Methane | ND | ND | N/A |
| Carbon Dioxide | 115 | 116 | +0.87 |

### 3.3.4.3 Summary of the CERP/Technikon Testing

1. The pre-production CH (non-AO) versus CI (AO) trial used sodium silicate cores and green sand that originated from a full-scale foundry where it had been re-circulated multiple times. The green sand had a 5.0-5.3% LOI and 30-32% water-to-MB clay ratios. Hydrogen peroxide was applied for AO conditions at 160 ppm. AO treatment caused a drop in hydrocarbon, sum VOC, and sum HAP emissions of 43-46%, and it caused a reduction in individual analytes of between 37-79%.

2. The pre-production CV-Tap versus CV-AO trial included 1.1% cored sands with phenolic urethane binder (0.9 lb binder/ton of total green sand) while using near-virgin green sand materials. The green sand had a 3.6-3.9% LOI and 20-22% water-to-MB clay ratios. Hydrogen peroxide was applied at 495ppm. AO treatment caused a drop in hydrocarbon, sum VOC, and sum HAP emissions of 24-27%. AO processing caused an 18% drop in phenol emissions, and most of this drop could only be due to the AO-treated green sand mold adsorbing or capturing phenol emissions that released from the smoldering phenolic urethane core.

3. When AO treatment ceased in a green sand that had just previously received AO conditions (CX trial), the green sand retained most of its emission-capturing properties for at least 11 more turns.

4. The pre-production CE (non-AO) versus CF (AO) trial used 1.74% "high" core sands with phenolic urethane binder (1.4-1.5 lb binder/ton total green sand). The green sand had a 5.0-5.4% LOI and 28% water-to-MB clay ratios. AO treatment achieved no statistically significant reduction in emissions. Also, no statistically significant reductions in emissions were observed when the green sand contained 1.74% core sands but no coal.

5. The pre-production trials varying western to southern bentonite ratios used sodium silicate cores and virgin green sand materials. The green sands had 4.8-5.0% LOI and 22.8-24.7% water-to-MB clay ratios. AO processing included either 160 or 495 ppm hydrogen peroxide. AO treatment caused no statistically *significant* change in emissions for any of the clay ratios: 20 western / 80 southern, 50w / 50s, or 80w / 20s. However, AO did cause a slight (10-23%) drop in nearly all emissions for the 50 western / 50 southern green sand.

6. The continuous feed production-level trials included star patterns and no organic core. The green sand had 7.8-8.0% MB clay, 31-33% water-to-MB clay ratios, and a 5.0% LOI for non-AO conditions and a 3.6% LOI for AO conditions. The AO treatment induced drops of 49-64% in hydrocarbons, sum of VOCs, and sum of HAPs. AO treatment also reduced naphthalene and other polyaromatic organic molecules to non-detectable levels. About half of these declines could be attributed to a lower LOI (i.e. indirect AO effect on common system process by reducing coal and clay contents). The other half could be attributed to the direct effects of AO treatment on reducing emissions from a given batch of green sand.

### 3.3.5 Summary of Section 3.3

1. The emissions performance of AO-CW and AO-DBW systems has been evaluated in a series of pre-production-scale tests at CERP/Technikon and during stack testing at three production foundries. In particular, the CERP/Technikon testing is useful to focus and interpret the stack test results from the production foundries, where the long-term direct effects of AO systems on emissions combined with the beneficial effects of AO-driven sand system optimization on sand system emissions are revealed.

2. For AO-CW systems, foundry benzene reductions of from 10-30% and total VOC reductions of 20-40% can be expected. For AO-DBW systems, foundry benzene reductions of 20-50% can be expected along with total VOC emission reductions of 30-75%.

3. VOC emissions, and benzene emissions in particular, are created from the decomposition of organic core binders during pouring, cooling, and shakeout.

## 3.4 SAND SYSTEM PERFORMANCE – LABORATORY STUDIES

### 3.4.1 AO-Clean Water Mulling Trials

#### 3.4.1.1 Introduction

Penn State laboratory tests were conducted to study the effect of AO water on green compressive strength and compactibility. The laboratory tests were conducted with both new green sand (consisting of new sand and western bentonite) and with production green sands obtained from two high-production iron foundries.

The new sand trials used synthetic green sand mixtures made from silica sand, western bentonite clay and water. The proportions of these ingredients were similar to those found in the production green sands, however, no other additional additives, such as coal were added. This allowed the effects of AO on clay activation to be evaluated for a simple sand/clay system. Since the clay was new and had not been subjected to the casting cycle, it did not contain any injured or dead clays from repeated molding cycles.

The production sand trials used green sand obtained from both Neenah Foundry and Wheland Foundries. Since this production sand was taken directly from their sand systems, it contained fines, seacoal, dead clay and injured clay. The Wheland Foundry used a 70:30 mixture of both western and southern bentonites, while Neenah Foundry sands were only bonded with western bentonites. Complete details of the procedures and results presented in section 3.4.1 can be found in the Penn State thesis by Hannigan (2000).

#### 3.4.1.2 Methods

The new sand tests consisted of mull-down trials with temper curve information developed from multiple mull-down trials. In the mull-down trials, the sand, clay and water were mulled for a specific period of time in a laboratory muller, then removed from the muller and tested for compactibility, green compressive strength (GCS), and moisture content. This entire test protocol occurred at ambient temperature.

After property testing, the sand mixture was put back into the muller, mulled for additional time and re-tested. These mull-down trials permitted the development of sand properties as the mulling time progressed. The final mulling time data points were used to develop temper curves. However, these were not standard temper curves, since the mulling had been interrupted several times to collect the mull-down data.

Three replicate samples were tested for the compactibility and green compressive strength to assess repeatability. The reported test values were the averages of the three samples. Only one moisture content sample was tested, however, because of the length of time needed to complete a moisture test. The mulling times and tests performed on the new sands are shown in Table 3.4-1.

**Table 3.4-1: Sand tests performed on new sands.**

| Cumulative Mulling Time (Minutes) | Sand Tests Performed |
|---|---|
| 0.5 | Compactibility, 3 replicates; GCS, 3 replicates |
| 1.0 | Compactibility, 3 replicates; GCS, 3 replicates; moisture content |
| 1.5 | Compactibility, 3 replicates; GCS, 3 replicates |
| 2.0 | Compactibility, 3 replicates; GCS, 3 replicates |
| 3.0 | Compactibility, 3 replicates; GCS, 3 replicates |
| 5.0 | Compactibility, 3 replicates; GCS, 3 replicates |
| 10.0 | Compactibility, 3 replicates; GCS, 3 replicates<br>Wet tensile strength, 3 replicates; moisture content |

The mull-down trials were performed on the various synthetic green sand mixes with different amounts of clay, different moisture/clay ratios, and with both tap water and AO processed water ($O_3$ saturation, 150 ppm $H_2O_2$, sonication). Green sands containing either 8 wt% or 12 wt% western bentonite (WB) clay were evaluated. The new sand test matrix is shown in Table 3.4-2.

For each test run, 9 lbs. of new sand were added to a Simpson-Gerosa laboratory muller with an appropriate amount of western bentonite clay. The mixture was dry-mixed for 30 seconds. The appropriate amount of either tap water or AO processed water was then added to the muller. The sand was mulled for 0.5 minutes, then taken out and tested. The sand, including the specimens used during testing, was placed back into the muller and mulled for an additional 0.5 minutes. This procedure was repeated until the properties at cumulative mulling times shown in Table 3.4-1 were obtained.

The testing of production green sands using green sand provided by Neenah Foundry and Wheland Foundry were conducted in the same manner as the new sand trials (also at ambient temperature). Mull-down trials, with the end points being used to generate temper curves, were similarly conducted. The mulling times and tests performed on the production sands are shown in Table 3.4-3.

The mulling times for the production sand were chosen based on some initial tests to determine the operating mulling range of the production sands. Non-uniform properties were observed after mulling for times less than 1 minute. After 5 minutes of mulling, the production sands were already over-mulled, so nothing was gained from extending the mulling times beyond 5 minutes.

Moisture percentages were measured at 1.5 minutes of mulling and 5.0 minutes of mulling. The testing procedures for these sand tests on the production sands were identical to the procedures described previously for the new sand tests. The mull-down trials for the production sands were performed with the various conditions shown in Table 3.4-4.

The first set of tests was run using Neenah Foundry Plant 3 green sand (from

1999) that had been production treated with AO processed water. The rest of the tests were done with Neenah Foundry Plant 2 or Wheland Broad Street Foundry production sands that had not been previously treated with AO. The target moistures for the trials were selected to replicate the moisture levels used in production.

**Table 3.4-2: New sand test matrix.**

| Clay Addition (%) | Target Moisture (%) | MB Clay Content (%) | Moisture/ MB Clay Ratio | Water Type |
|---|---|---|---|---|
| 8 | 1.6 | 7.2 | 22 | Tap |
| 8 | 1.9 | 7.2 | 26 | Tap |
| 8 | 2.2 | 7.2 | 31 | Tap |
| 8 | 2.5 | 7.2 | 35 | Tap |
| 8 | 2.8 | 7.2 | 39 | Tap |
| | | | | |
| 12 | 2.8 | 10.8 | 26 | Tap |
| 12 | 3.3 | 10.8 | 31 | Tap |
| 12 | 3.8 | 10.8 | 35 | Tap |
| 12 | 4.2 | 10.8 | 39 | Tap |
| 12 | 4.3 | 10.8 | 40 | Tap |
| | | | | |
| 8 | 1.6 | 7.2 | 22 | AO Processed |
| 8 | 1.9 | 7.2 | 26 | AO Processed |
| 8 | 2.2 | 7.2 | 31 | AO Processed |
| 8 | 2.5 | 7.2 | 35 | AO Processed |
| 8 | 2.8 | 7.2 | 39 | AO Processed |
| | | | | |
| 12 | 2.8 | 10.8 | 26 | AO Processed |
| 12 | 3.3 | 10.8 | 31 | AO Processed |
| 12 | 3.8 | 10.8 | 35 | AO Processed |
| 12 | 4.2 | 10.8 | 39 | AO Processed |
| 12 | 4.3 | 10.8 | 40 | AO Processed |

**Table 3.4-3: Mulling times and sand tests for production sand trials.**

| Cumulative Mulling Time (Minutes) | Sand Tests Performed |
|---|---|
| 1.0 | Compactibility, 3 replicates; GCS, 3 replicates |
| 1.5 | Compactibility, 3 replicates; GCS, 3 replicates; moisture content |
| 2.0 | Compactibility, 3 replicates; GCS, 3 replicates |
| 3.0 | Compactibility, 3 replicates; GCS, 3 replicates |
| 5.0 | Compactibility, 3 replicates; GCS, 3 replicates<br>Wet tensile strength, 3 replicates; moisture content |

**Table 3.4-4: Production sand test matrix.**

| Sand Type | Target Moisture (%) | Re-moisturized Water Type |
|---|---|---|
| Neenah Plant 3 (AO) | 3.5 | Non-AO |
| Neenah Plant 3 (AO) | 3.5 | AO |
| | | |
| Neenah Plant 2 (non-AO) | 2.8 | Non-AO |
| Neenah Plant 2 (non-AO) | 2.8 | AO |
| | | |
| Wheland (non-AO) | 3.0 | Non-AO |
| Wheland (non-AO) | 3.0 | AO |
| Wheland (non-AO) | 3.7 | Non-AO |
| Wheland (non-AO) | 3.7 | AO |

### 3.4.1.3 Results and Discussion

The first set of new sand trials was run with 12% western bentonite (WB) clay additions. Figures 3.4-1 and 3.4-2 show the green compressive strength and compactibility as a function of the mulling time with 3.2% nominal moisture. Similar mull-down trials were performed at 3.8% moisture and 12% WB, as shown in Figures 3.4-3 and 3.4-4.

Test results at specific mulling times were used to develop temper curves. Three types of temper curves were completed: compactibility versus moisture, green compressive strength versus moisture, and green compressive strength versus compactibility. All of the curves were plotted for the 1.5-minute mull, which is representative of a typical foundry mulling time, and for the 10-minute mull, which is representative of complete mulling. Figures 3.4-5 through 3.4-10 illustrate mull-down behavior and temper curves for tap water (TW) and AO water (AOW) trials.

The mull-down and tempering behaviors of synthetic 12% WB green sands show no significant difference between the mull-down or temper curve behavior of AO and non-AO sands. The influence of AO on sand properties and mulling behavior observed in the foundries was not replicated in the laboratory for these 12% western bentonite mulling trials on virgin materials. A few possibilities why the AO did not show the same effects here as found in the foundry are that: (a) the sands experienced only one AO application in the laboratory setting; sand in a foundry is recirculated and exposed to AO water numerous times; (b) the new, or virgin, sand materials used had not been previously mixed, mulled, and so forth – they had not been previously conditioned – while production sands during molding are never "virgin;" (c) the new sand mixtures did not contain any of the injured clays that are part of production sand systems. Work at Penn State has shown that (a), multiple turns of AO, is probably the most prominent reason (see section 3.4-2).

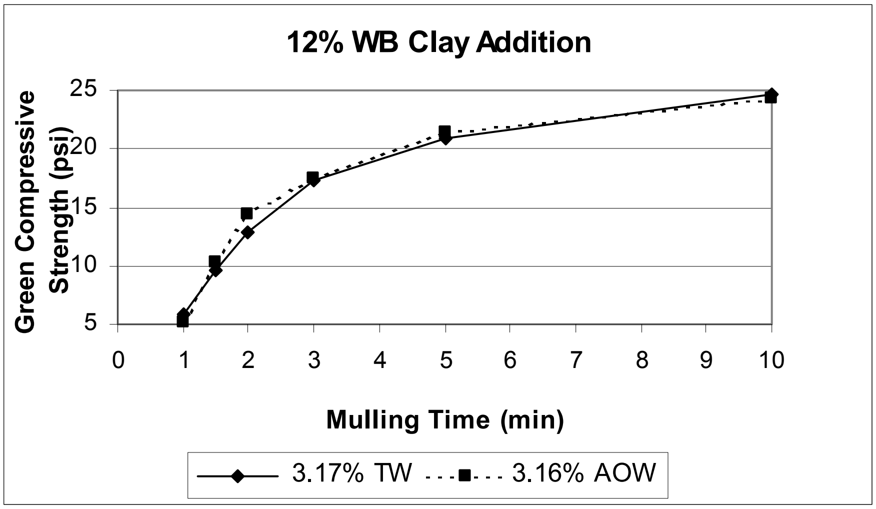


**Figure 3.4-1: Green compressive strength (GCS) mull-down behavior – 12% western bentonite (WB) clay, 3.2% target moisture.**

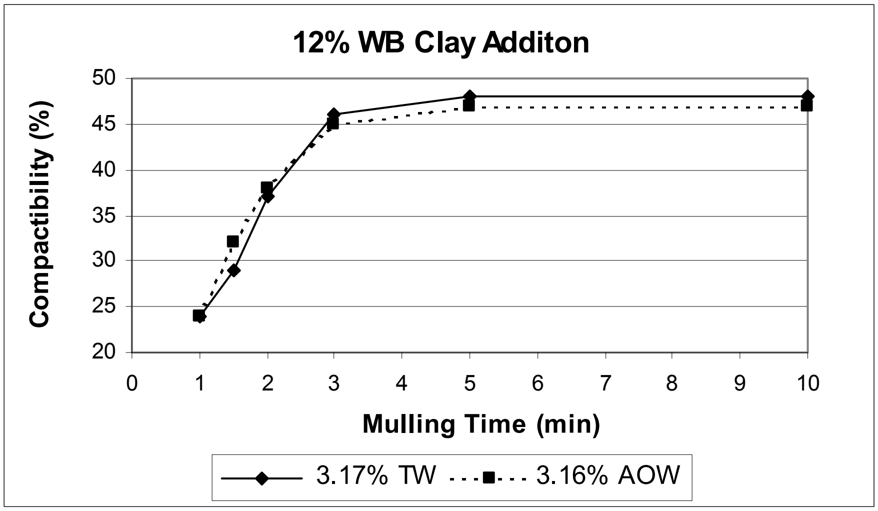


**Figure 3.4-2: Compactibility mull-down behavior – 12% WB, 3.2% target moisture.**

*[Note: AOW = AO processed water, TW = Tap water. All plotted data are averages of three replicate tests; all tests were performed at ambient temperatures and without involving molten metal]*

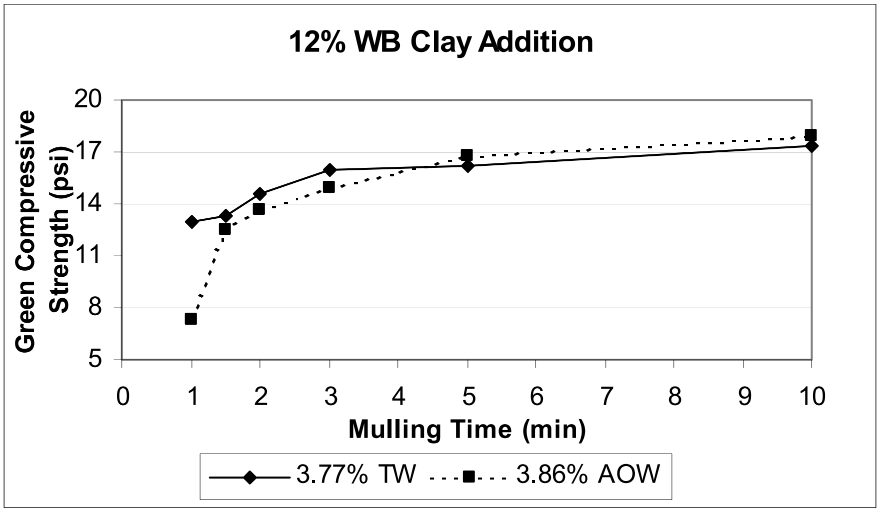


Figure 3.4-3: GCS mull-down behavior – 12% WB, 3.8-3.9% actual moisture.

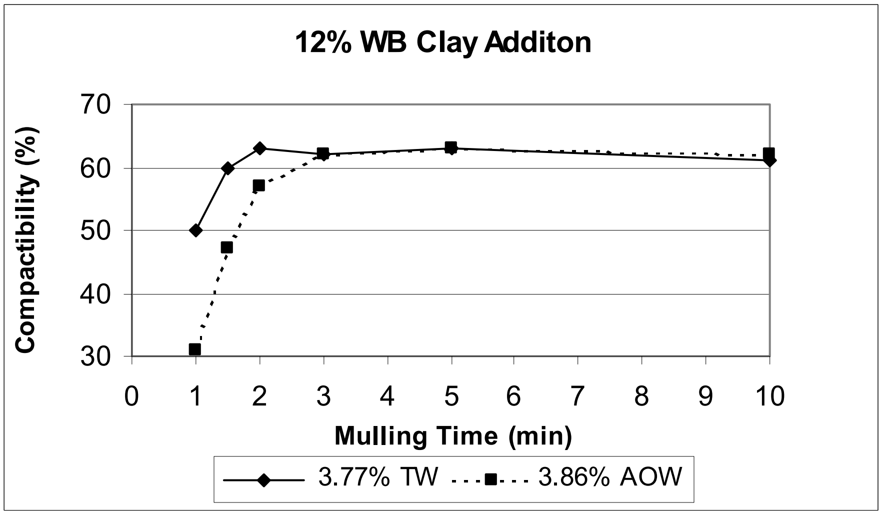


Figure 3.4-4: Compactibility mull-down behavior – 12% WB, 3.8-3.9% actual moisture.

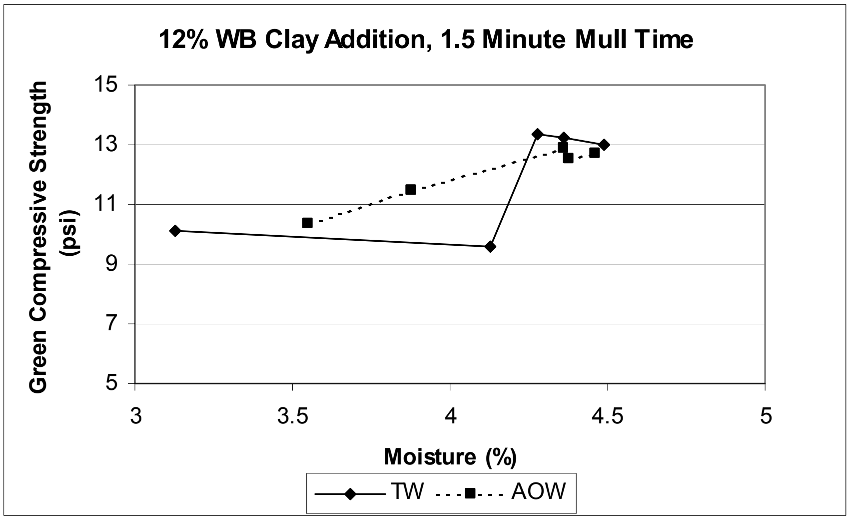


Figure 3.4-5: 12% WB GCS temper curve, 1.5 minute mull.

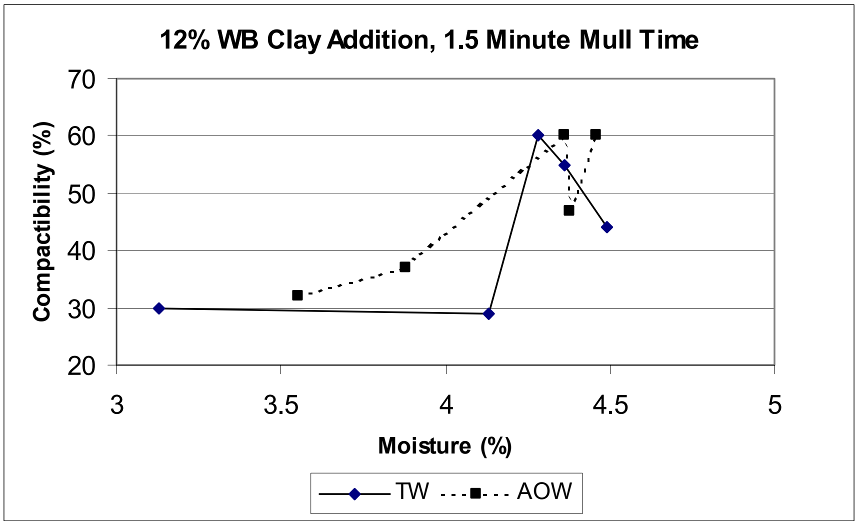


Figure 3.4-6: 12% WB compactibility temper curve, 1.5 minute mull.

