Incorporating Advanced Oxidation into Your Operation for Management and Engineers

November 20, 2003

By
Steve Lewallen, Neenah Foundry Company
and
Jim Furness, Furness-Newburge, Inc.

What is Advanced Oxidation (AO) as used in the foundry industry ?

- Advanced oxidants (and reductants) are created in sand system process water with the addition of small amounts of ozone, hydrogen peroxide, and in the presence of intense sonication

  <u>AO-Clean Water</u>: sand system water treatment only

  <u>AO-Black Water</u>: dust reactivation and return in an AO treated blackwater slurry

  <u>AO-Core Room Odor Scrubbing</u>

Basis for Beginning the Process at Neenah Foundry Company

- WI Air Toxics Rule - NR445 (Table 3) Compounds
  - 300 lb./yr. benzene
  - 250 lb./yr. formaldehyde
  - LAER (Lowest Available Emission Rate) Incineration cost: $3,500,000/yr. Fuel estimate ***per (Disa) molding line***
  - VARIANCE = BACT (Best Available Control Technology) Worked with the WDNR on sand system optimization while pursuing Advanced Oxidation options

Neenah's Implementation

- Began with "sand system optimization"
- Developed and implemented sand system based mathematical modeling*. Sand system "art" started to become a predictable science.
- Plant 3 = 1st Neenah AO process implementation. Research began in 1995.
  - Clear water
  - Clay and coal recycle