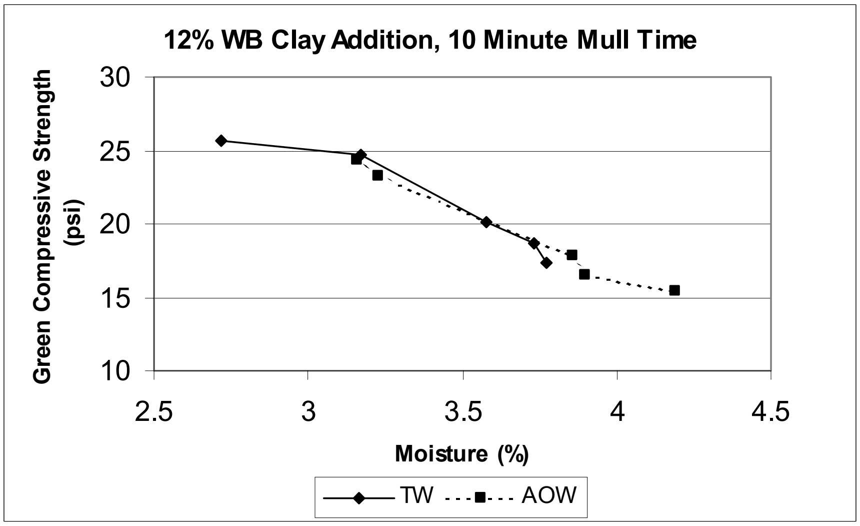


Figure 3.4-7: 12% WB GCS temper curve, 10 minute mull.

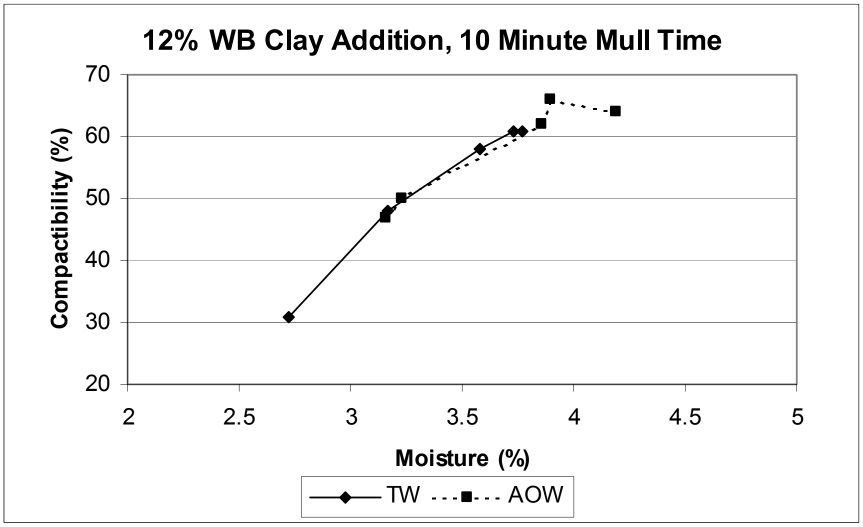


Figure 3.4-8: 12% WB compactibility temper curve, 10 minute mull.

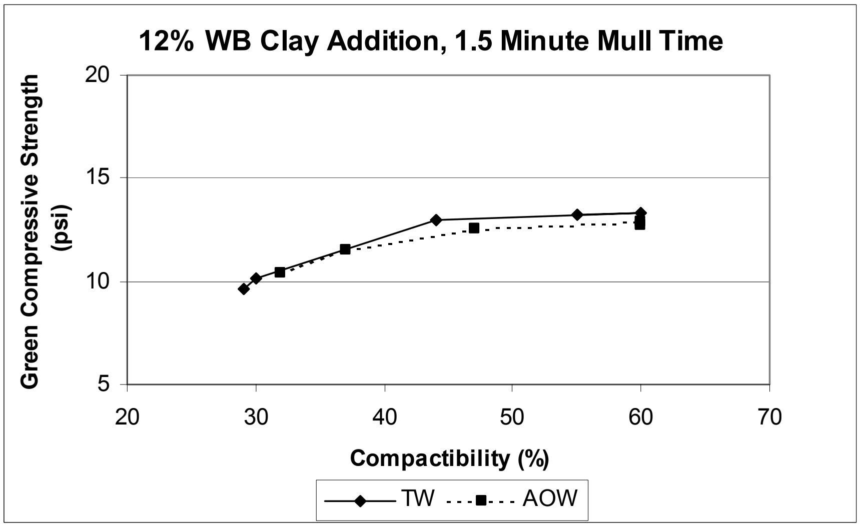


Figure 3.4-9: 12% WB GCS vs. compactibility, 1.5 minute mull.

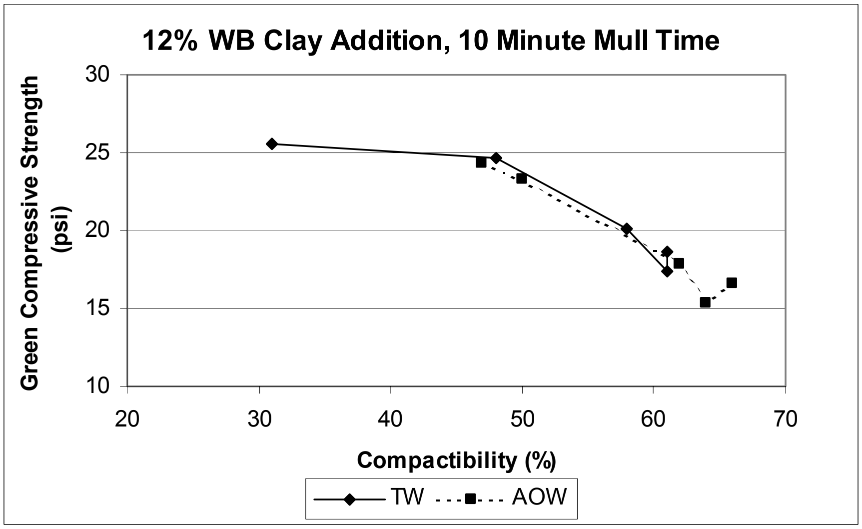


Figure 3.4-10: 12% WB GCS vs. compactibility, 10 minute mull.

Similar new sand trials with 8% western bentonite were run. Though the results from the 12% WB trials showed no significant AO effect, it was necessary to confirm these results on synthetic green sands with 8% WB. Figures 3.4-11 and 3.4-12 show the green compressive strength and compactibility mull-down curves for the 8% WB new sands at a moisture level much lower than used for the 12% WB mull-down trials.

The low moisture levels for these tests (2.0%) prevented uniform distribution and the test-to-test variability was high. Testable samples could not be obtained for tap water tests after 1 minute of mulling. The AO-processed water samples, however, were testable at these short mulling times. Significant increases in green compressive strength and compactibility for AO samples were observed at these low clay and moisture levels. Figures 3.4-13 and 3.4-14 show the mulling behavior for green compressive strength and compactibility at higher moisture (2.5%) target levels.

The development of green compressive strength and compactibility in the higher moisture tests was similar for the tap and the AO-processed waters, indicating that AO water again did not enhance the mulling properties for synthetic sands with new clays. Initially, slightly enhanced properties were observed at short mulling times for the AO water tests. However, after 3 minutes of mulling the compactibility and GCS for both AO and tap water appear to be very similar.

Additional mull-downs of 8% WB sands at even higher (2.8%) moisture (not shown in this report) showed similar results to the 8% WB 2.5% moisture sands. Initially, GCS and compactibility were somewhat greater for AO water green sands, but by the 5 minute mull time both properties had converged to that found with tap water.

Once again, temper curves after 1.5 and 10 minute mulling times were developed for the 8% MB clay sands from the data obtained during the mull-down trials. The results are shown in Figures 3.4-15 through 3.4-20.

The temper curves for 8% WB are very similar to the 12% WB temper curves. As with the 12% WB temper curves, the 8% temper curves also indicated that the AO-processed water did not enhance the properties of the synthetic green sand mixtures to any statistical significance after a certain amount of mull time. However, as shown in Figure 3.4-20, enhanced GCS was observed at low compactibility values for AO-treated synthetic sand mixtures.

Tests to generate mull-down and temper curves similar to those performed on the new sands were performed on production green sands. Green sand from an AO water molding line was obtained from Neenah Foundry Plant 3, which was (and is currently) operating an AO clean water (AO-CW) system. The purpose of this set of testing was to determine if any property enhancement took place when sand that had previously been treated with AO was tested in the laboratory after tap water or AO water additions.

In Figure 3.4-21, it can be seen that the green compressive strength for the tap water and AO-processed water re-moisturized green sands were very similar for all mulling times. This was confirmed by a statistical analysis of variance. Similarly, the compactibilities were also statistically similar, as shown in Figure 3.4-22. However, similar to that for the new sands, AO-treated samples could be prepared for testing at short mulling times (< 30 sec), but tap water treated samples could not.

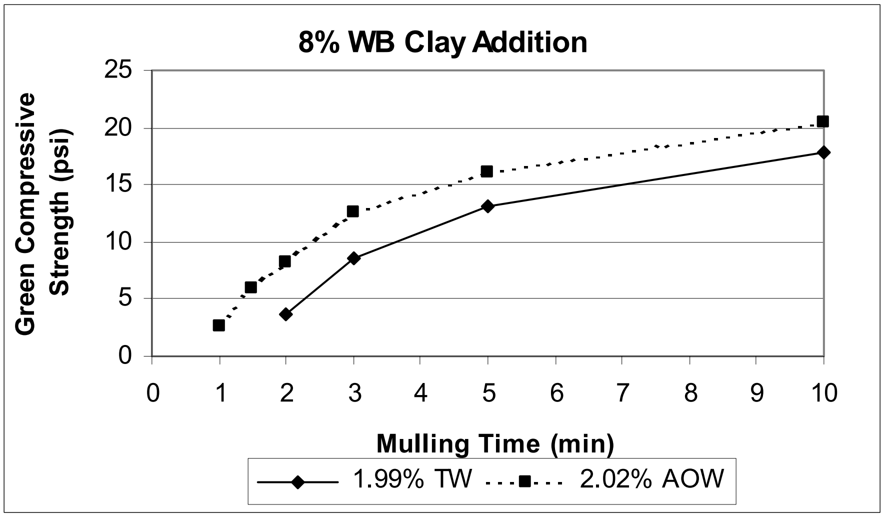


Figure 3.4-11: GCS mull-down behavior – 8% WB, 2.0% target moisture.

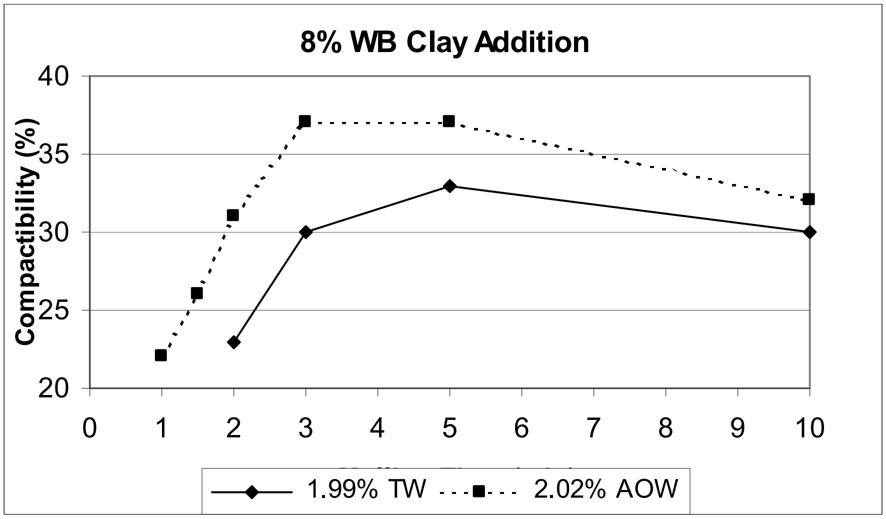


Figure 3.4-12: Compactibility mull-down behavior – 8% WB, 2.0% target moisture.

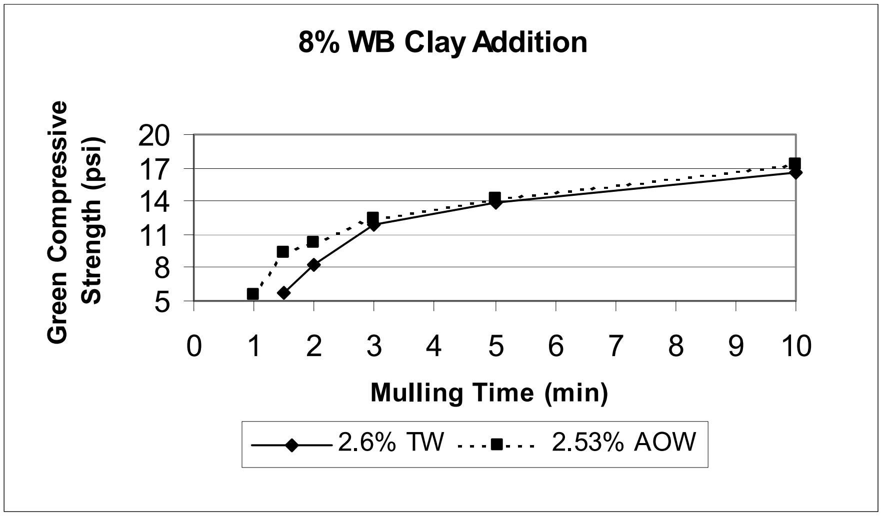


Figure 3.4-13: GCS mull-down behavior – 8% WB, 2.5% target moisture.

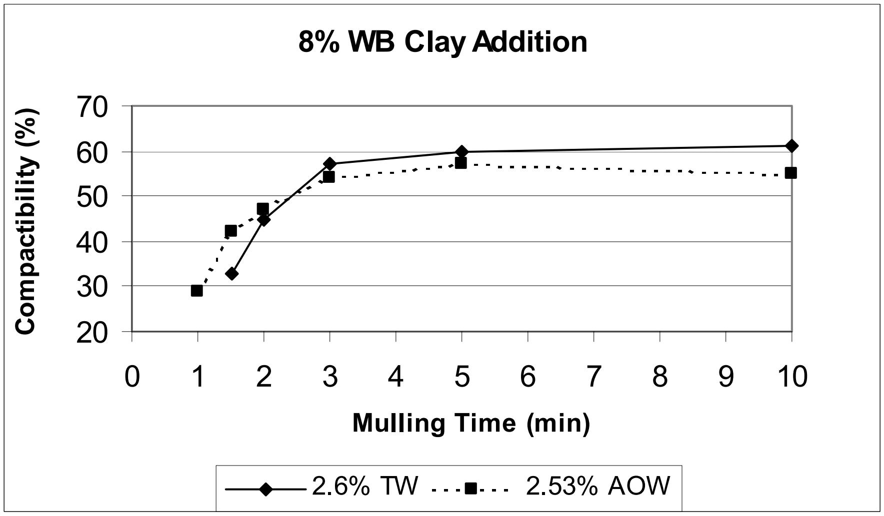


Figure 3.4-14: Compactibility mull-down behavior – 8% WB, 2.5% target moisture.

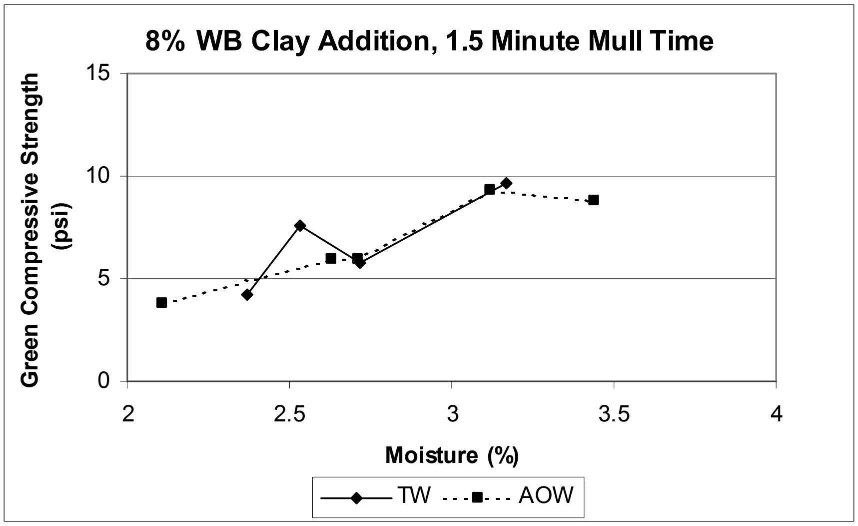


Figure 3.4-15: 8%WB GCS temper curve, 1.5 minute mull.

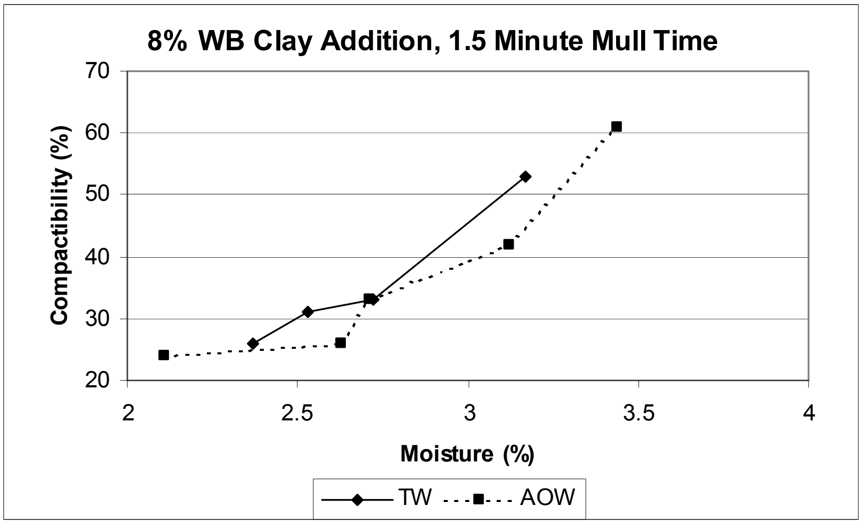


Figure 3.4-16: 8% WB compactibility temper curve, 1.5 minute mull.

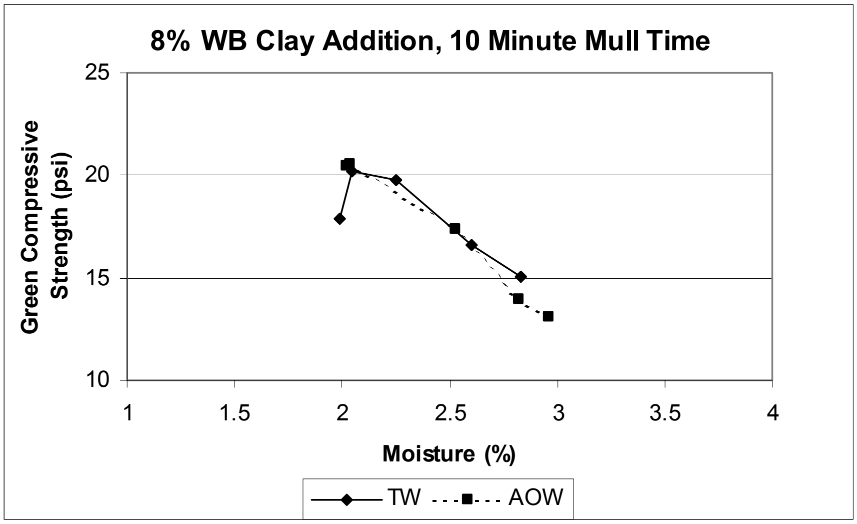


Figure 3.4-17: 8% WB GCS temper curve, 10 minute mull.

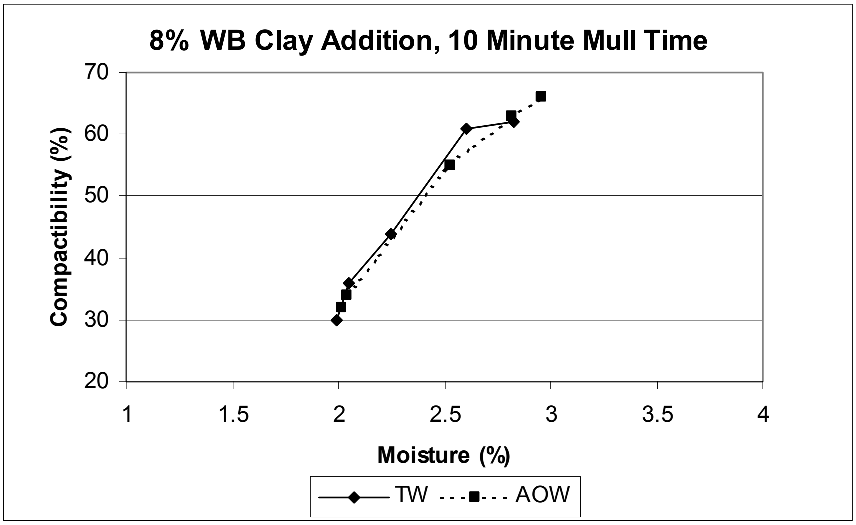


Figure 3.4-18: 8% WB compactibility temper curve, 10 minute mull.