*See XL file

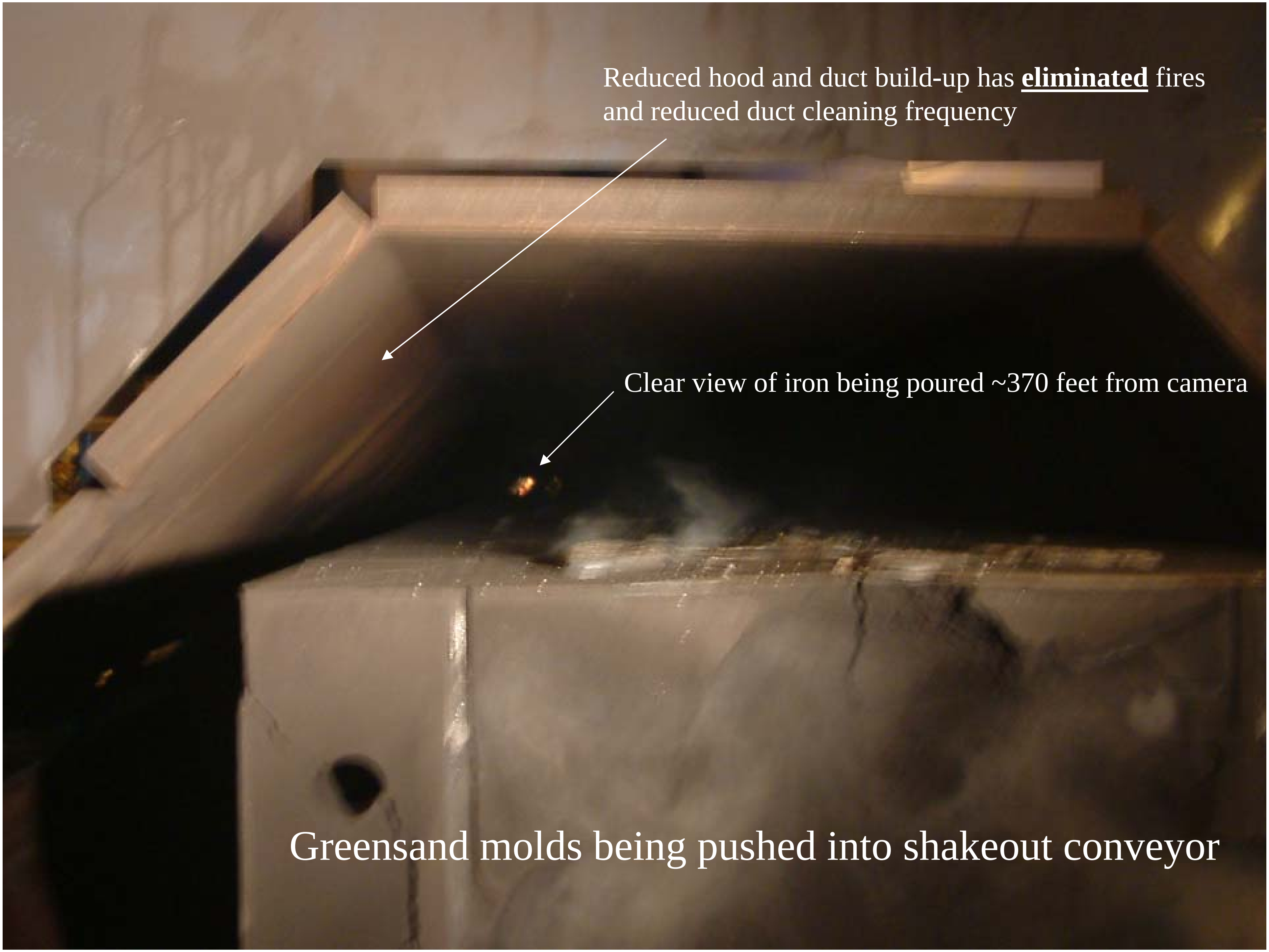
Neenah's Implementation

- Sand System Optimization: The ongoing process of investigating and documenting the sand system changes and equipment changes needed to reduce organic emissions to the minimum level that will allow production of quality castings without increasing scrap.

Neenah's Implementation

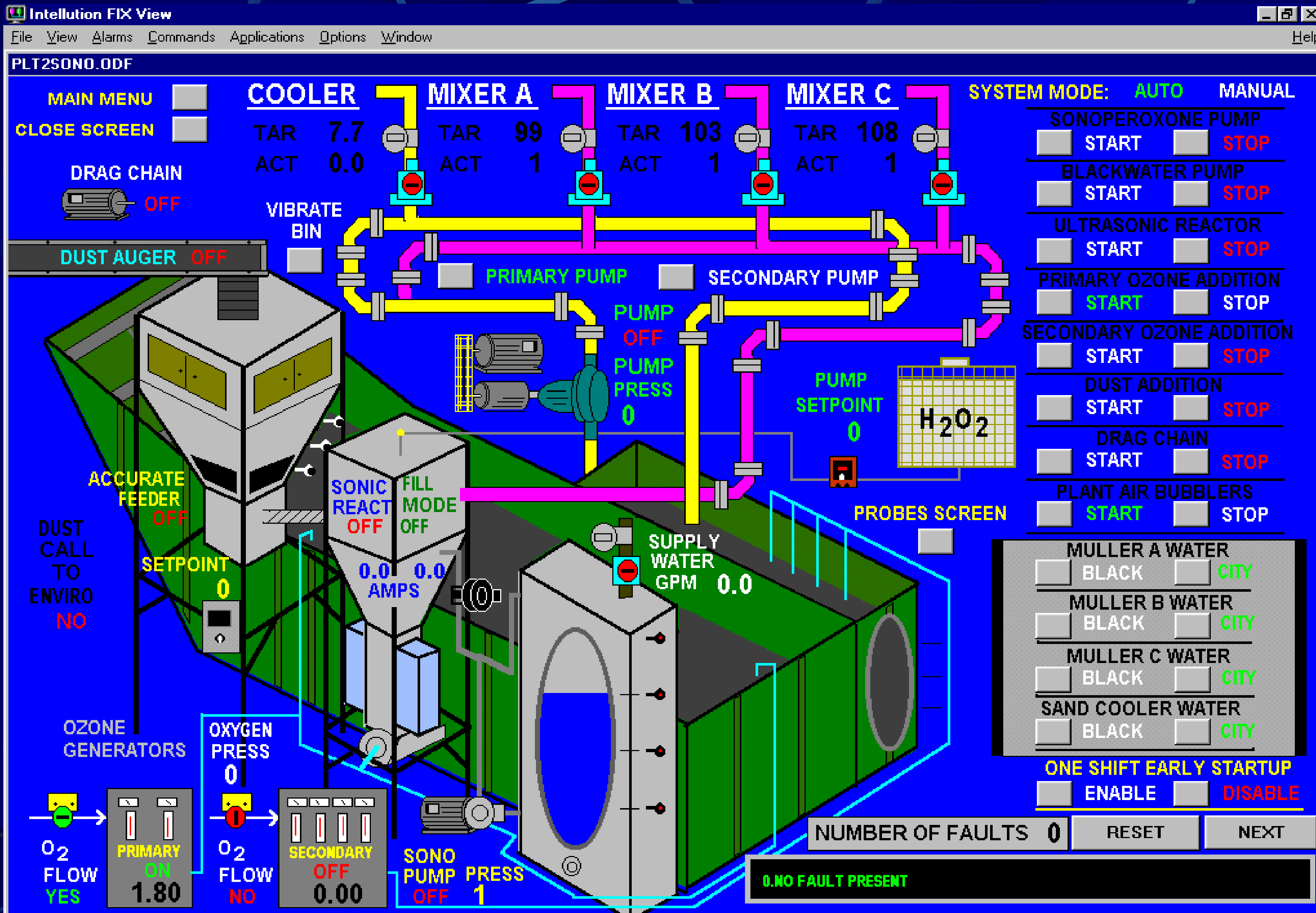
- Established the proper grain sizing of core and make-up sand to minimize sand additions to the green sand system and therefore reduce premix additions.
- Reduced the combustible levels to a minimum to reduce material cost and reduce emissions.
- Made adjustments to the dust collection system to minimize carry out.
- Did a complete review of pre-mix addition practices and formulas used to determine addition rates.
- Added an Advanced Oxidation-Clean Water System.
- Used a caustic to chemically treat the bentonite and control pH.
- Reintroduced baghouse material through the AO system making it an Advanced Oxidation Dust to Black Water System.