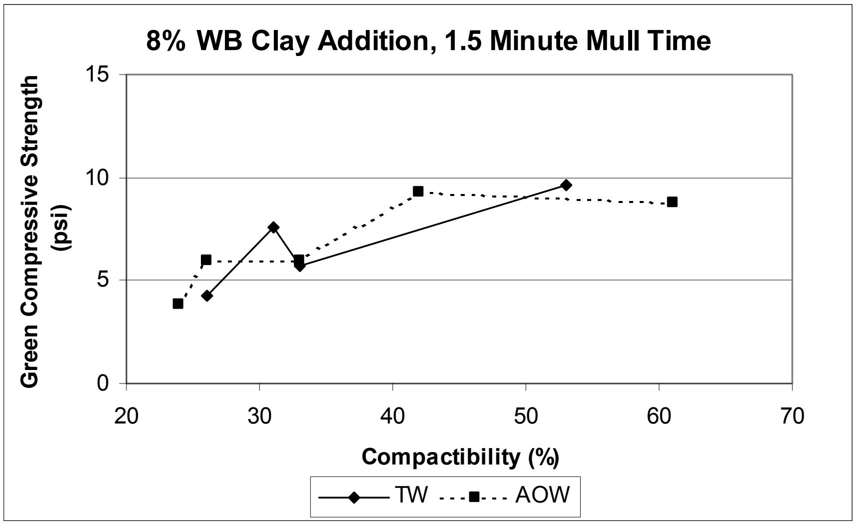


Figure 3.4-19: 8% WB GCS vs. compactibility, 1.5 minute mull.

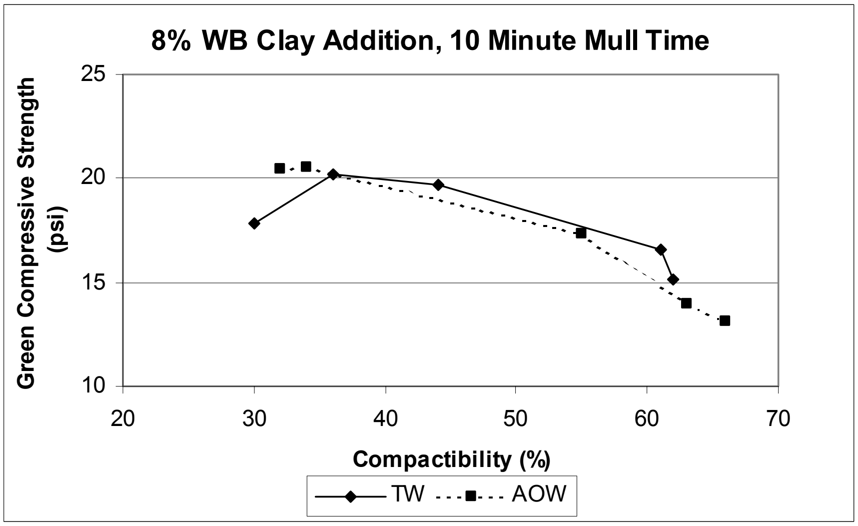


Figure 3.4-20: 8% WB GCS vs. compactibility, 10 minute mull.

Production green sands that were not previously treated with AO were similarly tested. Tests were run on Neenah Foundry Plant 2 sand that at the time had not been exposed to AO processing (AO processing has since commenced at the plant). The results are shown in Figures 3.4-23 and 3.4-24. The green compressive strengths of the tap water AO water re-moisturized green sands did not differ significantly after 3 minutes of mulling; however, as seen in Figure 3.4-24, the AO water re-moisturized sand experienced a 20% increase in compactibility for all mulling times.

Similar results were found using Wheland Foundry sand that had not been processed with AO, as shown in Figures 3.4-25 and 3.4-26. As with the Neenah sand, there was not a statistically significant difference between the green compressive strength of the tap and the AO water re-moisturized sands for any mulling times. However, again significant increases were found in the compactibility for AO water re-moisturized sands. For the AO-processed water additions, the compactibility reached its maximum after 1.5 minutes of mulling and then leveled off. For the tap water additions, the compactibility did not level off until after 2 minutes of mulling. AO-processed water allowed the Wheland non-AO production sand mixture to reach its maximum compactibility with less mulling time.

Figures 3.4-27 and 3.4-28 show the results of additional tests performed using Wheland Foundry production sand at higher (3.7%) moisture levels. The green compressive strength was not significantly different between the tap and AO water re-moisturized sands except at 1 minute. While the compactibility difference in means was significant after 1 minute, the 20% shift in compactibility previously observed was not observed in this particular case. This indicated that at higher moisture levels (outside the percent moisture operating range for this foundry) the AO and tap water re-moisturized sands behave more similarly.

The data from the production sand mull-down curves were also used to develop partial temper curves. Figures 3.4-29 and 3.4-30 are compactibility and green compressive strength temper curves after 1.5 minutes of mulling. Figures 3.4-31 and 3.4-32 are similar plots after 5 minutes of mulling.

The sand property changes observed for these laboratory tests must be interpreted with respect to the corresponding effects of AO observed in production sand systems, which are discussed in Chapter 3.5.

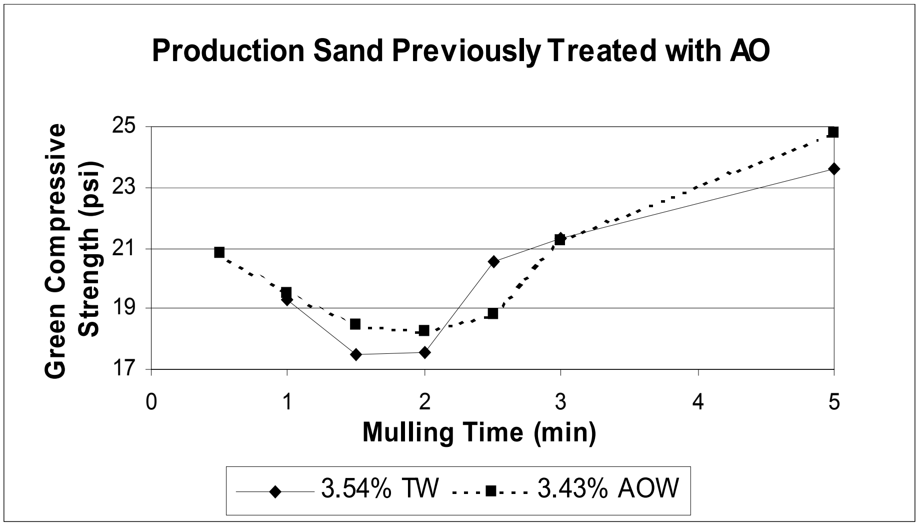


Figure 3.4-21: GCS mull-down behavior of production sand from a Neenah AO-CW treated molding line, re-moisturized to 3.5%.

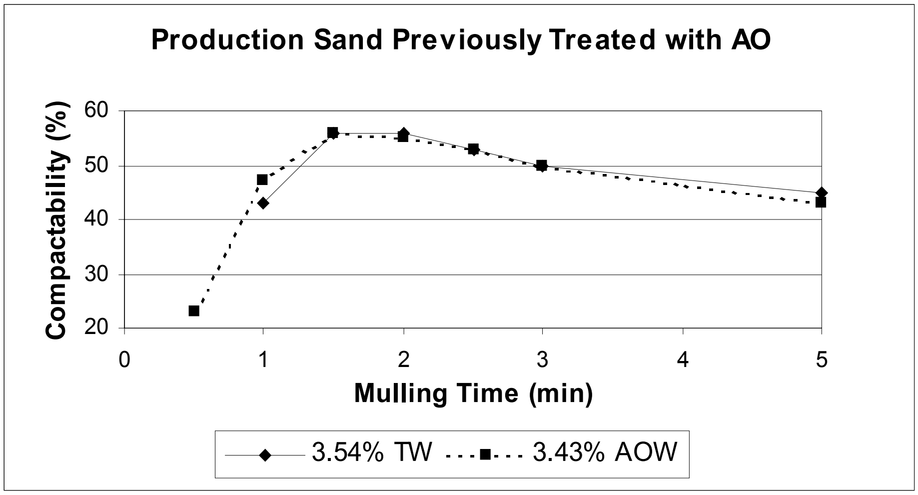


Figure 3.4-22: Compactibility mull-down behavior of production sand from a Neenah AO-CW treated molding line, re-moisturized to 3.5%.

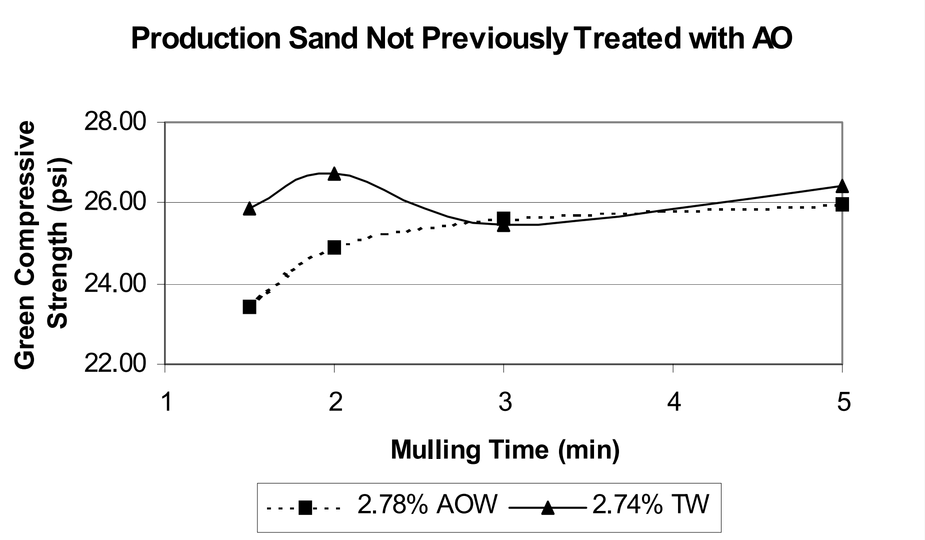


**Figure 3.4-23: GCS mull-down behavior of production sand from a Neenah non-AO treated molding line, re-moisturized to 2.7%.**

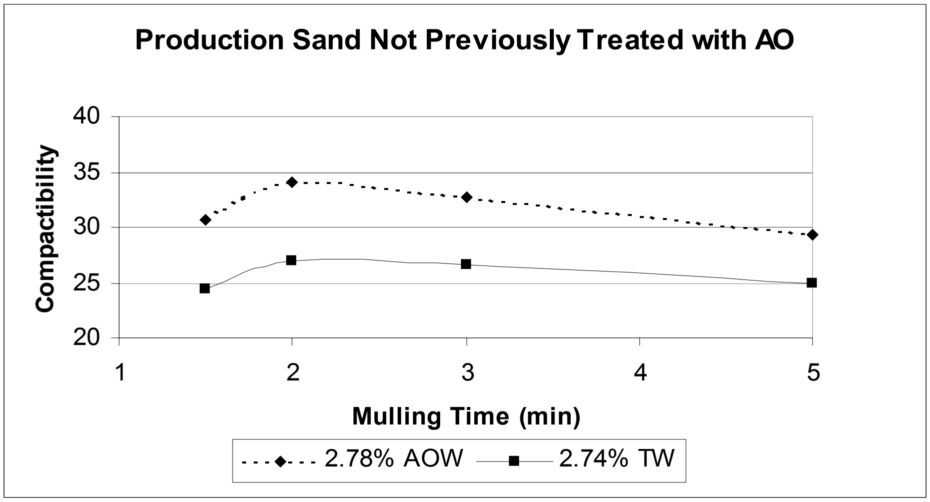


**Figure 3.4-24: Compactibility mull-down behavior of production sand from a Neenah non-AO treated molding line, re-moisturized to 2.7%.**

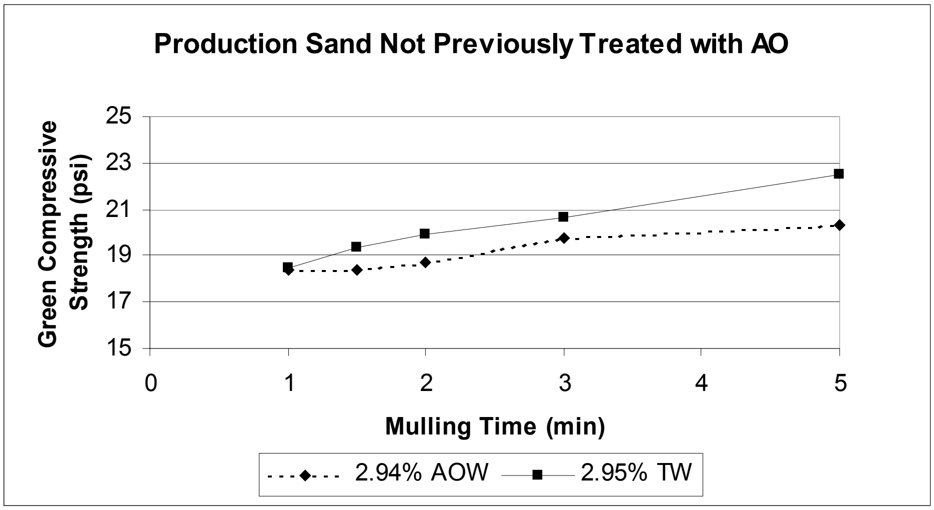


Figure 3.4-25: GCS mull-down behavior of production sand from a Wheland non-AO treated molding line, re-moisturized to 2.9%.

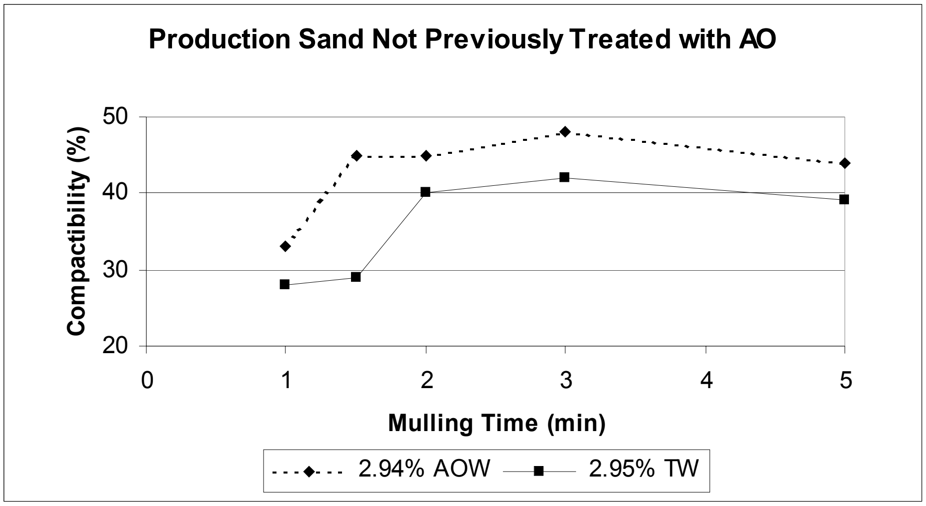


Figure 3.4-26: Compactibility mull-down behavior of production sand from a Wheland non-AO treated molding line, re-moisturized to 2.9%.

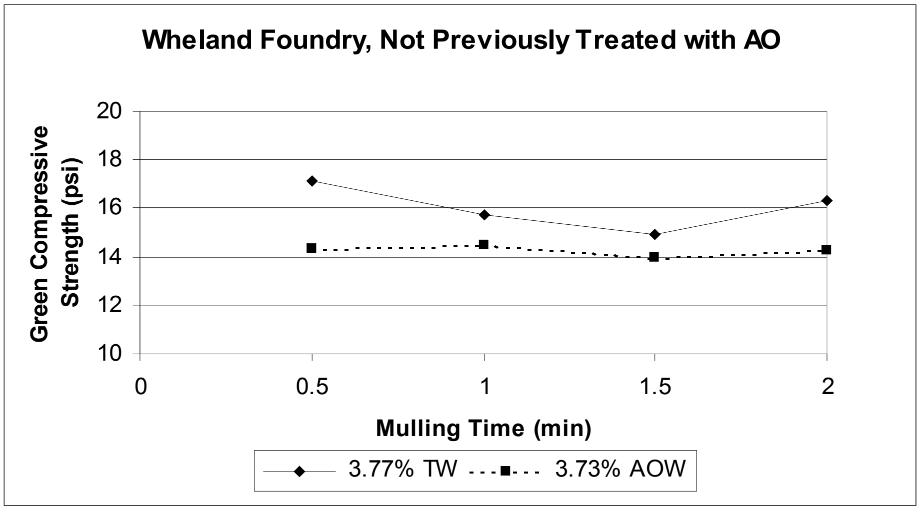


**Figure 3.4-27: GCS mull-down behavior of production sand from a Wheland non-AO treated molding line, re-moisturized to 3.7%.**

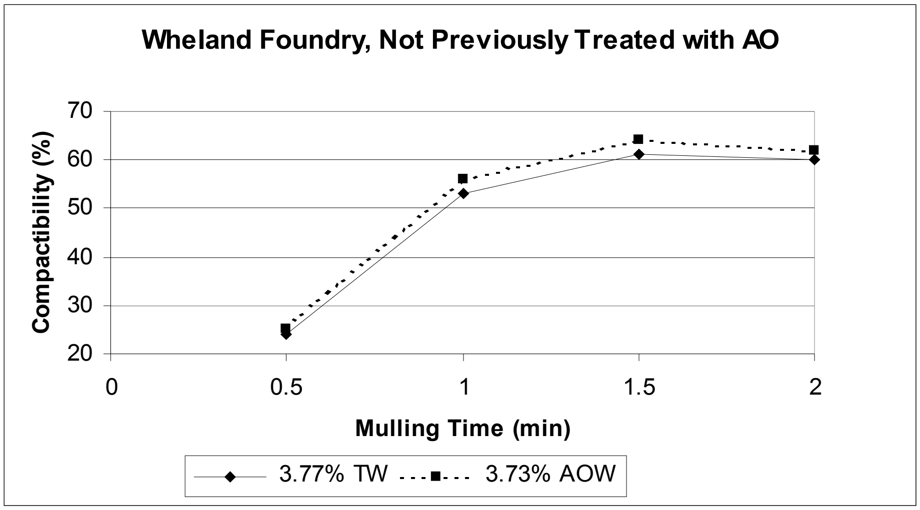


**Figure 3.4-28: Compactibility mull-down behavior of production sand from a Wheland non-AO treated molding line, re-moisturized to 3.7%.**

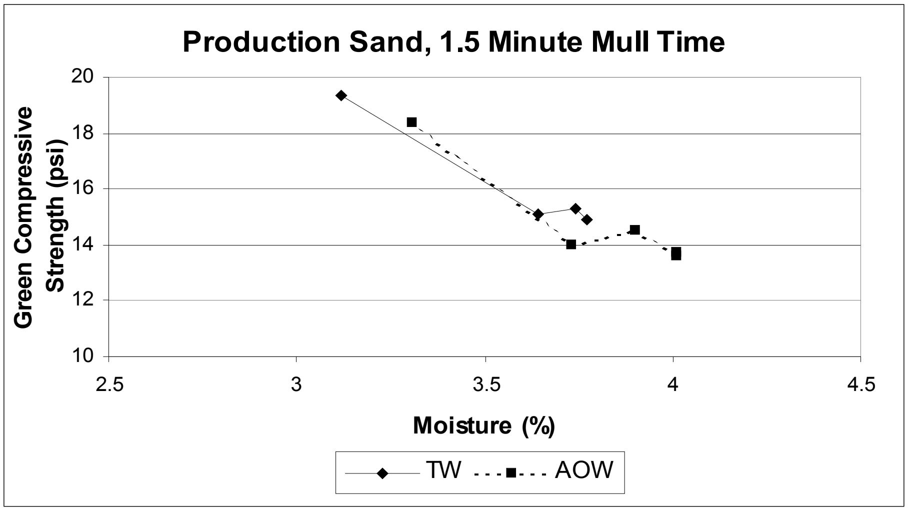


Figure 3.4-29: Production sand GCS temper curve, 1.5 minute mull.

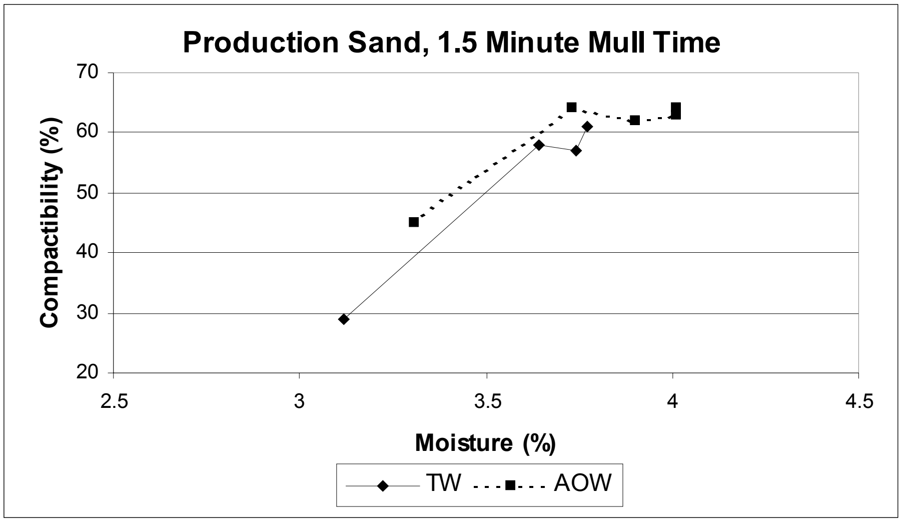


Figure 3.4-30: Production sand compactibility temper curve, 1.5 minute mull.

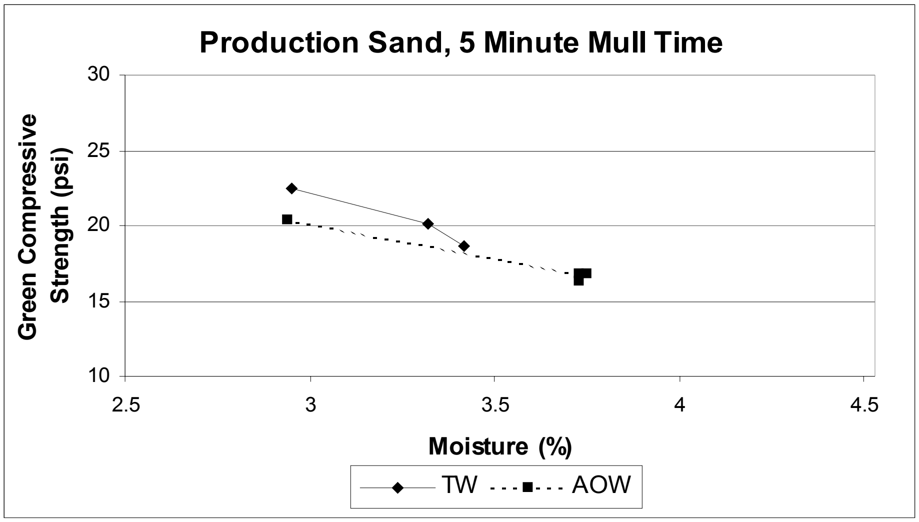


Figure 3.4-31: Production sand GCS temper curve, 5 minute mull.

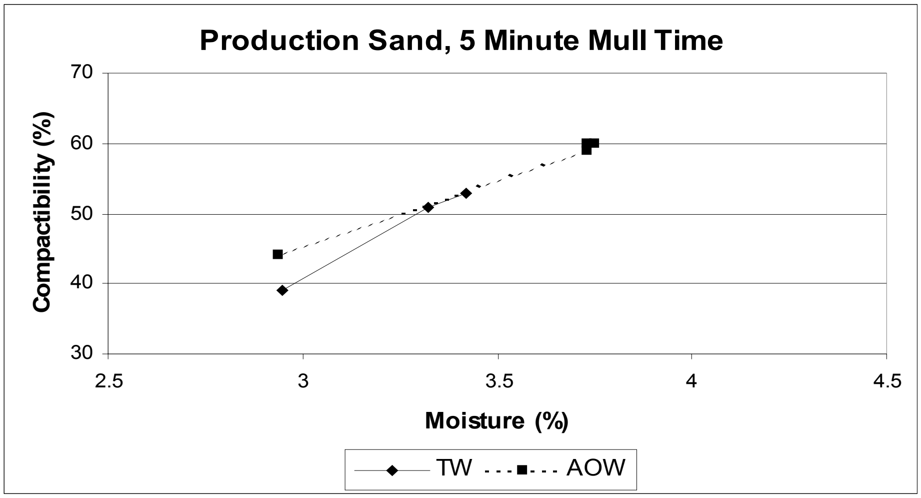


Figure 3.4-32: Production sand compactibility temper curve, 5 minute mull.

### 3.4.1.4 Summary of AO-CW Mulling Trials

Laboratory muller trials at ambient temperature using a single treatment of AO water or tap water on both synthetic sands and foundry system sands can be summarized as follows:

- Synthetic green sands did not show any property changes with the addition of AO water.
- Production green sands previously treated with AO did not show any effects of AO re-moisturization except for short mull times, where strength and compactibility developed more quickly for AO sands than non-AO.
- Production sands not previously treated with AO did show a 20% increase in compactibility when treated with AO; GCS was not affected.

## 3.4.2 AO-Clean Water Cycling Trials

### 3.4.2.1 Introduction

Previous AO-CW laboratory trials employed only a single mulling and AO addition cycle before sand property changes were assessed. These laboratory trials did not mimic the repeated cycling of the sand that occurs in foundries nor did they mimic the temperatures typically seen by the bulk green sand. Laboratory mull-down cycling trials were conducted to evaluate the influence of repeated AO and tap water cycles on the performance of a production non-AO green sand. Emphasis was placed on short mulling cycles that are more typical of production mulling. These tests were performed using the same laboratory muller and mulling protocols used in previous single cycle tests. The non-AO production sand used in this trial, however, was different than the non-AO production sands used in previous trials.

### 3.4.2.2 Results and Discussion

Two sand batches were hydrated, one with tap water and the other with AO water, to target 3.9% moisture (moisture-clay ratio = 33%) and mulled for 20, 30, 40, and 60 seconds. After each mull, five GCS, three compactibility, and a moisture reading were taken. Each batch was then placed in a 350°C oven and dried for 30 minutes. The batches were then re-hydrated, mulled, and tested again through 5 additional cycles. Through the course of the experiment the only difference between the batches was that one batch was always re-hydrated with AO water ($O_3$ saturation, 150 ppm $H_2O_2$, sonication) and the other with tap water. The green sand was foundry production sand from a company other than those described in section 3.4.1. The green sand properties were as follows: 5.72% LOI, 10.15% MB clay, AFS grain fineness of 66.5, and 16.6 AFS clay.

Table 3.4-5 shows the testing matrix evaluated as well as the average GCS and compactibility response. Figures 3.4-33 to 3.4-36 illustrate the changes in compactibility and green compressive strength as a function of the mulling time for cycles one, three, and six. Results were analyzed for statistical significance using conventional analysis of variance (ANOVA) techniques. The percent moisture was included in the ANOVA analysis as a covariant factor to account for its natural and uncontrollable variability. Tables 3.4-6 and 3.4-7 summarize the ANOVA results.

The cycling test results show that AO additions significantly increase compactibility, but do not directly affect green compressive strength. The changes in compactibility increased with multiple cycles of AO treatment. This is not observed for tap water treatments. These behaviors were observed at all mulling times used in this study.

For a typical compactibility-controlled sand system at a constant clay level, the net influence of AO-CW additions as observed from these multiple-cycle trials would be to drive the sand system set points to higher moisture and thereby alter the green compressive strength. The AO processing in this experiment decreased the compactibility. To compensate, a foundry would have to raise the moisture content of the green sand to keep compactibility constant (see Figure 3.4-18, for example). (It should be noted that these same effects are not necessarily what have been observed at the foundries that employ AO-CW.) It is not straightforward what effect the increased moisture content would have on the green compressive strength, as GCS for compactibilities less than about 50% increases with moisture, reaches a maximum, then decreases as moisture is increased in the sand system (Heine, *et al*., 1993). Most foundries operate near that maximum. Therefore, GCS may either increase or decrease upon application of AO.

The results obtained from these multiple-cycle trials seem to contradict the results found by the single-cycle tests on the non-AO production sand described in section 3.4.1. It is not apparent why the compactibility increased significantly for non-AO production sand with only one application of AO, yet decreased from application of AO water in the multiple-cycle trials. The test conditions were not exactly the same, but it can be reasoned that the multiple-cycle tests rather than single-cycle tests should better mimic production sand system results. However, variables such as different green sands used between the tests, different moisture, moisture/clay ratios, and mull times (typically shorter for the multiple cycle trials) confound the situation. Figures 3.4-24 (2.7% moisture Neenah sand), 3.4-26 (2.9% moisture Wheland sand), and 3.4-28 (3.7% Wheland sand) show the compactibility response for the non-AO single-cycle production sands. Figures 3.4-33 and 3.4-34 show the compactibility response for the multiple-cycle trials. It may be coincidental, but the Wheland 3.7% moisture sand (Figure 3.4-28) did not show as large of a compactibility percentage increase as did the other two lower

### Table 3.4-5: Experimental data for six-cycle production sand trials.

| Treatment | Cycle | Mull Time (sec) | Ave Comp. | Ave GCS | % Moisture |
|---|---|---|---|---|---|
| AO | 1 | 20 | 20 | 12.8 | - |
| AO | 1 | 30 | 28 | 16.1 | 3.71 |
| AO | 1 | 40 | 37 | 18.0 | 3.69 |
| AO | 1 | 60 | 43 | 21.0 | 3.62 |
| AO | 2 | 20 | 18 | 14.3 | - |
| AO | 2 | 30 | 24 | 18.4 | 4.43 |
| AO | 2 | 40 | 30 | 20.6 | 3.72 |
| AO | 2 | 60 | 37 | 20.6 | 3.72 |
| AO | 3 | 20 | 24 | 12.8 | - |
| AO | 3 | 30 | 25 | 18.8 | 3.83 |
| AO | 3 | 40 | 31 | 19.7 | 3.64 |
| AO | 3 | 60 | 38 | 21.3 | 3.52 |
| AO | 4 | 20 | 23 | 13.3 | - |
| AO | 4 | 30 | 30 | 18.7 | 3.93 |
| AO | 4 | 40 | 36 | 20.1 | 3.46 |
| AO | 4 | 60 | 39 | 22.1 | 3.48 |
| AO | 5 | 20 | 22 | 16.7 | - |
| AO | 5 | 30 | 31 | 19.7 | 3.96 |
| AO | 5 | 40 | 39 | 20.7 | 3.75 |
| AO | 5 | 60 | 42 | 22 | 3.69 |
| AO | 6 | 20 | 18 | 12.5 | - |
| AO | 6 | 30 | 20 | 17.0 | 5.54 |
| AO | 6 | 40 | 28 | 19.9 | 2.84 |
| AO | 6 | 60 | 32 | 21.4 | 3.69 |
| Tap | 1 | 20 | 22 | 12.5 | - |
| Tap | 1 | 30 | 30 | 15.9 | 3.57 |
| Tap | 1 | 40 | 36 | 18.1 | 3.72 |
| Tap | 1 | 60 | 43 | 20.4 | 3.62 |
| Tap | 2 | 20 | 19 | 15.0 | - |
| Tap | 2 | 30 | 25 | 19.0 | 4.32 |
| Tap | 2 | 40 | 33 | 20.0 | 3.41 |
| Tap | 2 | 60 | 40 | 21.0 | 3.6 |
| Tap | 3 | 20 | 21 | 14.4 | - |
| Tap | 3 | 30 | 30 | 18.0 | 3.89 |
| Tap | 3 | 40 | 39 | 20.4 | 3.68 |
| Tap | 3 | 60 | 43 | 21.4 | 3.53 |
| Tap | 4 | 20 | 24 | 13.1 | - |
| Tap | 4 | 30 | 28 | 17.1 | 3.85 |
| Tap | 4 | 40 | 37 | 19.4 | 3.58 |
| Tap | 4 | 60 | 43 | 20.9 | 3.62 |
| Tap | 5 | 20 | 22 | 15.2 | - |
| Tap | 5 | 30 | 34 | 19.0 | 3.83 |
| Tap | 5 | 40 | 45 | 18.9 | 3.6 |
| Tap | 5 | 60 | 47 | 21.3 | 3.77 |
| Tap | 6 | 20 | 25 | 14.7 | - |
| Tap | 6 | 30 | 36 | 19.2 | 3.84 |
| Tap | 6 | 40 | 41 | 21.1 | 3.19 |
| Tap | 6 | 60 | 43 | 22.1 | 3.4 |

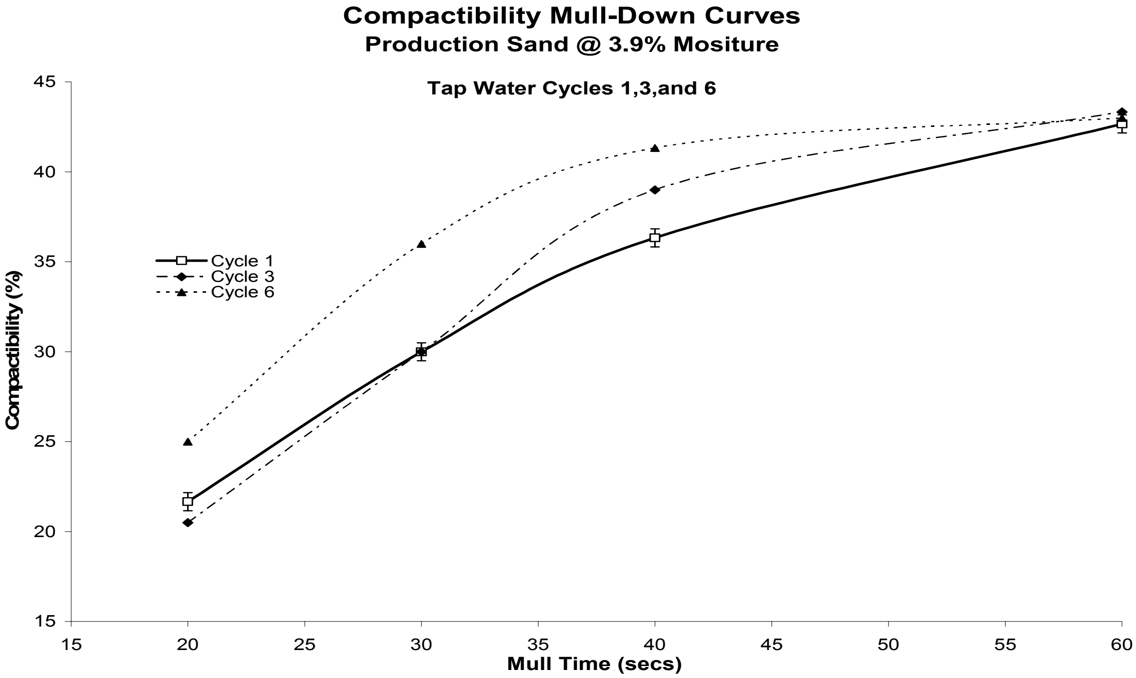


Figure 3.4-33: Compactibility response after 1, 3 and 6 cycles of TAP treatment.

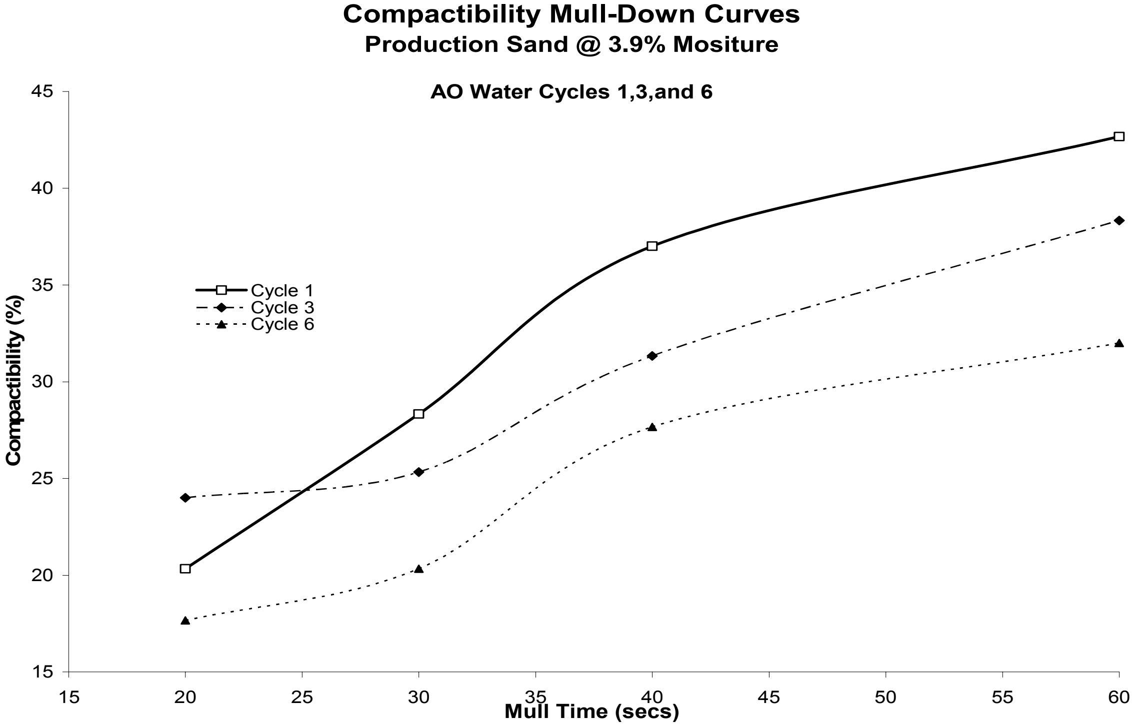


Figure 3.4-34: Compactibility response after 1, 3 and 6 cycles of AO treatment.

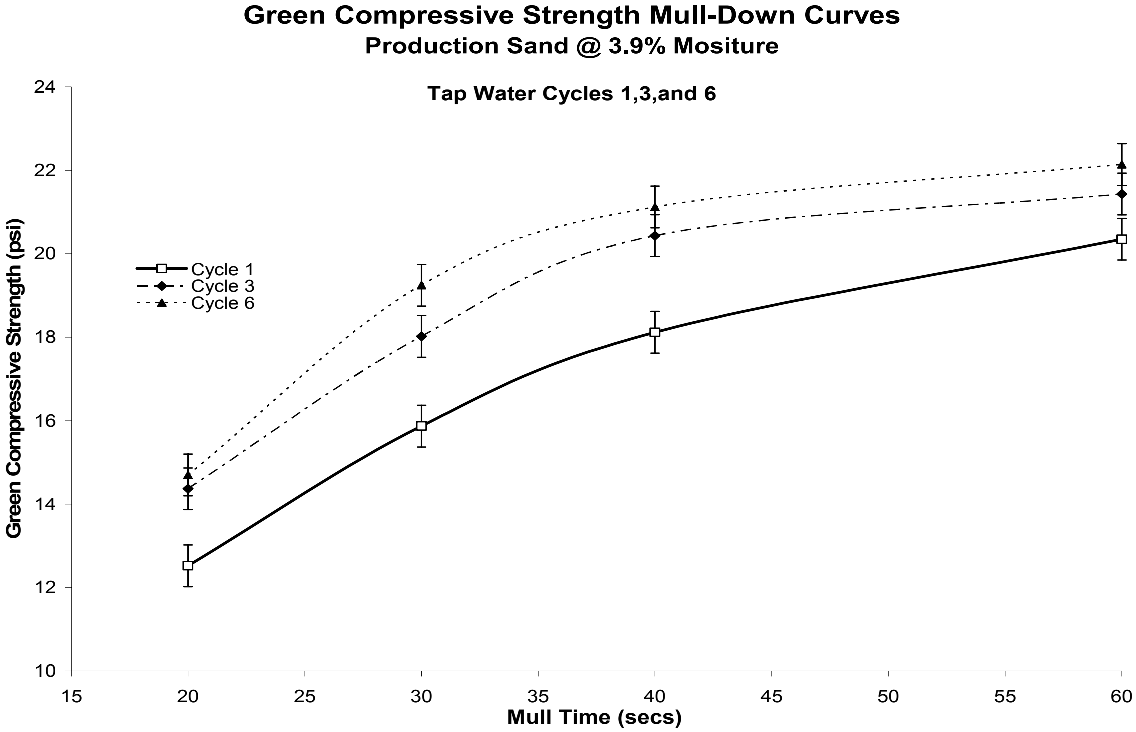


Figure 3.4-35: GCS response after 1, 3, and 6 cycles of TAP treatment.

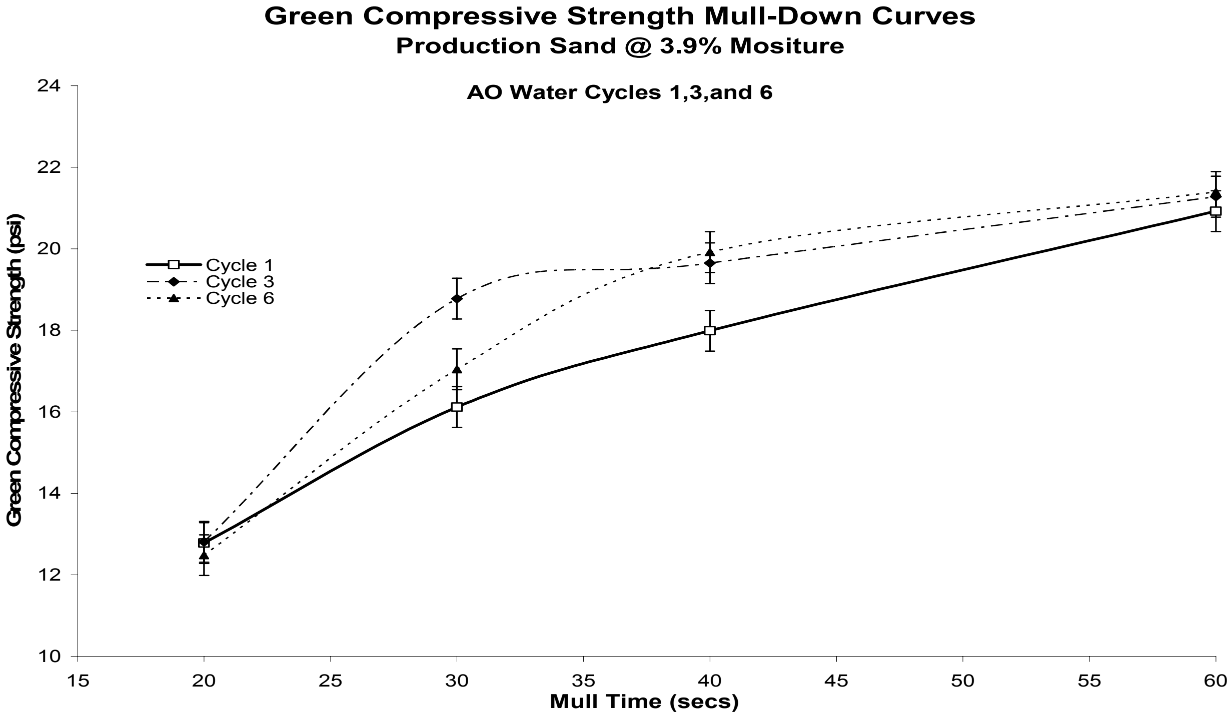


Figure 3.4-36: GCS response after 1, 3, and 6 cycles of AO treatment.