Ultrasonic Reactor
Peroxide Tote
& Secondary Containment


Reduced hood and duct build-up has **eliminated** fires and reduced duct cleaning frequency
Clear view of iron being poured ~370 feet from camera
Greensand molds being pushed into shakeout conveyor

Dust feed from new baghouses
Dust mixer and acoustic system
5000 gallon system retained from replaced wet dust collecting system

Black Water System



Active clays can be more effectively recovered in AO-BW and AO-DBW systems.

Blackwater Clarifier Properties:	Baghouse Dust	Waste Sludge	Blackwater
MB Clay, %	34	3	51
LOI, %	20	11	22
Percent Sand, %	47	86	27

Baghouse Dust Processed, [Ave Tons per day]	11**
Blackwater Processed, [Ave Tons per day]	84
Waste Sludge Processed, [Ave Tons per day]	6
System Clay as recycled from BWC, %	23
System Coal as recycled from BWC, %	30

AO system performance summary

	AO-CW	AO-BW	AO-DBW
Emissions	10-30% Benzene 20-40% VOC	20-50% Benzene 30-75% VOC	50% Benzene 30-75% VOC
Sand System Performance	15-35% Clay less consumption	20-35% Clay less consumption	27%-42% Clay less consumption
Other Benefits	Reduced in-plant smoke and odor Reduced stack odor Reduced build-up of condensables in ductwork		

Existing Neenah Group Installations

- Neenah Plant 3 – “clean water” system (Ductile Iron)
- Neenah Plant 2 - clay/coal recycle “blackwater” system (Gray Iron)
- Dalton Warsaw – “clean water” system (Gray Iron)
- Gregg Industries – integrated core room odor scrubber with clay/coal recycle “blackwater” system (Ductile & Gray Iron)

Future Neenah Group Installations

- Dalton Warsaw – Converting and expanding existing system to clay/coal recycle “Blackwater” system
- Neenah Plant 2 - Engineering an expansion of existing “Blackwater” system
- Neenah Plant 3 - Engineered conversion of clean water system to a “Blackwater” system

Neenah Foundry Conclusions at one installation

- Emissions Reductions Realized
  VOCs are down 48% due to optimization conditions, down more than 84% from mid 1990s testing (98% in latest testing)
- Bond Reductions Realized
  200#/ton prior to Optimization (32% pre-mix coal)
  187#/ton after Optimization (25.5% pre-mix coal)
  127#/ton after AO (22.4% pre-mix coal)
- Cost Savings Realized
  $4.80/ton poured $1,460,000/yr. with AO
  $1.04/ton poured $ 260,000/yr.Optimized only
  (yearly value assumed 1000ton/day)

Jim Furness discovered the foundry green sand advanced oxidation reaction in the late 1980s while researching chemical reactions associated with relatively standard ultraviolet-ozone destruction of drinking water disinfection by-products.

The dusty environment of a sand system caused the ultraviolet lamps in this early device to stop producing the reaction within minutes.

This problem was solved several years later by Jim's development of the radically different "ultrasonic-peroxide-ozone" foundry specfic *PROCESS.*

A Pollution Prevention Process

The PROCESS is a "***non-end of pipe***" pollution prevention process that treats the city water used in a foundry's sand molding operations with advanced oxidants – ozone, hydrogen peroxide, and high intensity sonication.

The original concept was expanded to ultrasonically recycle the normally land fill disposed coal and clay from a foundry's particulate collection systems.

After equipment start-up, the sand systems begin responding much more predictably to clay/coal additions. Consequently, the PROCESS must include "re-optimization" of the sand system **properties and control methods**.

Discussion of “Generic” Terminology

The acronym **AOP** for Advanced Oxidation Process, is a generally accepted term for ***<u>any</u>*** process that generates the “super oxidant” OH radical in water. This “super oxidant” can be created with a wide variety of methods. These methods can range from:

- illuminating water with a simple UV lamp
- adding some ozone or peroxide
- blasting the water with electron beams

If the generic term “AO” is used “stand alone” when describing what is actually being done in the foundry industry, it is a very deceptive use of the term. The synergistic use of acoustic science and post equipment installation operational changes are, in most cases, much more important to the foundry than the mere generation of “super-oxidants”.

To be much more technically correct and non-commercial as possible, for the rest of this presentation we will be using the generic, non-trademarked acronym *AAOP* (Acoustic Advanced Oxidation Process) where *practical* when describing the *equipment* used in the foundry *PROCESS.*

AAOP System

Motivations for Installation

Reduce organic pollutant emissions

- Reduce smoke and odor in foundries
- Reduce neighborhood odor complaints and associated legal costs
- Reduce benzene and VOC emissions to meet regulatory limits
- Reduce solid wastes

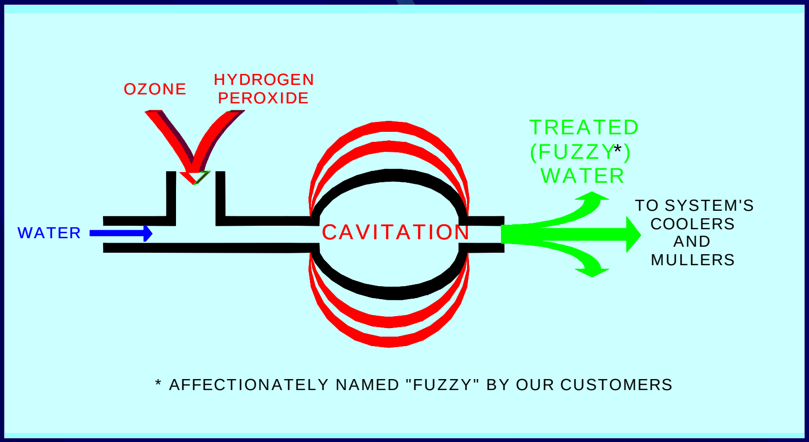
Improve sand system performance

- Improve sand strengths → reduce mold cracking
- Reduce bond consumption → save money
- Improve the predictability of sand system properties

The existing types and an installation layout of AAOP equipment presently in use in the foundry industry

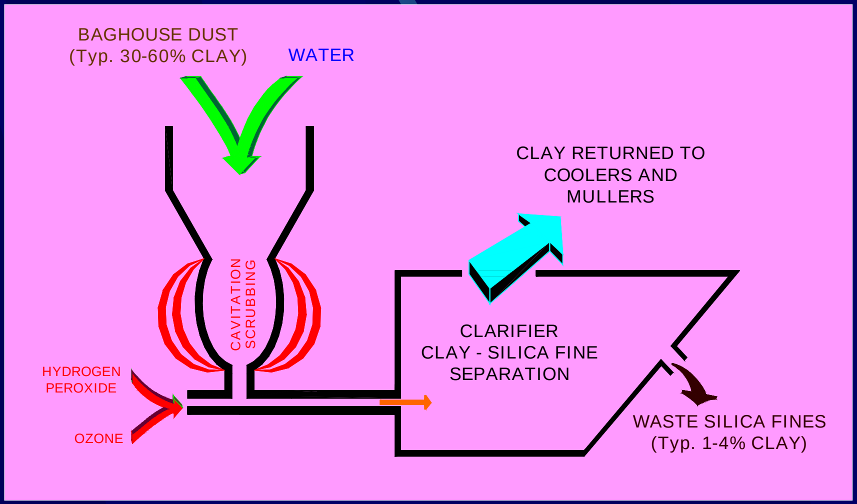
AAOP Clean Water System

The CLEAN WATER systems treat the city water used in a foundry's greensand molding and sand cooling operations with advanced oxidants generated from the combination of ozone, hydrogen peroxide, and sonication.