**Table 3.4-6: ANOVA table of the compactibility response.**

| Factor: | DF | SS | Adj SS | Adj MS | F | P |
|---|---|---|---|---|---|---|
| Moisture | 1 | 425.185 | 3.573 | 3.573 | 2.23 | 0.169 |
| **AO Treatment** | **1** | **116.603** | **148.649** | **148.649** | **6.57** | **0.051** |
| **Time** | **2** | **581.629** | **412.876** | **206.438** | **136.70** | **0.000** |
| AO Treat*Time | 2 | 4.433 | 2.955 | 1.478 | 0.92 | 0.432 |
| Cycle | 5 | 223.164 | 220.501 | 44.100 | 1.77 | 0.274 |
| **AOTreat*Cyc** | **5** | **160.178** | **122.098** | **24.420** | **15.27** | **0.000** |
| Time*Cycle | 10 | 26.844 | 26.844 | 2.684 | 1.68 | 0.224 |
| Error | 9 | 14.394 | 14.394 | 1.599 | | |
| Total | 35 | 1552.431 | | | | |

*** Bold type indicates significance to the 95% confidence level.**

**Table 3.4-7: ANOVA table of the green compressive strength response.**

| Factor: | DF | SS | Adj SS | Adj MS | F | P |
|---|---|---|---|---|---|---|
| Moisture | 1 | 17.3686 | 0.2186 | 0.2186 | 0.99 | 0.346 |
| AO Treatment | 1 | 1.2664 | 0.3846 | 0.3846 | 0.57 | 0.504 |
| **Time** | **2** | **44.1482** | **32.1126** | **16.0563** | **228.99** | **0.000** |
| AO Treat*Time | 2 | 0.0208 | 0.0299 | 0.0149 | 0.07 | 0.935 |
| Cycle | 5 | 17.7215 | 16.6255 | 3.3251 | 3.55 | 0.097 |
| **AOTreat*Cyc** | **5** | **5.5609** | **4.6068** | **0.9214** | **4.16** | **0.031** |
| Time*Cycle | 10 | 5.7564 | 5.7564 | 0.5756 | 2.60 | 0.083 |
| Error | 9 | 1.9909 | 1.9909 | 0.2212 | | |
| Total | 35 | 93.8336 | | | | |

*** Bold type indicates significance to the 95% confidence level**

moisture sands (however, the increase was statistically significant). The 3.7% moisture of this sand was more comparable to the 3.9% moisture of the multiple-cycle sand. It may be that the moisture content of the sand has a large effect on whether AO increases or decreases compactibility.

### 3.4.2.3 Summary of AO-CW cycling trials.

- The primary effect observed by cycling green sand through AO treatment and exposure to 350°C for 30 minutes is to decrease compactibility. The green compressive strength was not shown to be significantly affected by AO.
- Compactibility decreases due to AO became more significant as the number of cycles increased.

## 3.5 SAND SYSTEM PERFORMANCE – PLANT TRIALS

### 3.5.1 AO-BW System – Wheland Foundry

#### 3.5.1.1 Introduction

The green sand system performance for Wheland Foundry's Middlestreet Plant was compared before and after the installation of an AO system. Wheland Foundry incorporated AO processing into their existing blackwater wet scrubber system. AO (ozone, peroxide and sonication) was introduced directly into the blackwater clarifier.

Some of the AO-treated black water effluent transfers to the sand cooler. Another portion of the AO-treated black water effluent is introduced into the muller along with re-circulated green sand and virgin make-up sand and premix. A fraction of the green sand is disposed to maintain the core/sand balance while the majority returns to the sand system. The exhaust air from the mold cooling, shakeout and the green sand preparation and return areas vents to a dust collection system that captures fine particulates, and these fine particulates are pneumatically conveyed to a wet scrubber or bag house dust collector. This cycle repeats itself with continuing rounds of mulling, molding, pouring, shakeout, particle venting, AO-clarifier segregation of clays, and reuse of clays from the black water system.

Wheland commenced operation of an AO system in May-July, 1997 on their vertical parting molding line pouring an average of 550 tons of ductile iron per day during the time period studied. The foundry dust is collected via wet dust collectors, and the resulting slurry passes through an ultrasonic field before entering a clarifier. The clarifier water receives 150 ppm hydrogen peroxide and a near-saturation level of ozone. Effluent black water flows to a continuous muller and sand cooler. Mulled green sand supplies two vertical parting line molding machines. Sand property data has been collected for quality control over three years: one year prior to AO, and two years with AO. The sand properties and the successive changes due to the AO system have been examined.

#### 3.5.1.2 Results and Discussion

*(This section has been adapted from the paper by Neill, Cannon, Voigt, Furness, and Bigge, 2001.)*

Green sand properties at Wheland Foundry before and after AO system installation are displayed in Table 3.5-1 and Figures 3.5-1 to 3.5-7). From June, 1996 through April 14, 1997, a number of non-AO sand optimization strategies were implemented, improving green sand properties somewhat. On April 15, 1997, the advanced oxidation system commenced operation. This was followed by a two-month stabilization and learning period, during which the green sand system was adjusting to AO conditions. This period offers some useful information regarding how AO influenced green sand properties. It should be noted that from April 15, 1997 to May 15, 1997, the green compressive strength was reading false-low values (this was unknown to the foundry personnel). The July, 1997 though September, 1999 time frame reflects a time when the green sand system was becoming optimized with respect to the advanced oxidation process. It should be noted that the proportion of heavily cored jobs and thus, core sand added to the system, diminished slightly starting in April, 1998.

There are several useful comparisons that could be gleaned from the data. One such is how the non-AO optimized sand system (October, 1996 to March, 1997) compared with the AO-optimized sand system (April to September, 1999). When comparing the non-AO optimized system to the with-AO optimized system, one observes from Table 3.5-1 (last column) that green compressive strength improved 9%, from 28 psi to 30-31 psi while the compactibility remained the same (a compactibility-controlled system). Premix declined from 147 to 108 lb/ton of metal poured (down 27%), and total new sand declined from 520 to 325 lb/ton of metal poured (down 37%). Moreover, total scrap rate declined 34%, and sand-related scrap rate declined 19%, while available clay increased 13%, working clay increased 9%, and muller efficiency increased 5%. The change in premix rates was statistically significant at the 95% confidence level, and the change in total new sand addition was statistically significant at the 85% confidence level. In comparison, the changes in green compressive strength, total scrap, and sand-related scrap were not significant to the 85% confidence levels. The decrease in total new sand per ton of metal poured was statistically significant to the 95% confidence level, if the July, 1999 value (excessively high) is not included. The July, 1999 value was high because one molding line was down, causing an unusual balance between sand and metal.

Another useful comparison is to appraise how green sand properties changed while AO optimization progressed, which represented a learning curve for the new process. These trends are discerned by comparing the initially stabilized AO system of July-August, 1997 to the AO-optimized system of summer, 1999. During the span of this time, the foundry personnel recognized that acceptable levels for green compressive strength and other properties could be achieved with less material additions. Thus, during this time period green compressive strength decreased from a higher-than-needed 31-32 psi to 31-30 psi and muller efficiency decreased from a higher-than-needed 68% to 65%. Premix declined from 120 to 108 lb/ton of metal poured, total new sand additions (core plus non-core) declined from 400 to 300 lb/ton of metal poured, methylene blue (MB) clay rose from 8.6 to 9.4 and loss on ignition (LOI) rose from 2.8 to 3.2% (see Table 3.5-1 and Figures 3.5-1 to 3.5-7). It should be noted that at least part of the sand addition drop could be attributed to a slight decline in heavily cored jobs and, therefore core sand after April, 1998. Consequently, this core sand decline could have resulted in a gradual decline in premix additions.

Figures 3.5-1 to 3.5-7 reflect either daily averages of process data or monthly inventory values. The daily average values represent the averages of multiple tests taken

**Table 3.5-1: Sand system performance for Wheland Foundry – Middlestreet Plant before and after AO system installations.**

| Parameter | Before AO (6/14/96 to 4/14/97) | After AO Stabilization (6/16/97-9/30/99) | % Change (No AO vs. AO) |
|---|---|---|---|
| Green Compressive Strength (psi) | 24 up to 28.0* | 31.6 down to 30.4* | +9[1] |
| Compactibility (%) | 37-38 | 39-40 | - |
| Premix (lb/ton of metal poured) | 142 up to 147 | 120 down to 108 | -27[ss] |
| Total new sand (lb/ton of metal poured) | 520 | 400 down to 300 | -37 |
| Fines <#140 mesh (%) | 4.5 up to 5.0 | 4-5, 5.2-5.7[2] | NR[2] |
| Pan Fines < #270 mesh (%) | 1.1 | 1.1, 1.3[2] | NR[2] |
| Permeability | 130 up to 134 | 132-138<br>117 down to 105 | NR[2] |
| Total Scrap Rate (relative units) | 40 down to 35 | 26 down to 23 | -34 |
| Sand Related Scrap (relative units) | 18 down to 10.5 | 8.5 | -19 |
| Moisture (%) | 3.3 | 3.3 up to 3.5 | +6 |
| Methylene Blue Clay (%) | 8.8 (set point) | 8.6 up to 9.4 | +7 |
| Moisture to MB Clay ratio (%) | 34-39 | 34-43 | - |
| Available Clay (%) | 6.8 up to 7.3 | 7.7 up to 7.8 | +13 |
| Working Clay (%) | 4.0 up to 4.7 | 5.3 down to 5.1 | +9 |
| Muller Efficiency (%) | 57 up to 62 | 68 down to 65 | +5 |
| Loss on Ignition (%) | 3.5 down to 3.3 | 2.8 up to 3.2 | - |
| Volatile Carbonaceous Material (%) | 1.5 down to 1.3 | 1.2-1.3 | - |

[*] “Up to” and “down to” designations represents trends from the initial stabilization condition to the final optimized condition during this period.

[1] The change in GCS was statistically significant after AO start-up, but was not significant after optimization of the AO sand system.

[2] Fines, pan fines, and permeability were influenced by a change in the grain fineness number (55 to 60), which occurred in Nov 97; thus the % change in these values were not inherently related to AO system.

[ss] Statistically different at the 95% confidence level

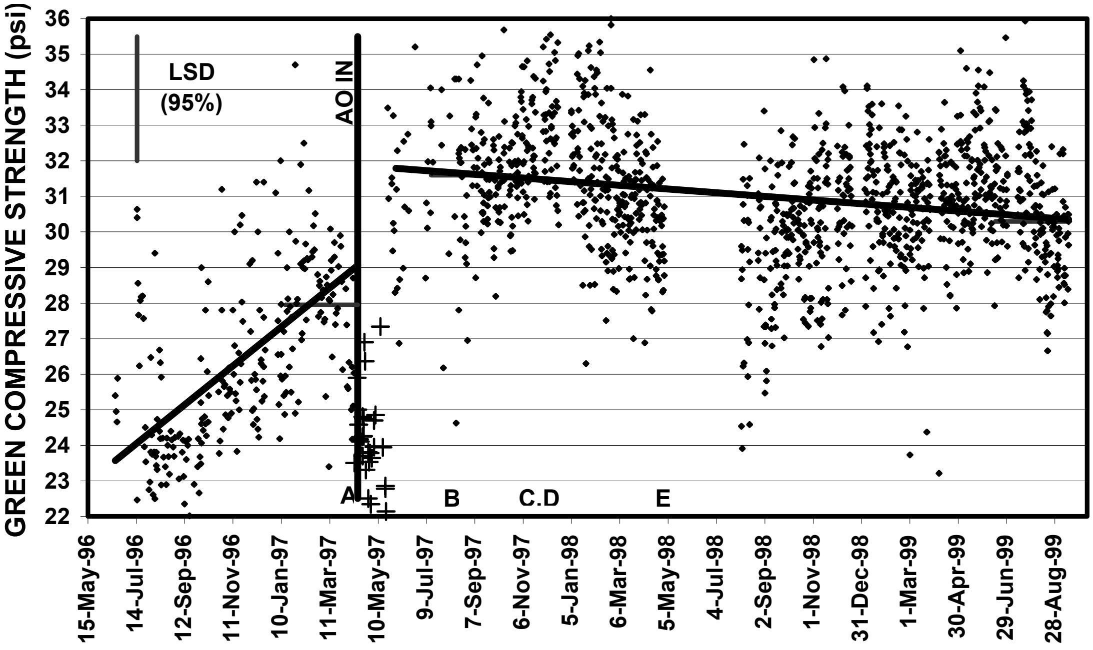
through the day, and these parameters were generally monitored every hour or every two hours. Monthly premix and sand inventories represent the total monthly amount of material used as normalized to the total monthly amount of metal poured. Fluctuations in inventory from one month to the next may represent carry-over of inventory from one month to another. The AO system was stabilizing for two months after it commenced operation. Thus, the inventory values during the transition months of April, May, and June, 1997 are not included when developing linear regressions of monthly inventories in the figures (although other useful comparisons are made with the May and June data, as discussed later. Scrap rates are presented as internally relative values (per suggestion of foundry personnel), and these values represent (a) the total relative amount of scrap generated per month or (b) what fraction of that scrap was considered sand-related scrap (see definition of sand-related scrap below). The linear regressions of the scrap data also exclude April, May, and June, 1997 in the figures. Several events, in addition to AO start-up, could have influenced some of the green sand properties, and these are listed in Table 3.5-2 and designated by letter in some of the figures.

Table 3.5-2: Significant events at Wheland Foundry during AO system start-up.

| Letter | Date | Event |
|---|---|---|
| AO IN | April 15, 1997 | AO system start up |
| A | April 15, 1997 to May 15, 1997 | GCS tester giving false low readings |
| B | August, 1997 | Premix ratio set at: 64% western, 18% southern, and 12.75% coal |
| C | November, 1997 | Grain fineness changed from 55 to 60. |
| D | November, 1997 | Premix ratio changed to 63.5% western, 17% southern, 13.75% coal |
| E | May, 1998 to August, 1998 | Labor stoppage; daily data excluded |

Green compressive strength and compactibility:

AO process start-up coincided with a significant increase in GCS as shown in Figure 3.5-1. Before AO installation, the GCS ranged from an average of 24 psi in June, 1996 to an average of 28 psi in mid-January to mid-April, 1997, and it was improving as non-AO sand optimization strategies were employed (such as increasing premix feed rate and new sand feed rate, as discussed later). AO operation commenced April 15, 1997. From April 15 to May 15, 1997, the GCS test machine read false low readings (the force was applied partly in compression and partly in shear); this data is denoted as + values on Figure 3.5-1. Once the GCS tester was repaired and accurate GCS reading were achieved, GCS values averaging 31-32 psi and as high as 40 psi were recorded. Foundries need not operate at such a high GCS, so foundry personnel decreased the premix and water feed rates which caused the GCS to drop slightly. The average GCS of 31.6 psi (mid-July to mid-October, 1997), after AO start-up and stabilization, was 13% higher than the average GCS of 28.0 psi (mid-January to mid-April, 1997) before AO start-up. These values were statistically different at the 95% confidence level shown by a least significant difference (LSD) of 3.5 psi and a measured difference of 3.6 psi. (If the LSD of a given confidence level is less than the measured difference, then the difference is significant to that confidence level.) Since July, 1997, the green compressive strength has gradually declined to 30-31 psi while premix likewise gradually declined (see respective graphs). The average GCS was 30.4 psi for mid-July to mid-September, 1999, after the AO system was optimized. The pre-AO optimized sand system GCS of 28.0 psi (for mid-January to mid-April, 1997) was not statistically different from the mid-July to mid-September, 1999 value to the 95% confidence level. The average GCS for these three time periods are shown in Figure 3.5-1.



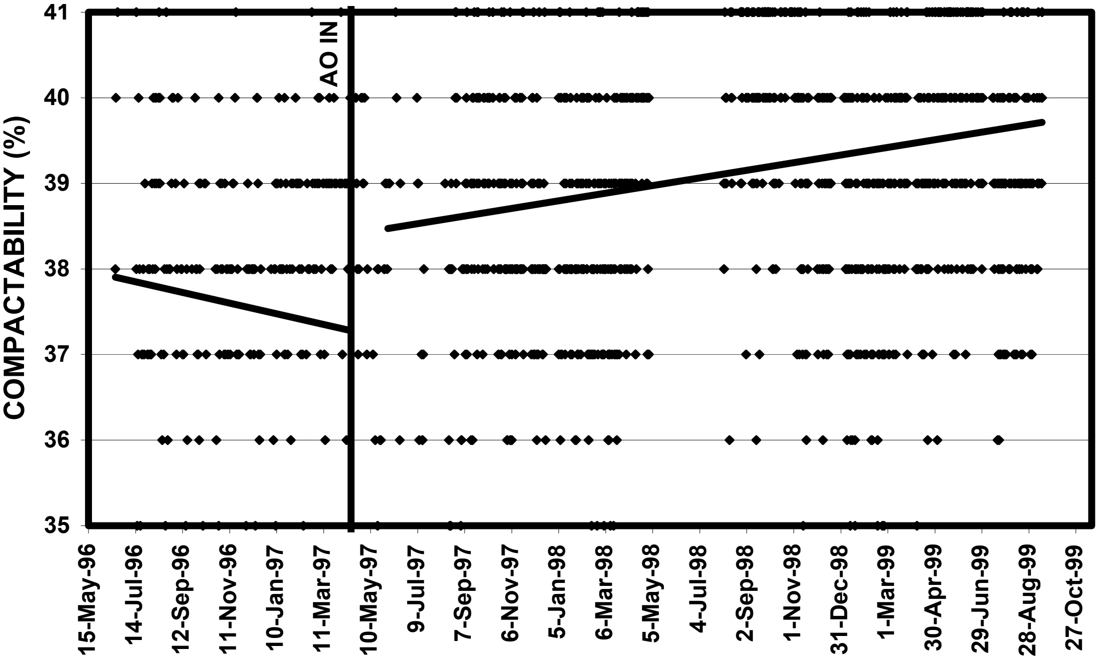


**Figure 3.5-1: GCS and compactibility at Wheland Foundry from June, 1996 to September, 1999.**

While green compressive strength rose as the AO process commenced operation, average lab compactibility remained constant at 38 to 40% (see Figure 3.5-1). This was a result of the compactibility-controlled system: due to automated compactibility controller feedback, when compactibility increased, the controller automatically reduced moisture addition to maintain the constant compactibility set point of the sand system, which was 38-40%.

Premix and total sand solutions:

AO process start-up also coincided with decreased premix and silica sand, as shown in Figure 3.5-2. Figure 3.5-2 depicts new premix (clay, sea coal and additives) that was blended into the green sand, normalized per ton of metal poured. Figure 3.5-2 also represents total silica sand (core plus non-core) per ton of metal poured. It should be noted that these figures represent materials inventories taken over the course of each month. Fluctuations from month-to-month may represent carry-over of materials from one month to the next. Thus, actual operational fluctuations in materials may have been less than the monthly inventory fluctuations in materials. The virgin premix feed rate decreased from an average of 147 lb/ton for the non-AO optimized sand system (October, 1996 to March, 1997) to 108 lb/ton following AO stabilization and optimization (May to October, 1999). This represented a 27% decrease in premix that needed to be purchased. Total new silica sand additions (core plus non-core) also diminished from 520 lb/ton during non-AO optimization to 325 lb/ton after the AO system was stabilized and optimized. This represented a 37% decrease in non-core sand use. The composition of the premix changed slightly on two occasions, as identified in Table 3.5-2. The reduction in premix consumption was statistically significant at the 95% confidence level, and the reduction in total new sand consumption was statistically significant at the 85% confidence level. Relative to the premix, the LSD (95%) was 37.9 lb/ton of metal poured compared to the measured difference of 38.6 lb/ton of metal poured. Relative to the total new sand, the LSD (95%) was 257 lb/ton of metal poured, the LSD (85%) was 176 and the measured difference was 196 lb/ton of metal poured. If the data in July, 1999 is excluded (where one molding line was down, causing an unusual balance between sand and metal), the difference is statistically significant at the 95% confidence level.

When comparing Figure 3.5-1 with Figure 3.5-2, it should be noted that before installing the AO system, green compressive strength was raised from a low 24 psi to a more acceptable 28 psi by implementing a concurrent raise in premix from 142 to 147 lb/ton metal (among other optimization strategies). However, after the AO system had become installed and stabilized (i.e. by July, 1997), the yet-higher GCS of 31-32 psi was achieved even though premix feed dropped to 120 lb/ton of metal.

It is useful to track the ratio of premix addition to sand addition through the course of this 3-year study. For the non-AO optimized system (October, 1996 to March, 1997), this premix-to-sand ratio was 0.282. When the AO system was first initiated in June-August, 1997, this ratio remained at 0.283. Ultimately, when the AO system had been optimized, this ratio had risen to 0.332. Thus, the initial start-up of the AO system offered the opportunity for making a non-confounded and direct comparison between

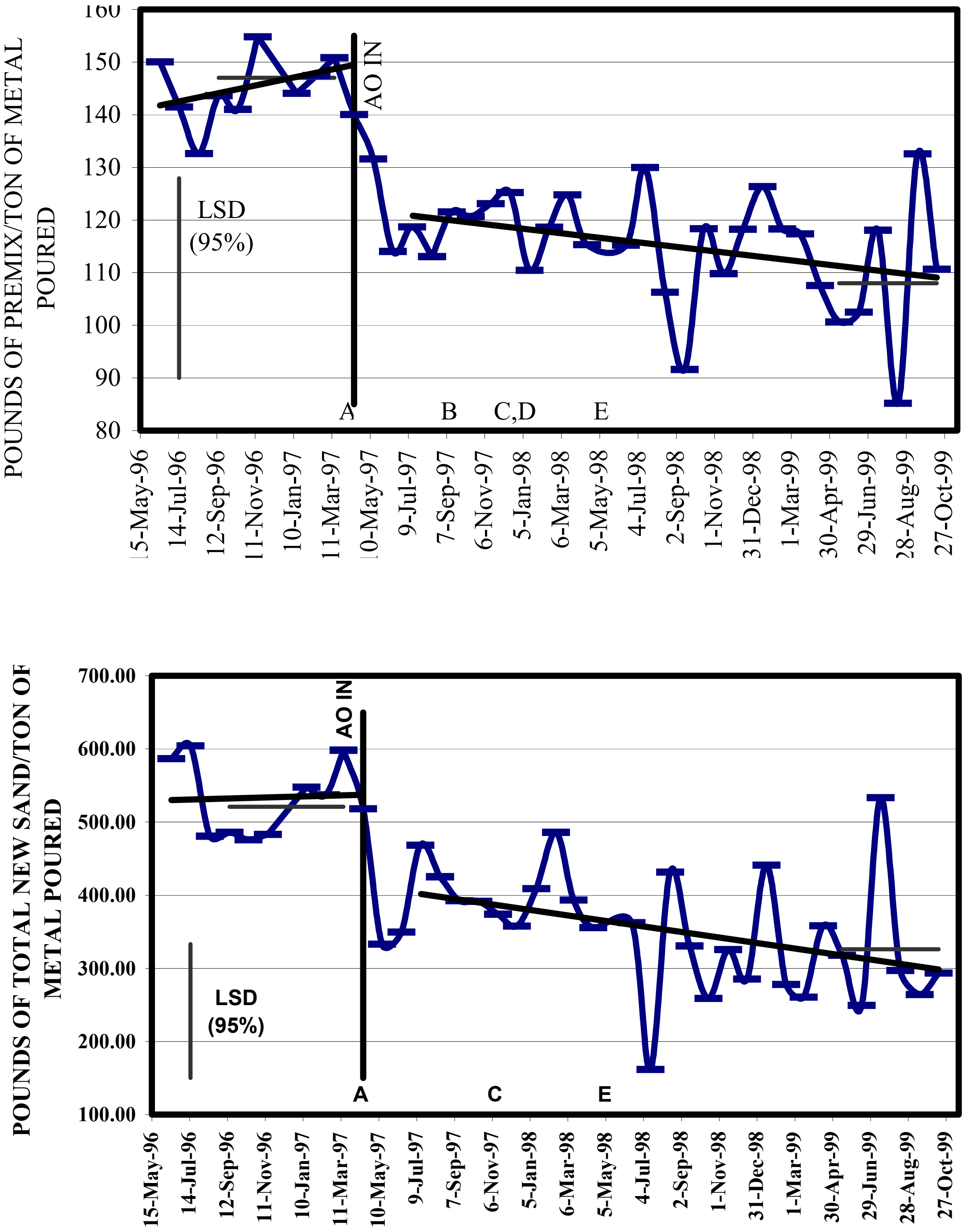


**Figure 3.5-2: Pre-mix and total new sand consumption as pounds per ton of iron poured at Wheland Foundry from June, 1996 to October, 1999.**

non-AO and with-AO performance. Specifically, when comparing the non-AO optimized versus initial with-AO systems, while the premix-to-sand ratios were the same, it can be observed that the AO process caused green compressive strength to rise from 28.0 to 31.6, a true difference at the 95% confidence level.