AAOP Blackwater System

The BLACKWATER systems apply additional acoustic techniques to advanced oxidation treatment concepts in order to recycle the coal and clay from a foundry's dust collection systems to reduce solid waste disposal and to further reduce bond consumption.



Foundry Industry Odor Removal

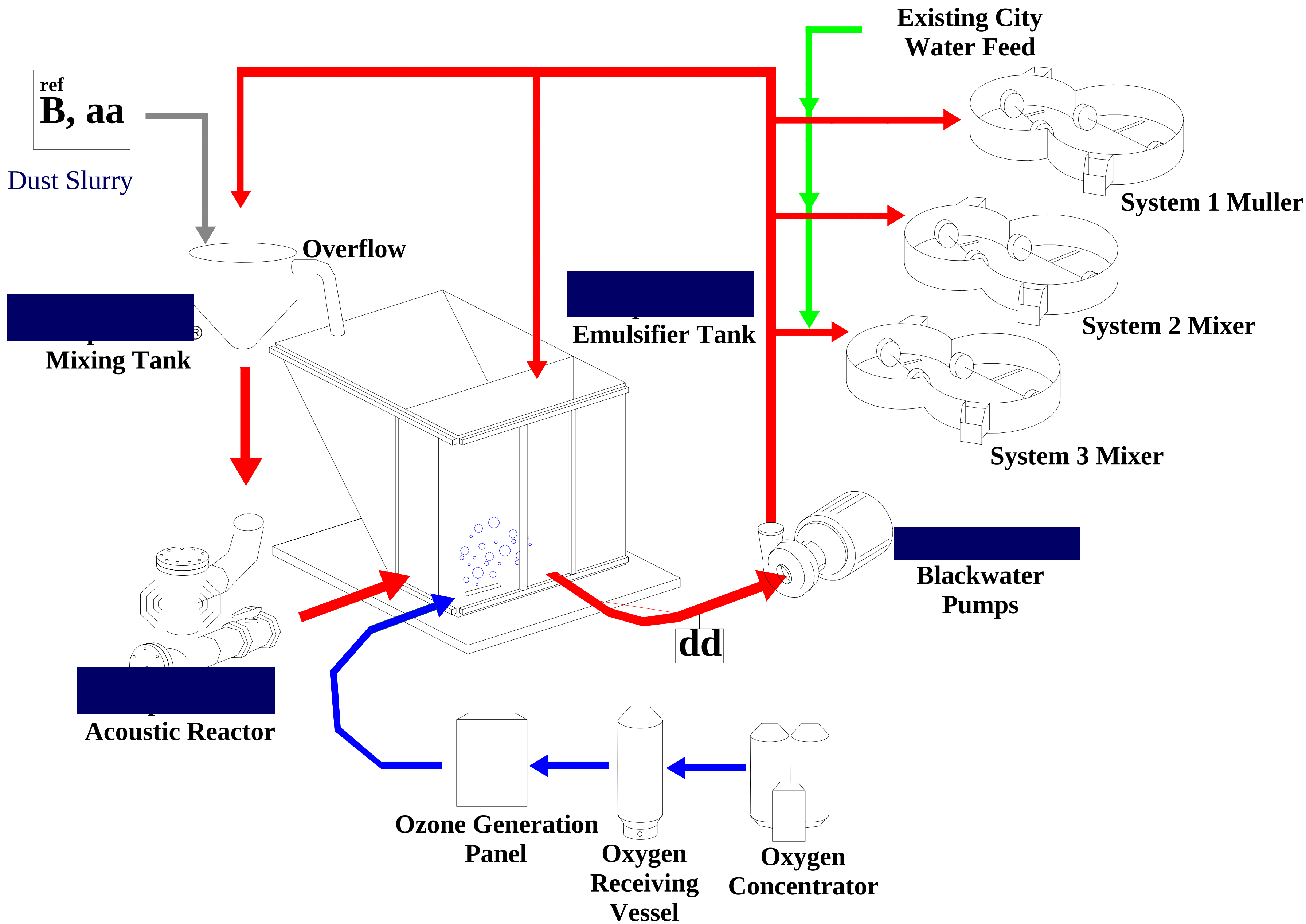
AAOP System for Core Room Odor Scrubber --Removes objectionable odors emitted during core room operations and potentially replaces sulfuric acid scrubbing.

Innovative Clean Air Technologies contract funded by California Air Resources Board and the South Coast Air Quality Management District. Work on contract started July, 2002.