It is also observed that without AO, excessive new sand additions were unable to be reduced much below the 520 lb/ton metal level. Before AO, Wheland had unsuccessfully attempted to reduce the sand addition rates below this level (to 480 lb/ton metal) in July to November, 1996 (Figure 3.5-2), but fines building up in the system (to 4.8% fines < #140 mesh and 1.1-1.2% pan fines < #270 mesh, per Figure 3.5-3) appeared to cause an increase in the total scrap rate (to 40-43 relative units, per Figure 3.5-4) at these lower sand addition levels. This fines buildup was reduced and controllable with the AO system operation, per Figure 3.5-3 (July-November, 1997, before introduction of smaller-grained sand). On the surface, the reduction in new sand addition alone might be construed to represent a major source of bond reduction as the AO system became optimized. However, foundry personnel have observed that whenever their AO systems are down for maintenance, they find their sand systems quickly and consistently returning to at or near pre-AO bond consumption rates without an increase in new sand feed rates.

Fines and permeability:

The percent fines in the re-circulated green sand (Figure 3.5-3) reflect one manifestation of green sand performance. As a foundry re-circulates sand, abrasion causes fines to develop. The more green sand is re-circulated, the more its fines build up. The dust collector system normally controls the level of fines by extracting some of the fines portion of the sand. Unfortunately, this process has traditionally also removed valuable clay and sea coal. Some fines are desired in the sand to help stabilize the system and absorb excess moisture; however excessive fines can lead to metal defects.

The data in Figure 3.5-3 show that prior to AO, the fraction of fines less than #140 mesh (< ~106 μm) resided in the 4-5% range. Once the AO process was stabilized, during June to December, 1997, the fines remained at the same level of 4-5%. Likewise, the fraction of fines less than #270 mesh (< ~53 μm) dropped from 1.1% before AO to 0.9% after AO was stabilized. These acceptably low levels were maintained despite the fact that considerably less sand and premix was used after AO installation, and this corresponded to grains experiencing more turns and more abrasion before they were disposed of. The grain fineness of the silica sand was changed from a 55 grain fineness number (GFN) before November, 1997, to a 60 GFN thereafter. With this smaller grain size, the foundry could create a less porous mold surface for the casting while maintaining a reduced premix addition (Figure 3.5-2). This change in GFN translated to increasing the < #140 fines to 5-6% and the < #270 pan fines to 1.4%. Permeability remained unchanged while the system transitioned from the non-AO condition (130-140 units) to the with-AO condition (130-140 units), as shown in Figure 3.5-3. Permeability remained at this level until the virgin grain fineness number was changed from the 55 GFN before November, 1997, to the 60 GFN after November, 1997, at which point permeability dropped initially to 115 units and then ultimately to 105 units.

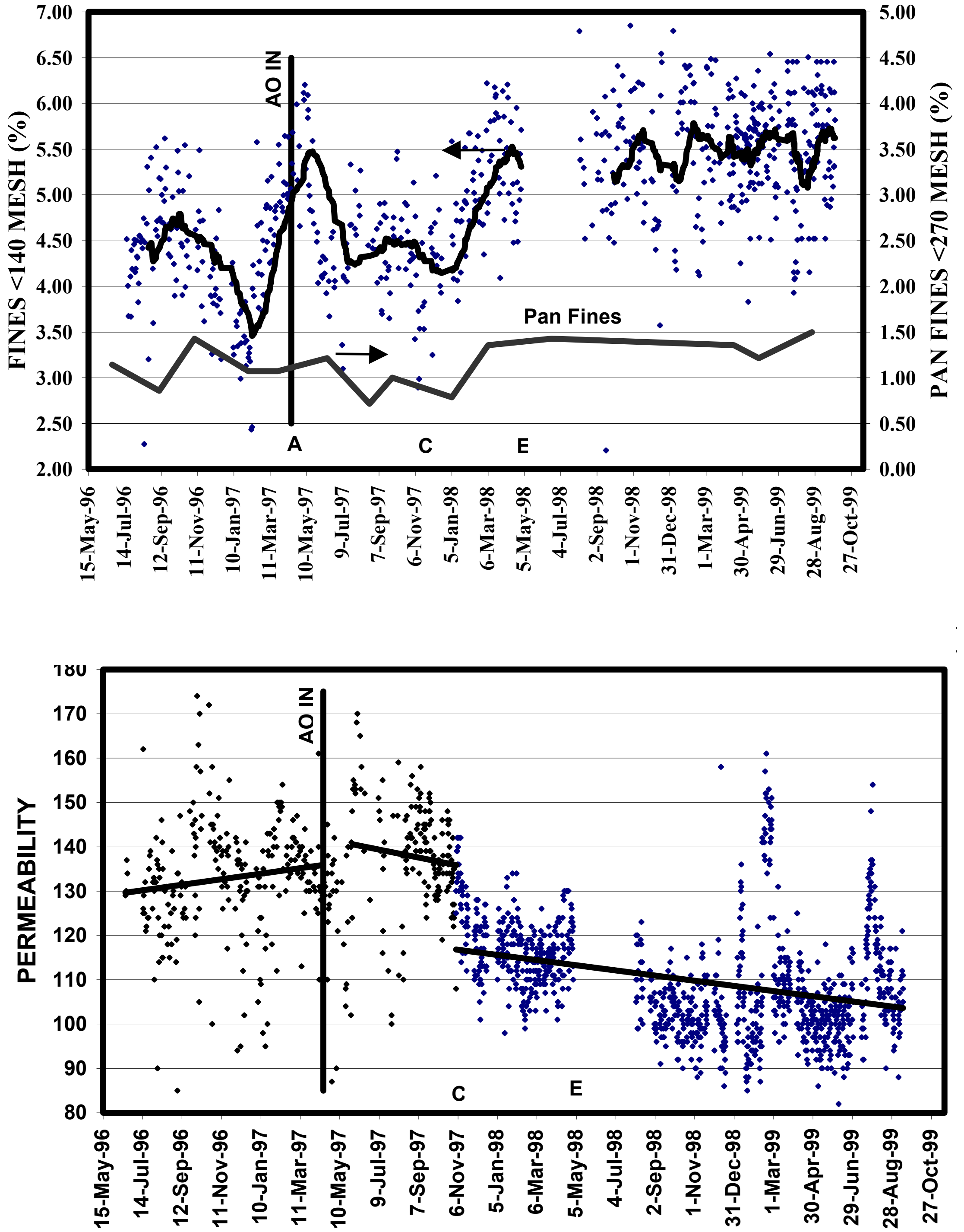


**Figure 3.5-3: Percent fines and permeability levels at Wheland Foundry from June, 1996 to September, 1999.**

## Total scrap and sand-related scrap:

The total scrap rate and the sand-related scrap rate are plotted in Figure 3.5-4. These scrap values are presented as internally compared relative rates, rather than as a percent of total metal poured. The total scrap rate declined from the non-AO optimized value of 35 relative units (October, 1996 to March, 1997) to the with-AO optimized average value of 23 relative units (May to October, 1999) as shown in Figure 3.5-4. This represents a 34% reduction. Likewise, sand-related scrap declined from a non-AO optimized average value of 10.5 relative units to a with-AO optimized average value of 8.5 relative units, as shown in Figure 3.5-4. This represents a 19% reduction. However, neither of these reductions was statistically significant at the 95% confidence level. Sand-related scrap represents iron pieces that were rejected because of burn-ins, cracked molds, run-out, rats, swell, slag, and sand holes.

## Moisture and methylene blue clay:

The percent moisture was 3.3% before AO, and also 3.3% at the onset of AO operation, as shown in Figure 3.5-5. Then moisture gradually rose to a 3.5% level as the AO system became optimized by June-September, 1999. Concurrently, the methylene blue (MB) clay set point was 8.8% prior to AO, and this increased to an AO-optimized value of 9.4%, as shown in Figure 3.5-5. Before July, 1997, the MB clay set point was 8.8%, and the system generally operated close to this set point, per discussions with foundry personnel; however, the actual MB clay values before July, 1997 were not logged into the currently-available computer data base.

The moisture-to-MB clay ratios are shown in Figure 3.5-6, along with a 30-day running average of this ratio. Green sand optimization experience has shown that best system casting quality performance can be achieved for this green sand system when the moisture-to-MB clay ratio remains between 36-42%. (The most favorable range varies slightly from one green sand system to another). As the moisture-to-MB clay ratio increases, more water is available to the clay for activation, and this is good up to a point. As a counter-balance, if the ratio gets too high, free water conditions can exist, and this can lead to increased defects.

This optimum 36-42% range was maintained for most of the 3-year study period, as shown in Figure 3.5-6. It was noticed that during the June, 1997 to September, 1999 time frame, each time the running average of moisture-to-MB clay value exceeded 42% or dropped below 36%, the sand-related scrap rate increased. The moisture-to-MB clay ratio dropped below 36% during November, 1997; February, 1999; and July, 1999; and the ratio exceeded 42% in February, 1998. During each of these intervals, there was a corresponding increase in sand-related scrap rate (Figure 3.5-4). It should also be noted that foundry production was cut to half from January 30 to February 6, 1999; and from July 15-22, 1999. Either the down-time or the hindered operations before the equipment defects were discovered could also have contributed to increased scrap. Moreover, changes in production rate could have precipitated changes in the moisture-to-MB clay ratio and other green sand balancing parameters.

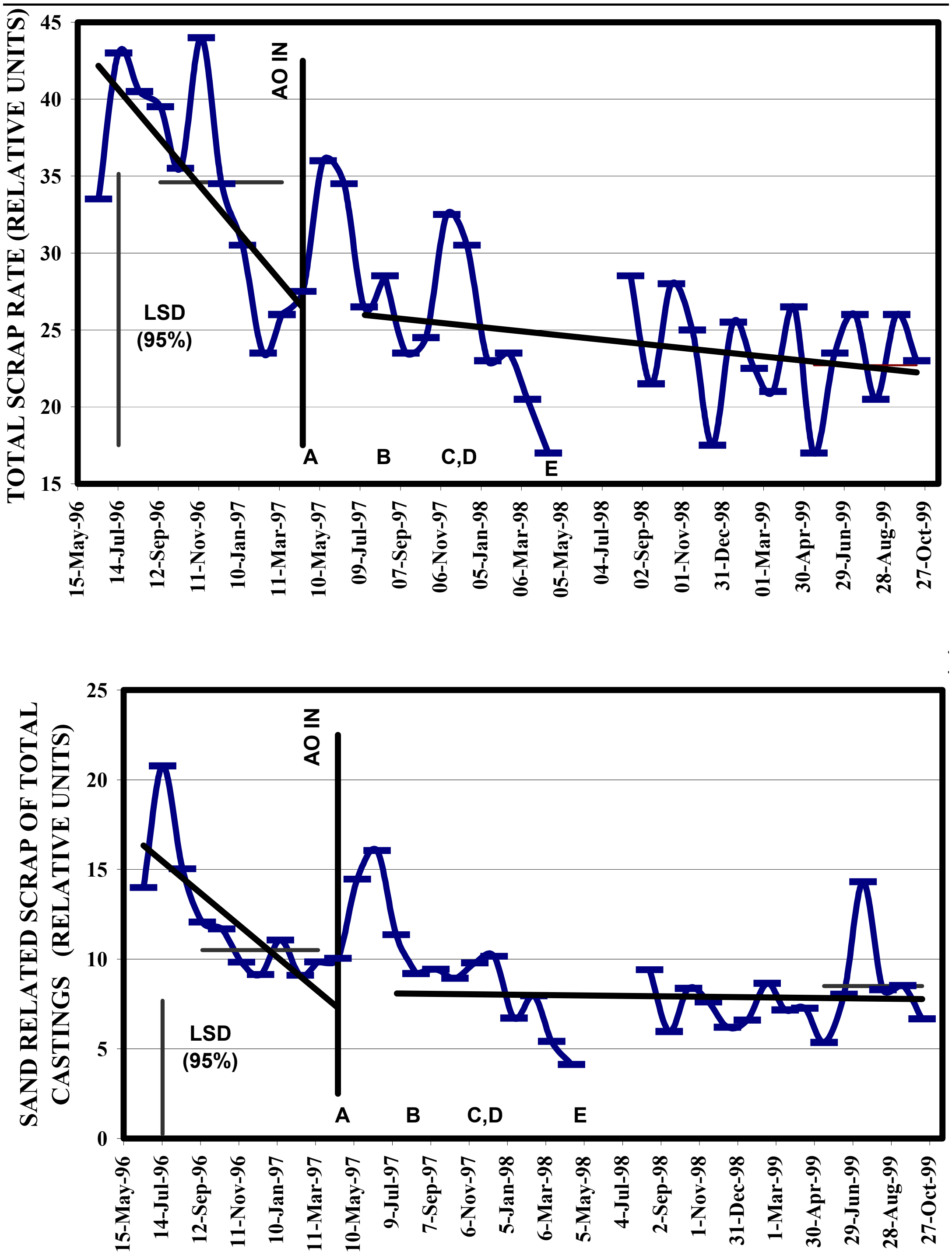
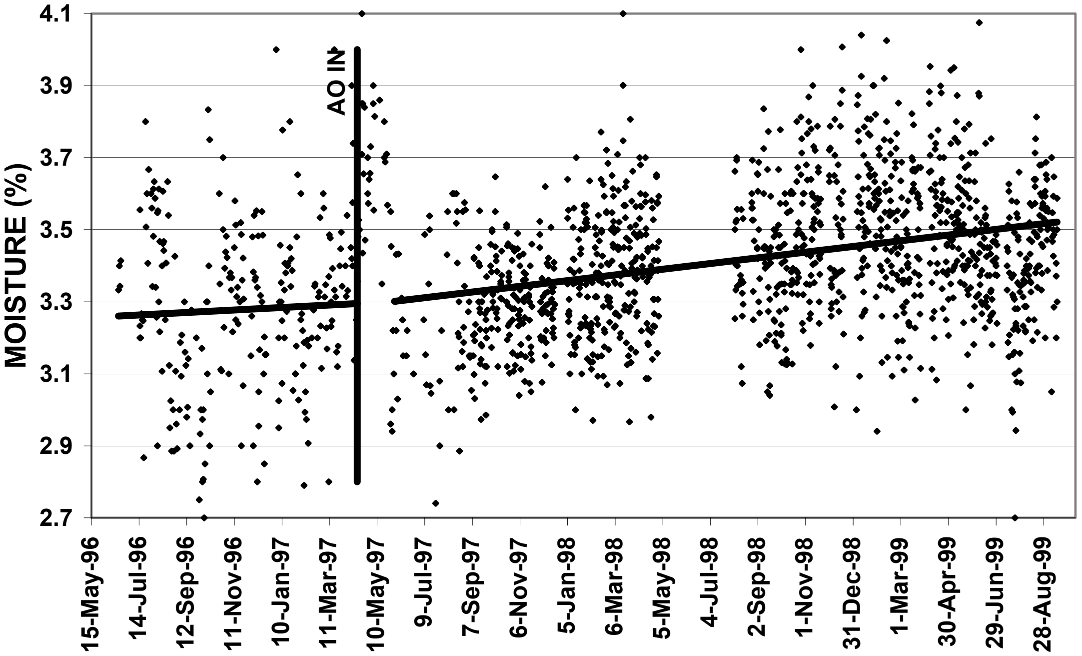


**Figure 3.5-4: Total and sand-related scrap rates at Wheland Foundry from June, 1996 to October, 1999.**



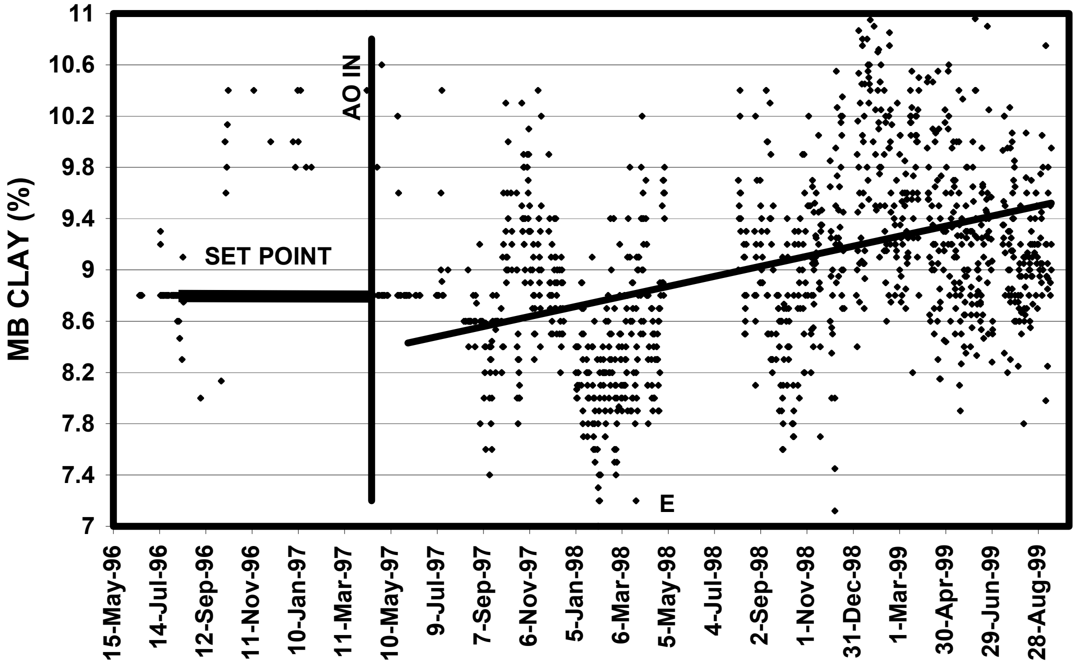


**Figure 3.5-5: Moisture and MB clay levels at Wheland Foundry from June, 1996 to September, 1999.**

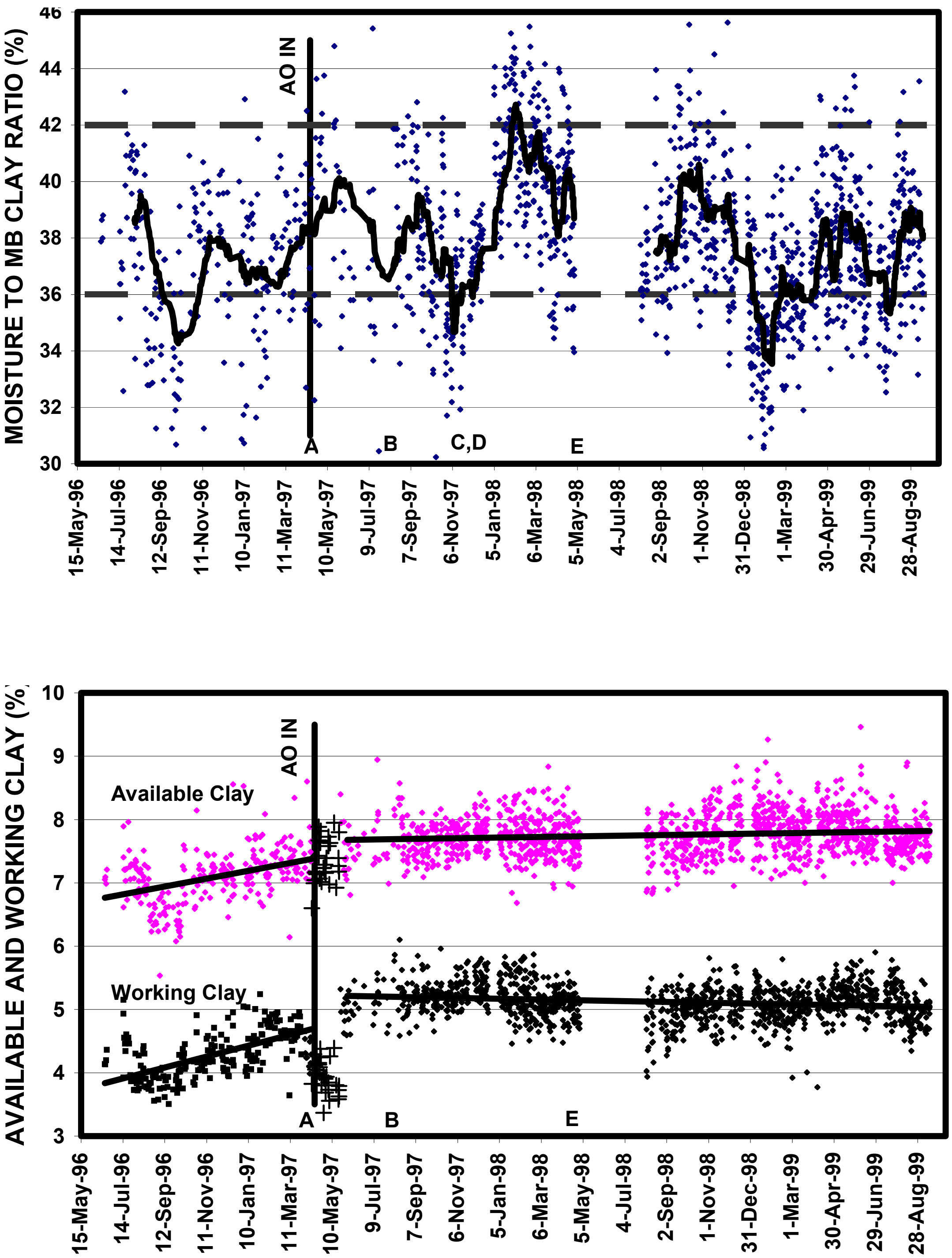


**Figure 3.5-6: Moisture-to-clay ratio and available and working clay levels at Wheland Foundry from June, 1996 to September, 1999.**

Available clay, working clay and muller efficiency:

Available clay (bond) and working clay (bond) levels are iterative properties which can help to characterize the efficiency of the clay activation in the system. When green sand is mulled, ideally the temper moisture will be added and the maximum strength will be developed. However, maximum strength may not be developed because of production demands on the sand system that dictate short cycle times in batch mullers and short residence times in continuous mullers. Also, the clays are not the only items absorbing the moisture. Sand fines, coal, latent and dead clays and additives also absorb this moisture. It becomes important to know how much of the moisture is going to clay activation, and therefore, to strength development. Working clay (bond) can be considered as the amount of clay that is actually being utilized for strength, while the available clay (bond) can be considered as the total amount of moisture-absorbing material in the sand (American Colloid Company, 1983). The plot of these values is found in Figure 3.5-6. As one can see, both available and working bond levels increased slightly when the AO system was operating. Specifically, comparing optimized non-AO versus optimized with-AO values, the AO process corresponded with an increase in working clay level of 4.7% to 5.1% (9% improvement); The AO process also corresponded with an increase in available bond of 7.3% to 7.8% (13% improvement). Again, it should be noted that these improvements occurred while premix feed rate decreased. According to the definitions above, this means that the clay utilization improved within the sand system when the AO process was operating.

Clays will absorb a variety of organic compounds on their surfaces (Odom, 1988; Odom, 1992), and these organic compounds can mask the surface charge of the clays in a manner that reduces the clay's ability to achieve a high green compressive strength. Advanced oxidants are capable of removing this organic "rain coat" from the surfaces of glass (Brant and Cannon, 1996), and the same would be expected for clay surfaces at both ambient and slightly elevated temperatures. The evaluation of the green compressive strength conforms to this interpretation, although other factors may have also played a role. In a dust collection-blackwater system, AO radicals can react to form radical scavengers when they react with such components as coal, $CO_3^-$, benzequenone (Pignatello and Chen, 1999), metals, and VOCs at ambient temperature. This establishes the seeds for much faster reactions at the high temperatures of a mold environment. Radical scavengers react slowly at ambient temperatures, but Arhennius kinetics would dictate that they react far more rapidly at the high temperatures near molten metal. Therefore, this AO-clay cleaning phenomenon should occur more rapidly in a heated mold environment than at ambient conditions.

Muller efficiency rose from non-AO optimized values averaging 62% (mid-October, 1996 to mid-March, 1997) to an initially-stabilized AO value of 68% (mid-July to mid-October, 1997) as shown in Figure 3.5-7. When it was recognized that premix feed rate could be dropped further after initial AO stabilization, a subsequent reduction in premix feed rate (Figure 3.5-2) was linked to a concurrent reduction in muller efficiency to 65%, as shown in Figure 3.5-7. The muller efficiency depicts the clay utilization in the sand system. The higher the muller efficiency, the greater the clay utilization and the lower the clay demand. It thus follows that if the sand system uses the clay more effectively, less clay will be required to develop the same strengths.

In a typical foundry, the reduction in the premix feed set point increases the muller efficiency. The way this works can be explained by illustrating that working of the clay in the sand mix to develop strength is the reason the muller motor current draw increases toward the end of the muller cycle. Muller cycle time is usually a compromise between sand property development and production needs. If this cycle time is held constant and the clay to be worked into the sand mix is reduced, the amount of energy per unit of clay is increased. Coupled with the initial increase in sand properties in an AO sand system, the stage is set for the next level of optimization. The premix feed rate could be decreased yet again as long as friability does not become an issue. Also, shorter muller cycles could be run because of the quicker development of the sand properties due to the increased muller efficiency.

### Loss on ignition and volatile carbonaceous material:

Loss on ignition (LOI) and volatile carbonaceous material (VCM) values decreased slightly when the AO system commenced operation, with the LOI dropping from 3.3 % to 2.8 %, and the VCM decreasing slightly from 1.3 % to 1.2%. These comparisons reflect mid-October, 1996 to mid-March, 1997 values as compared to mid-July to mid-October, 1997 values. After stabilizing AO operation, foundry personnel perceived that it was necessary to increase the coal content of the premix in order to compensate for decreased addition rates and maintain a slightly higher LOI and VCM. Thus, in November of 1998, the foundry personnel increased the coal content of the premix by one percent (see Table 3.5-2). This change caused higher LOI and VCM values (Figure 3.5-7) once this change had time to work through the system.

The LOI and VCM tests effectively measure the amount of material available for combustion in the green sand. It is necessary to have this material in the sand to increase casting quality. Coal is important in the green sand of iron foundries for several reasons: (a) it creates a lustrous carbon deposit to assist in peel at shakeout, (b) it expands to fill the "gaps" between the sand grains so as to create a smoother surface, (c) at high temperature, the coal forms a malleable coke that prevents the penetration of molten iron, (d) it consumes oxygen at the molten metal interface and creates a reductive atmosphere to prevent metal oxidation (Bindernagel, *et al.*, 1975), (e) sea coal swells while clay shrinks at high temperature, and these two balance to maintain dimensional tolerances.

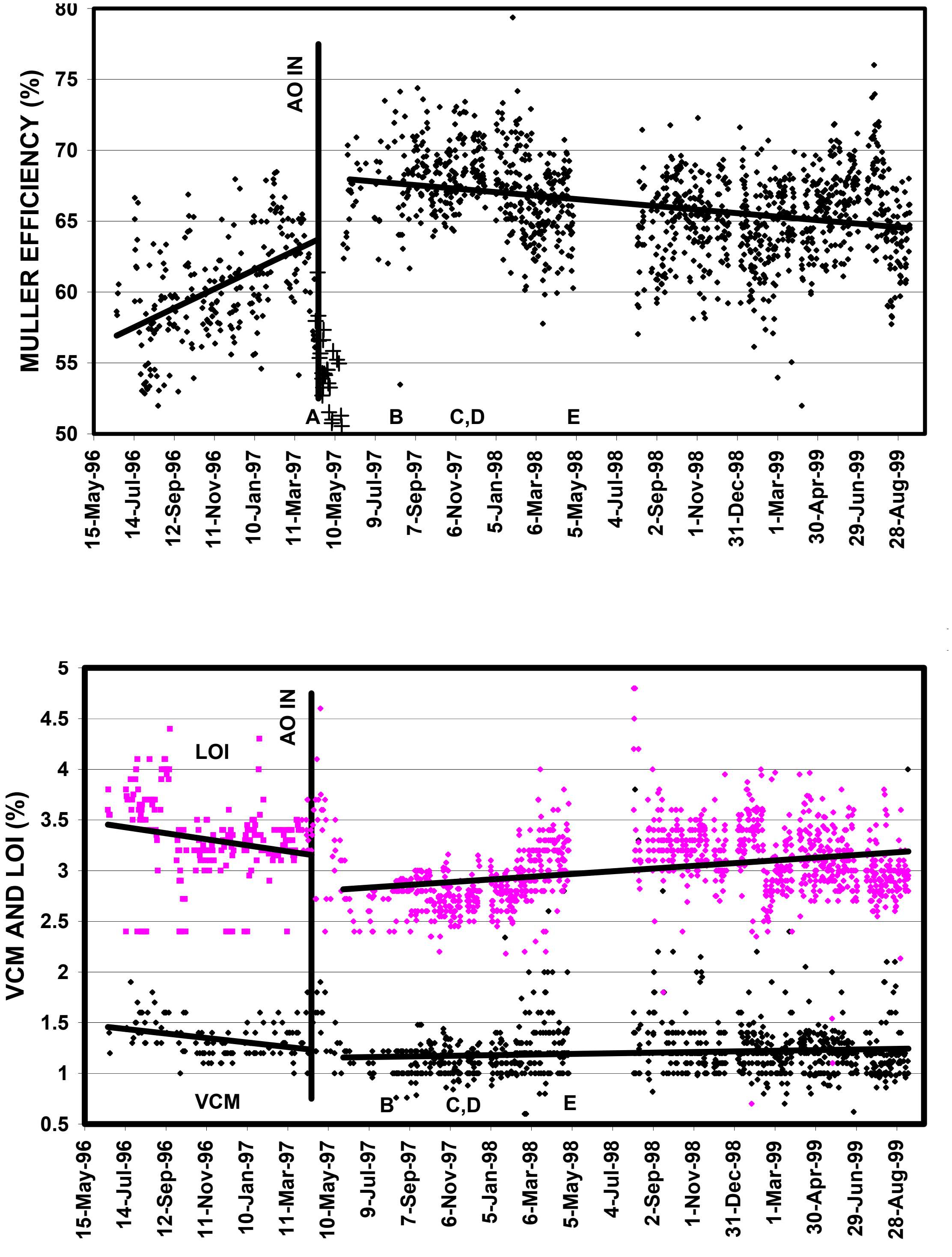


**Figure 3.5-7: Muller efficiency, LOI, and VCM levels at Wheland Foundry from June, 1996 to September, 1999.**

## 3.5.2 AO-DBW System – Neenah Plant No. 2

### 3.5.2.1 Introduction

Over the past several years, a number of iron foundries have incorporated advanced oxidants (AO) into their green sand systems to reduce emissions and/or to improve sand performance. Neenah Foundry has operated its Plant 2 green sand system for over 1½ years with an installed AO process. Sand system performance was fully documented prior to the phased installation of its initial AO-clear water (AO-CW) system, followed by the start-up of an AO-dry dust-to-black water (AO-DBW) system. Sand data throughout this start-up and transition was carefully monitored as were the control actions taken by foundry personnel to keep the sand system "under control".

The results presented in section 3.5.2 summarize data from an extensive sand property database at Neenah Foundry (Neenah, WI.) covering the period of non-AO baseline sand system performance, AO installation, AO phase-in, and final optimized AO operation. This database includes more than 20 sand properties sampled up to ten times a day for over three years. In addition, a detailed compilation of corresponding green sand control actions and sand system changes was developed to permit evaluation of the phased start-up of an AO-DBW system. After a sand system performance baseline was established, the AO-CW part of the AO system was started. After a one month period of system adjustment, the AO-DBW portion of the system was started up. Sand system evolution and controlled changes were continuously monitored and assessed for a 20-month period of time. Table 3.5-3 summarizes the equipment and capabilities of the sand system that is the basis for this study.

**Table 3.5-3: Neenah Foundry Plant 2 sand system equipment and capacities.**

| Equipment: | Capacities: |
|---|---|
| Model 2070 Disamatic molding machine | 10-20 tons iron / hour |
| 4000 lb capacity batch sand mullers (3) | 100-150 tons sand / hour |
| 180 ton/hour capacity sand cooler | 110-250 molds / hour |
| AO-DBW unit | |

### 3.5.2.2 Results and Discussion

*(This section has been adapted from the paper by Land, Voigt, Cannon, Furness, Goudzwaard, and Luebben, 2002.)*

The phased non-AO to AO-CW to AO-DBW start-up has been monitored for over 1.5 years. Table 3.5-4 presents a comparison between the baseline non-AO system sand properties and the current AO-DBW system. During this period of AO-driven sand system optimization, 27 events and/or process changes were implemented. Twelve of these events can be considered significant and these are identified as lettered events (A-L) on all of the following tables and graphs illlustrating sand system changes. Table 3.5-5 presents these sand system change events in chronological order along with the sand system performance response motivating the changes.

Figures 3.5-8 and 3.5-9 present monthly average trends of key sand properties over a two-year baseline period, the AO phased installation period, and the AO stabilization period. Signficant events are marked with dotted lines and identification letters. The open circles (o) before and after event lines mark the average from the beginning of the month to the event and the event to the end of the month, respectively. These are useful to interpret the immediate response of the sand system to the event as well as to gauge the direction of change.

AO and AO-driven system changes drive system performance toward new equilibriums which can clearly be seen in Table 3.5-4, where a "before" and "after" summary of key sand system performance parameters are presented. The indicated changes in sand system performance are driven by the influence of AO on fundamental clay-water-strength-compactibility relationships. For a sand system operated under conventional compactibility control, increases in system green compressive strength with AO drive the sand system to lower MB clay levels, lower moisture levels and ultimately to lower compactibility levels. This also results in increases in system processing efficiency (SPE) (Green and Heine 1989, 1991), which effectively continue this "AO-driven sand system optimization" process. Less sand system clay demand and clay recovery from the AO-DBW system significantly reduces the sand system bond consumption. AO sand systems run successfully at lower seacoal addition levels due to better coal utilization efficiency. This is seen in the 18.4% reduction in the %LOI / %MB clay ratio. It appears the beneficial moisture-carrying capability of the coked seacoal in the sand system may not be as necessary in AO-system sands due to the improved moisture retention capability of the clay. This improved moisture retention capability is demonstrated by the fact that the compactibility set-point at the muller has been reduced by 4 to 5 units in relation to the target compactibility at the molding machine since the introduction of the AO-DBW system. Sand system emissions, not reported here, also decreased due to both the AO reactions themselves and the reduced sand system LOI and VCM operating set-points possible with AO processing.

A more complete picture of the response of the sand system to the phased introduction of first AO-CW and then AO-DBW processing, as well as prior base-line performance can be seen by careful examination of Figures 3.5-8 and 3.5-9. In these figures, significant sand system control actions A-L from Table 3.5-4 are also indicated. A four-month sand system baseline performance period before AO system start-up is also shown (Sept., 1999 to Jan., 2000; prior to event A). Initially upon start-up of the AO-CW system in January, 2000, the green compressive strength of the system sand began to increase. AO system ozone levels were ramped up to specified levels as sand system performance was carefully monitored. In February, 2000, the AO-DBW clarifier and bond return system was started with an initial very low blackwater solids content of 5% (event B). The

**Table 3.5-4: Baseline and AO-DBW system performance comparison for Neenah Plant No. 2, production line 2.**

| Property | Baseline (non-AO) December 1999 | | AO-DBW System August 2001 | | Percent Change* |
|---|---|---|---|---|---|
| | Average | St. Dev. | Average | St. Dev. | |
| Compactibility, % | 40 | 1.1 | 35 | 1.0 | **-12%** |
| Moisture, % | 3.05 | 0.1 | 2.71 | 0.1 | **-11%** |
| Green compressive strength (GCS), psi | 33.3 | 1.2 | 34.6 | 1.6 | **+4%** |
| Methylene blue clay (MB Clay), % | 10.1 | 0.3 | 8.4 | 0.2 | **-17%** |
| Water-to-MB Clay ratio | 0.30 | 0.01 | 0.32 | 0.01 | **+8%** |
| Split tensile, psi | 6.4 | 0.4 | 6.6 | 0.4 | **+3%** |
| Dry strength, psi | 73.5 | 6.4 | 62.6 | 13.2 | **-15%** |
| Wet tensile, N / cm$^2$ (x10$^{-3}$) | 377 | 33.7 | 408 | 35.5 | +8% |
| Permeability | 80 | 3.4 | 79 | 4.3 | -1% |
| Friability | 7.0 | 2.0 | 8.6 | 5.6 | +23% |
| Specimen wt., g | 156 | 0.7 | 159 | 0.71 | +2% |
| AFS Clay, % | 11.1 | 1.0 | 10.9 | 0.5 | **-1%** |
| Loss on ignition (LOI, 1800$^o$F), % | 5.4 | 0.20 | 3.6 | 0.5 | **-33%** |
| Volatiles (VCM, 1200$^o$F), % | 2.4 | 0.5 | 1.7 | 0.2 | **-29%** |
| % LOI / MB Clay, % | 53.9 | | 44 | | **-18%** |
| Available bond, % | 7.5 | | 7.1 | | -4% |
| Working bond, % | 5.5 | | 5.4 | | -2% |
| Muller Efficeincy, % | 74 | | 76 | | +3% |
| System Processing Efficiency (MGS/MB Clay),% | 56 | | 69 | | **+23%** |
| New sand additions, lbs/ton iron | 83 | | 122 | | +47% |
| Core sand additions, lbs/ton iron | 174 | | 234 | | +35% |
| Preblend consumption, lbs premix/ton iron | 176 | | 139 | | -21% |
| Preblend composition: | | | | | |
| Clay, % | 72 | | 75 | | +4.2% |
| Coal, % | 26 | | 22.4 | | -13.8% |
| Cereal, % | 2 | | 2 | | 0% |
| Soda ash, % | 0 | | 0.7 | | - |
| Blackwater clarifier properties (after AO-DBW start-up): | | | *Baghouse Dust* | *Waste Sludge* | *Blackwater* |
| MB Clay, avg % | | | 34 | 3.2 | 51 |
| LOI, avg % | | | 19.5 | 10.8 | 21.7 |
| Percent Sand, avg % | | | 46.8 | 86 | 27.3 |
| Baghouse dust processed, avg tons/day | 10.7 | | | | |
| Blackwater processed, avg tons/day | 83.5 | | | | |
| Waste sludge produced, avg tons/day | 5.5 | | | | |
| System clay recycled from blackwater clarifier, % | 22.7 | | | | |
| System coal recycled from blackwater clarifier, % | 29.5 | | | | |

* *Bold type indicates a significant change at the 95% confidence level*

**Table 3.5-5: Chronology of AO-driven sand system changes on production line 2.**

| Event | Date | Sand System Changes | Reason for Changes |
|---|---|---|---|
| **A** | **18-Jan-00** | **AO-CW start-up. Ozone sparged in blackwater clarifier; hydrogen peroxide level at 100ppm (mistakenly)** | |
| - | 25-Jan-00 | Ozone generator voltage increased | Ozone concentration ramp-up to specified level |
| **B** | **22-Feb-00** | **Blackwater AO start-up (BW solids 5% by vol.)** | |
| | **28-Feb-00** | **Premix coal percentages decreased 2% (clay percentage increased 2%)** | **LOI had increased to 6.5% from 5% due to seacoal being recovered from blackwater (better coal utilization efficiency)** |
| **C** | **14-Mar-00** | **MB clay target reduced to 9.6%**<br>**Adjusted the bond addition formula to account for the clay recovered in the blackwater** | |
| | **15-Mar-00** | **Compactibility setpoint reduced from 42 to 40** | **Problems with heavy sand (poor flowabilty)** |
| | **21-Mar-00** | **MB clay target reduced to 9.4%** | |
| **D** | **13-Apr-00** | **MB clay target reduced to 9.2%** | **Reduce clay and still maintain strength** |
| - | 14-Apr-00 | Outlet point raised in the BW clairifier | Change the blackwater system to draw from the top cut. The middle cut had 4.7% clay. The top cut had 6.5% clay. |
| | 14-Apr-00 | BW system down. MB clay drops over 8hrs | |
| **E** | **8-May-00** | **MB clay target reduced to 9.0%** | **Reduce clay and still maintain strength** |
| - | 16-May-00 | Percent solids target in BW increased from to 6% to 10% by volume | |
| | 19-Jun-00 | Premix coal percentage decreased 1% (clay percentage increased 1%) | Decrease the LOI |
| **F** | **26-Jun-00** | **AO hydrogen peroxide addition increased. Ozone sparged moved to clearwell.** | **Correct $H_2O_2$ concentration** |
| **G** | **23-Oct-00** | **Premix soda ash percentage increased from .5% to .6% (coal percentage decreased .1%)** | **Correct for low wet tensile strength** |
| | **4-Dec-00** | **MB clay target reduced to 8.8%** | **Reduce clay and still maintain strength** |
| - | 7-Dec-00 | MB clay target raised back to 9.0% | Control mositure/clay ratio to maintain minimum scap levels |
| | 22-Mar-01 | BW solids increased to 12% solids by vol | |
| **H** | **5-Apr-01** | **Compactibility setpoint reduced from 41 to 40** | **Control mositure/clay ratio below 35% to maintain minimum scrap levels** |
| | **9-Apr-01** | **Compactibility setpoint reduced from 40 to 39** | |
| | **10-Apr-01** | **Compactibility setpoint reduced from 39 to 38** | |
| **I** | **19-Apr-01** | **MB clay target reduced to 8.8%** | **Reduce clay and still maintain strength** |
| **J** | **3-May-01** | **MB clay target reduced to 8.6%** | **Reduce clay and still maintain strength** |
| **K** | **24-May-01** | **MB clay target reduced to 8.4%** | **Reduce clay and still maintain strength** |
| **L** | **1-Aug-01** | **Compactibility setpoint reduced from 38 to 35 over a five-day period** | **Control mositure/clay ratio below 35% to maintain minimum scrap levels** |

* *Significant system events are indicated in bold and are marked with letters on Figures 3.5-8 to 3.5-11.*

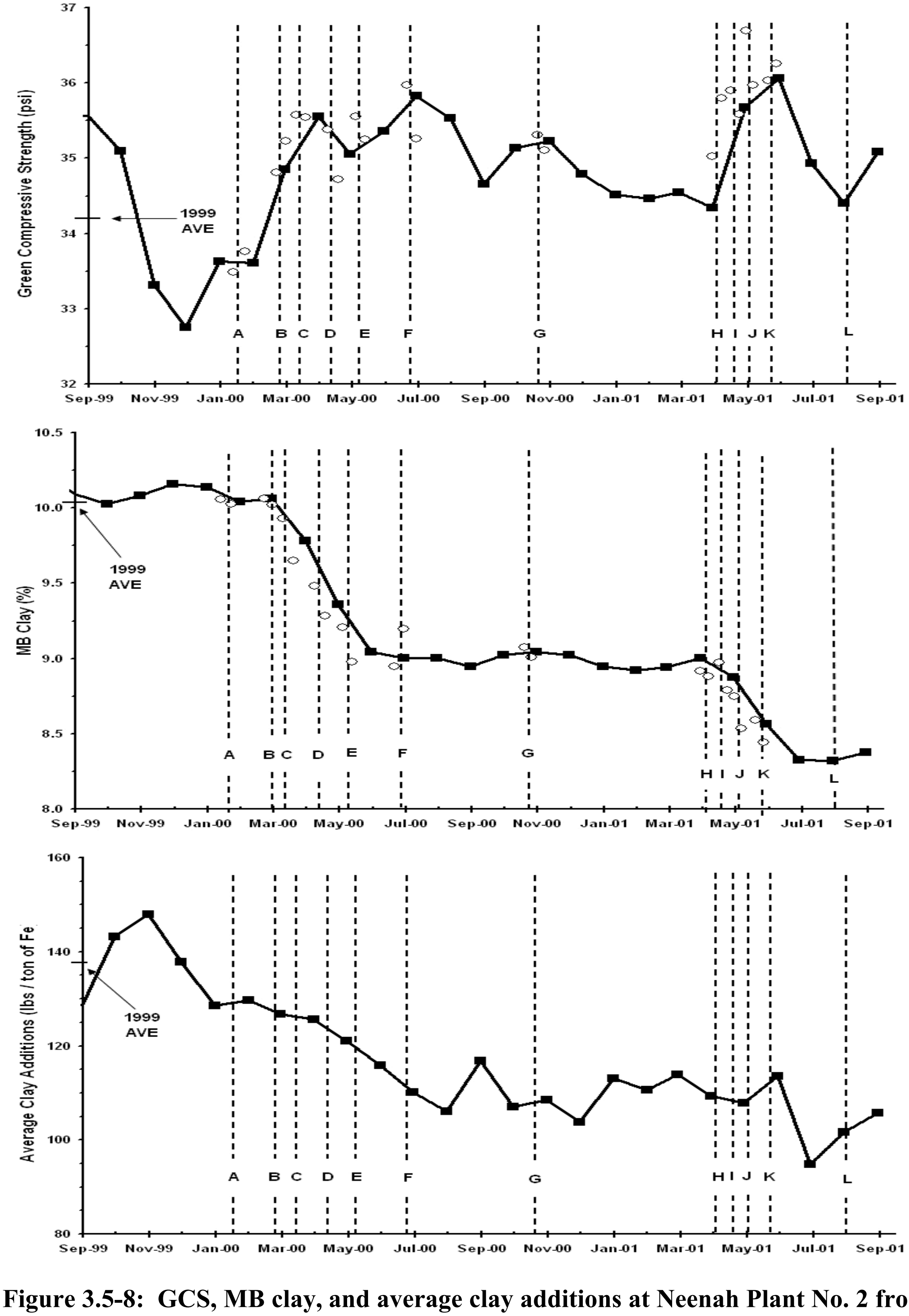


**Figure 3.5-8: GCS, MB clay, and average clay additions at Neenah Plant No. 2 from Sept., 1999 to Sept., 2001.**

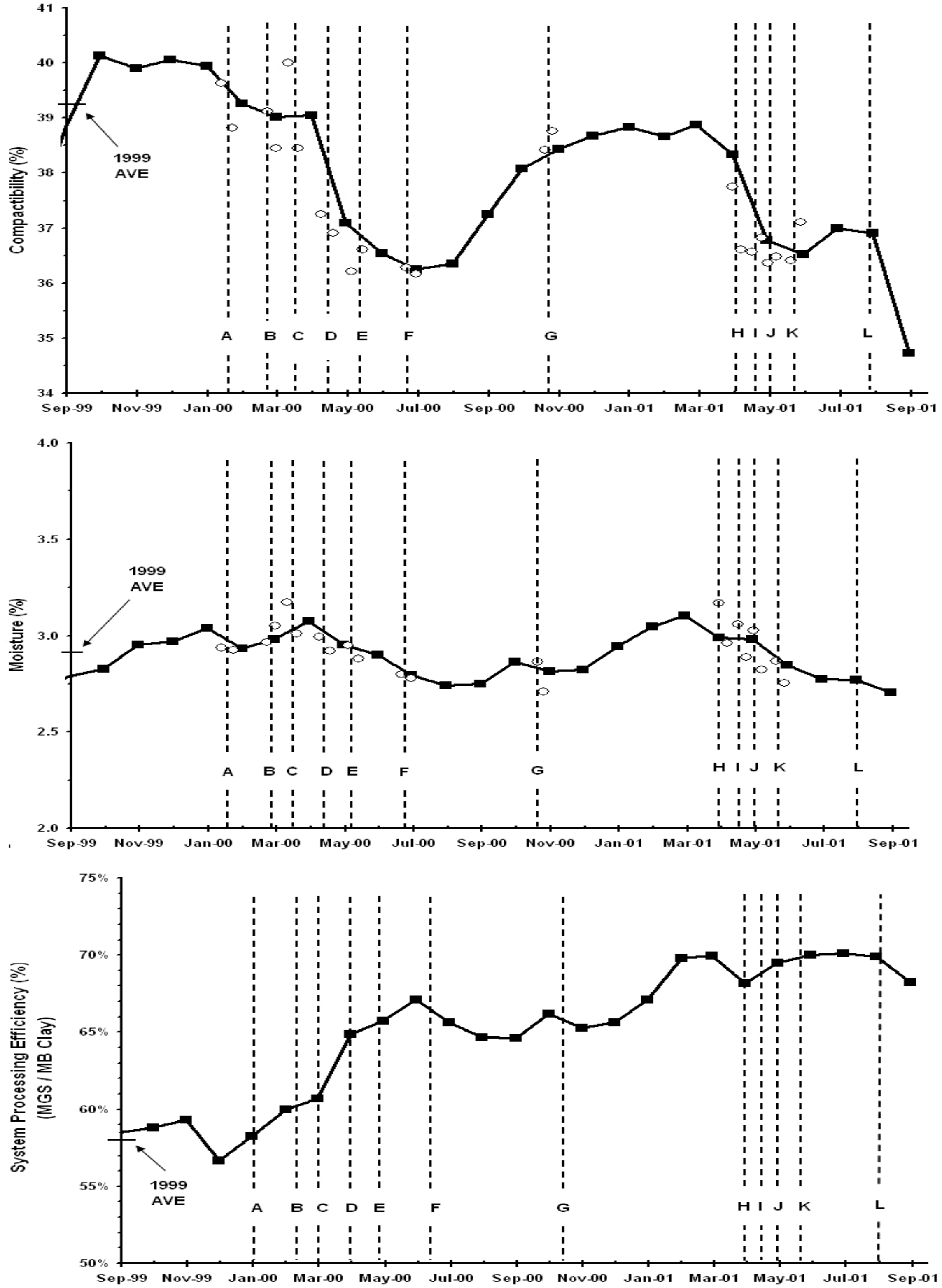


**Fig 3.5-9: Compactibility, %moisture, and system processing efficiency at Neenah Plant No. 2 from Sept., 1999 to Sept., 2001.**

resultant increases in green compressive strength led to a series of sand system MB clay reductions to keep green compressive strength below 36 psi. The MB clay reductions, combined with the blackwater clay and seacoal recovery, reduced muller premix additions first for light-section jobs and then for heavy-section jobs so that adequate shakeout could be achieved.

During the following months, small phased control actions were taken to keep the evolving sand system within acceptable property control set-points. In May, 2000 the solids loading in the blackwater system was increased to 8% and then again in March, 2001 to 12%. These increases in bond recovery from blackwater necessitated a proportional increase in soda ash and clay percentages in the premix to maintain the proper soda ash level and the proper clay/seacoal ratio (see bottom of Table 3.5-4).

The new green sand performance characteristics of the AO-DBW system can perhaps be best illustrated by Figure 3.5-10, where green compressive strength per unit of MB clay is plotted from September, 1999 to September, 2001. The AO-DBW processing system significantly increased not only clay recovery, but also clay utilization efficiency. This change in clay utilization efficiency is not due to blackwater additions alone, but is enhanced by AO additions as has been reported previously of other AO blackwater bond recovery systems (see section 3.5.1).

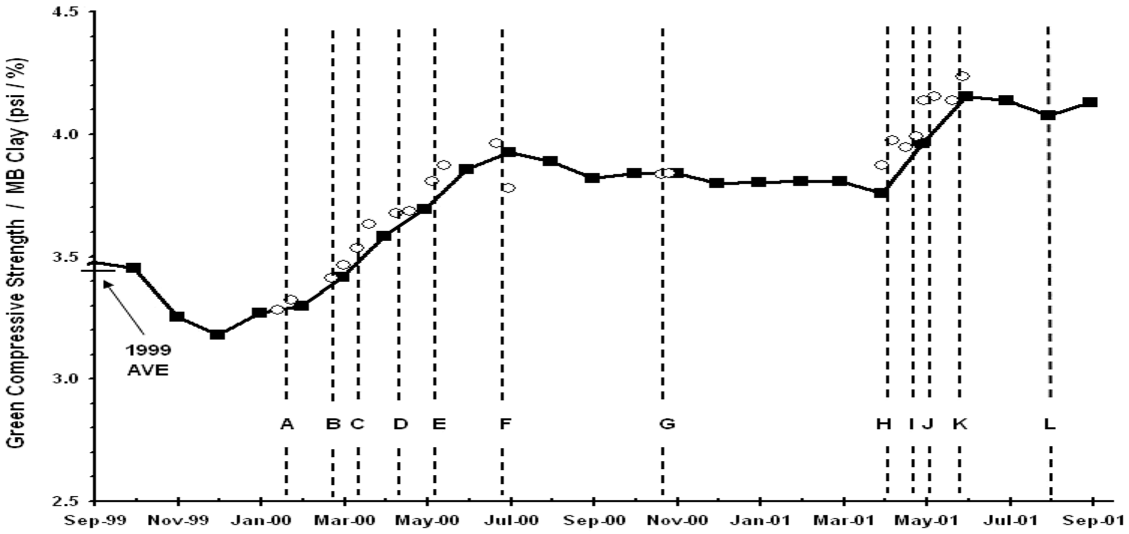


**Fig. 3.5-10: Green compressive strength per unit MB clay at Neenah Plant No. 2 from September, 1999 to September, 2001.**

Sand system control philosophies changed somewhat during the 1999-2001 time period. Now clay/moisture ratios are closely monitored and controlled rather then other secondary clay parameters such as working bond, available bond, or muller efficiency. The clay/moisture ratio was observed to correlate with casting quality and has demonstrated to improve system control. This parameter has motivated decreases in compactibility set points to maintain clay/moisture ratios within the proper limits.

Other operational characteristics of the AO-DBW green sand system also warrant mentioning. Throughout this time period no significant changes in sand-related scrap rates were observed. Success in avoiding sand defects such as scabbing can be attributed to careful monitoring and control of sand system wet tensile strength, as shown in Figure 3.5-11. Maintaining wet tensile strength above 0.350 N/cm$^2$ with soda ash additions is key to scab avoidance. AO-DBW processing does not appear to change this scabbing/wet tensile strength relationship. The AO-DBW sand system is easier to control from a compactibility standpoint and responds more quickly to sand system changes. Average losses of 4 compactibility units from the muller to the molding line have been reduced to 0-1.5 compactibility unit losses for the AO-DBW system.

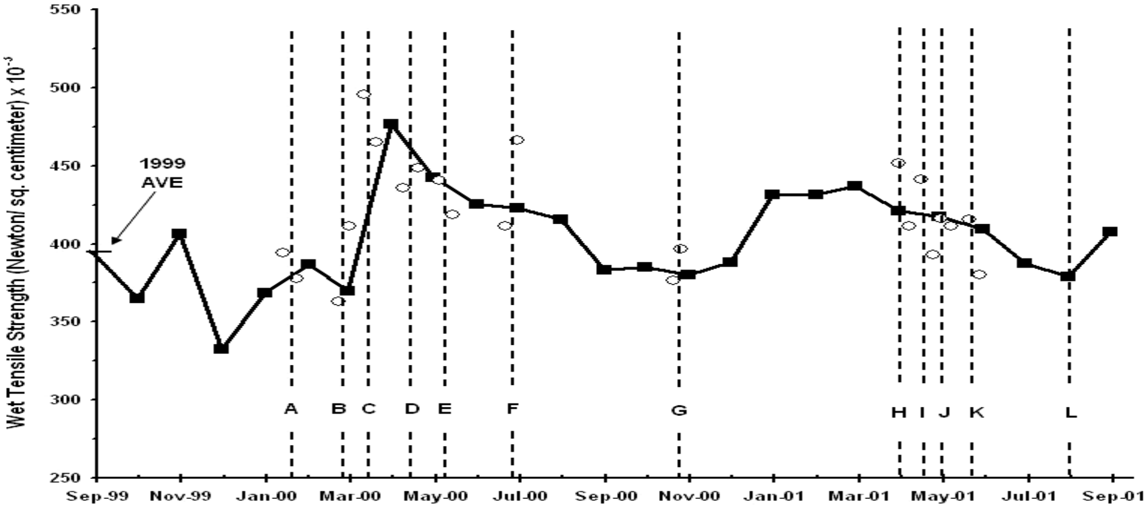


**Fig. 3.5-11: Wet tensile strength at Neenah Plant No. 2 from September, 1999 to September, 2001.**

Other system maintenance/control items should be noted. The AO blackwater clarifier does not require any special attention compared to a non-AO blackwater clarifier. In fact, the reduced MB clay content of the AO blackwater sludge to less than 4% makes disposal of this sludge easier than that for high MB Clay content clarifier sludge. Some additional wear has been observed for muller and cooler wear parts exposed directly to AO water; however, the increased wear is manageable.

In addition to emissions reductions measured during stack testing (not reported here), there has been a noticeable reduction in visible smoke generated during pouring, cooling and shakeout after AO start-up. Dust collection piping runs cleaner without an organic build-up that was typical before AO system start-up. The decreases in duct build-up and decreases in smoke with AO operations are very noticeable, but have not been quantified.

### 3.5.2.3 Summary of AO-DBW system – Neenah Foundry Plant No. 2

- A series of sand system benchmarks have been presented to summarize the performance of an AO-DBW system.
- Key aspects of AO-driven sand system optimization have been reported to show the impact of this potent sand additive on the short term and long-term performance of a sand system.
- Total premix reductions of 35% have been achieved with an improvement in sand system control and decreases in pouring, cooling, and shakeout smoke, odor, and duct build-up.
- Bond reductions are due to both improved bond recovery from an AO-DBW system and improved clay activation from the AO sand system.
- Similar sand system performance and control characteristics can be expected for other production green sand systems when AO processing is introduced.

# 4. SUMMARY

This initial study of the influence of advanced oxidation (AO) on green sand systems and the operating characteristics of foundry AO-clear water (AO-CW), AO-black water (AO-BW) and AO-dry dust-to-black water (AO-DBW) systems has just "scratched the surface" on our pathway to understanding AO system reactions. It has both answered questions and raised questions about the complex AO phenomena taking place in a green sand mold that influences pouring, cooling and shakeout emissions as well as sand properties. The major findings of this research, incorporating the combined research results from laboratory tests, pilot-scale tests and production foundries, are interpreted here.

It is important to note that each foundry green sand system is unique. A foundry AO system, whether AO-CW, AO-BW, or AO-DBW, will have unique operating and performance characteristics. Therefore specific percentage increases or percentage decreases in operating characteristics observed in this study may not be strictly expected in a different foundry setting. However, in general, results reported in this study in one setting or foundry have been reinforced by similar results obtained in another foundry setting. This indicates broad opportunities for AO technology adoption throughout the foundry industry. Similarly, results generated in the laboratory or from pilot-scale testing under "non-foundry conditions" must be interpreted within the context that these experiments were performed under. For these tests, the specific percentage changes in emissions and/or sand performance depend on the test materials and protocols employed. The laboratory and pilot-scale results have reinforced and clarified the results obtained from production foundries.

## 4.1 EMISSIONS

Penn State laboratory tests, as well as CERP/Technikon and foundry stack tests, indicate that significant volatile organic compound (VOC) emissions reductions can be expected when advanced oxidants are incorporated into a foundry's green sand system. VOC emissions reductions to be expected in a foundry are due to the direct effect of advanced oxidants as well as to the AO-driven sand system set point changes from bond (specifically, seacoal) reductions. VOC emissions reductions of 10-50% can be expected from the direct effects of AO additions (i.e. for identical loss on ignition (LOI) levels in the non-AO and the AO greensands). Production AO sand systems, operating with AO-driven lower seacoal levels can be expected to experience overall VOC emissions reductions of 15-75% from both the direct and AO-driven sand system changes. These reductions in emissions are fully observed after months of operation, when the green sand system has fully transitioned to an AO-optimized green sand system.

Emissions reductions can be expected for both cored and un-cored castings. Emissions from organic core binders are a major portion of overall green sand system emissions when there is significant core loading. Water that is laden with AO radicals cannot be mixed with phenolic urethane in the core sand. For this reason, AO radicals will not appear within the core sand when non-aqueous-based core binders are employed. Although these factors limit the positive effects of AO on core emissions, it is also true that during mold cooling, core emissions must typically pass through the AO green sand exterior of the mold before exiting the stack. Because of this, AO additions to green sand molds have actually reduced emissions from cored castings more than would be expected from a simple mass balance calculation.

Although not directly measured as part of this study, reductions in smoke and odor from pouring, cooling and shakeout have been consistently reported by foundries using AO systems. In addition, all foundries using AO systems have reported, but have not quantified, reductions in organic buildup in their ductwork.

CERP/Technikon emissions (HAP, VOC and POM) studies of an AO-CW system indicate that no new emission species were produced from AO-containing green sand molds. This is based on evaluation of a complete set of over 70 analytes from multiple tests specifically designed to identify any additional HAP products emitted during pouring, cooling and shakeout.

TGA mass loss tests, as well as TGA-FID and TGA-GAC tests for mass loss speciation, are effective laboratory tools for evaluating the emissions potential of foundry sands. Also, stepped LOI and MPTE emissions potential tests for system sands, developed by the Wisconsin Cast Metals Association, correlate well with measured stack emissions. Together these types of tests offer useful potential as analysis tools for foundries as part of emissions reduction efforts without conducting expensive stack tests.

## 4.2 GREEN SAND SYSTEM PERFORMANCE

Both AO-CW and AO-DBW systems have a significant impact on green sand system performance. The impact of AO on sand system performance and control has been characterized both in the laboratory and through careful study of the effects of AO on the performance and control of foundry green sand systems.

AO should be considered as a potent sand "addition" that drives a sand system toward lower MB clay and LOI operating set points. Premix reductions of up to 35% have been achieved for AO-DBW systems. These premix reductions in AO-DBW systems are due to both improved clay activation (as measured by an increase in GCS / MB clay) and the enhanced performance of blackwater clarifiers (as measured by increases in affluent MB clay levels). For AO-CW systems, reductions in premix consumption of up to 20% are the result of improved clay activation and mullability.

The effects of AO green sand systems have been evaluated for foundries using both western bentonite clays and western/southern bentonite mixes, although most of the sand system performance data is from foundry and laboratory study using 100% western bentonite systems. The primary effects of AO on the performance of foundry green sands are on the compactability and the mullability of green sands. AO additions thus result in an immediate increase in the green compressive strength for sand systems operating under compactability control, necessitating an immediate decrease in premix addition. This in turn increases the mulling energy input per unit of clay, further activating clay and increasing green compressive strength. This "ratcheting" effect significantly reduces the premix additions necessary to maintain green compressive strength over a period of months. The shutdown of AO systems for repair or maintenance requires an immediate increase in premix addition levels to avoid drops in green compressive strength. The drop in sand system coal (LOI) levels accompanying reduced MB clay levels is a major component of the overall emissions reductions that has been reported for "optimized" foundry AO sand systems. Casting surface finish remains acceptably high for AO sand systems even though seacoal levels are significantly reduced. These reductions in seacoal levels, without scrap increases, are not possible without AO additions.

# 5. FUTURE WORK

This initial study of AO system behavior has demonstrated both the emissions benefits and the green sand system performance improvements that can be achieved for iron foundries. The broad scope of this pioneering work is only a first step in developing a comprehensive understanding of the complex catalyzed AO reactions taking place in the sand mold during mulling, compaction, pouring, cooling, shakeout and sand recycling. Further study of the corresponding AO reactions and AO-driven influences on green sand molding systems in foundries is needed. Both fundamental and applied studies are necessary to further understand AO processing and to find ways to successfully enhance the effectiveness and control of AO reactions. In particular, the initial work performed in this study points to further research needed in the following areas:

## AO reactions

- Fundamental study is necessary of the complex, catalyzed, peroxone and sono-chemistry reactions taking place in green sand molds and in AO blackwater clarifiers at ambient and elevated temperatures.

- Investigate the hypothesis that AO emission reductions are driven by AO enhanced formation of activated carbons from seacoal in the mold environment.

- Develop a further understanding of temperature-dependent AO reaction kinetics.

## Emissions performance

- Additional CERP/Technikon and foundry stack testing to optimize AO system emissions performance and to optimize component additions (hydrogen peroxide, ozone and sonication).

- Characterize the reductions in in-plant smoke and odor and in ductwork condensable build-up that have been reported with AO system operation in foundries.

## Sand system performance

- Comprehensive evaluation of the influence of AO system components and their interactions on green sand system properties and control.

- Fundamental study of the influence of AO system and AO components on the activation of clays during sand system processing.

- Clarify the role of soda ash additions and other pH modifiers on AO system performance.

- For AO-BW and AO-DBW systems, characterize the performance of blackwater clarifiers with AO additions.

- Study the effectiveness of AO processing on other types of green sand systems, namely:
  - southern bentonite sand systems
  - non-ferrous sand systems (lower sand peak temperatures during pouring, cooling, and shakeout)
  - sand systems with olivine rather than silica sand

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# APPENDIX B: Extended Research Bibliography

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