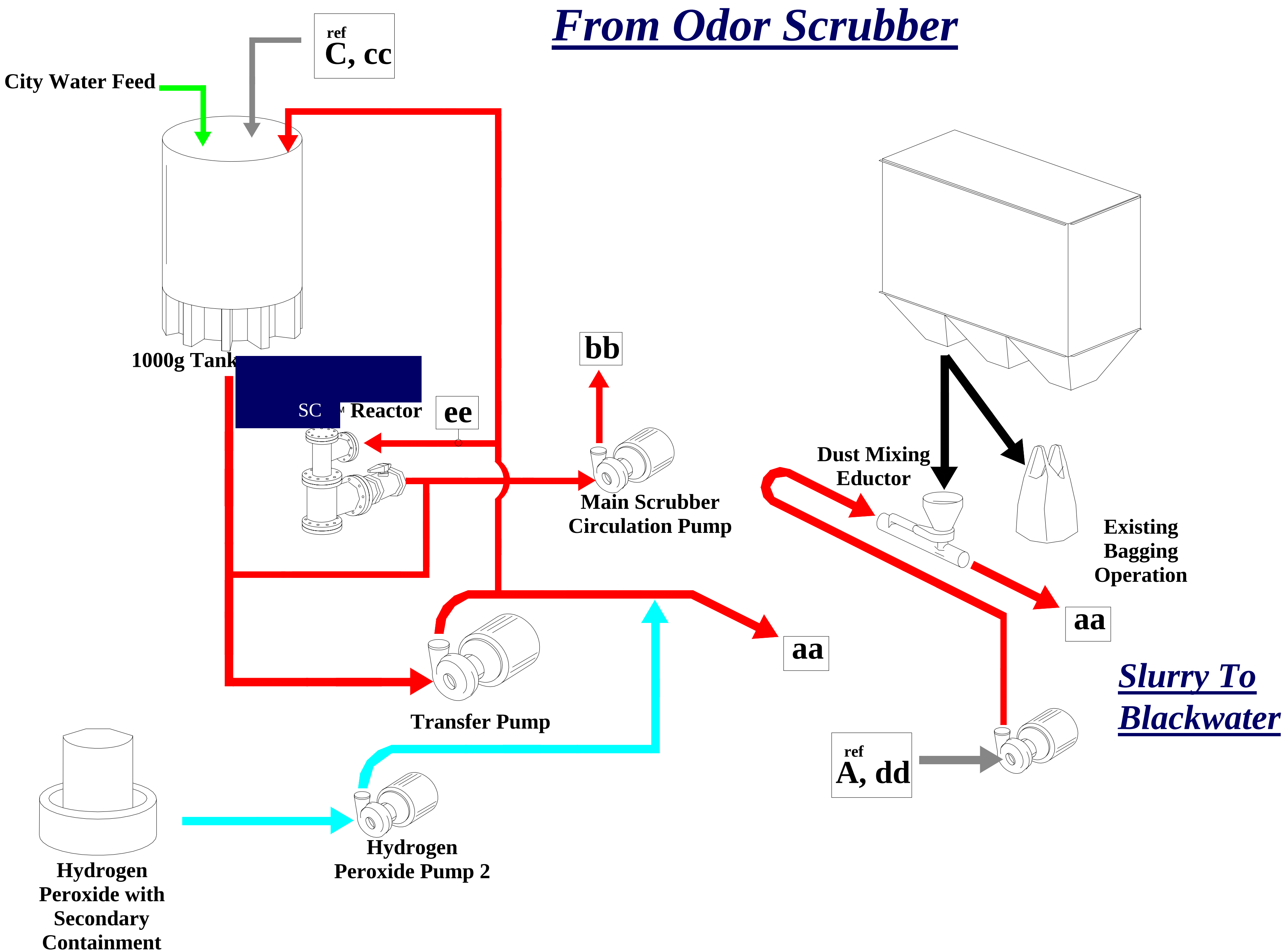
The team of Furness-Newburge, TechSavants, California State University at Pomona, Gregg Industries and Neenah Foundry are participants in this research. Gregg is now the first to have an integrated AAOP Clay Recycle System and an AAOP Core Room Odor Removal System. The AAOP systems provide much higher operating efficiencies for the foundry and minimize/eliminate handling and disposal of hazardous materials from a core room scrubbing system.

AAOP Core Room Odor Scrubber in operation at a California iron foundry. Integrates an advanced Sono-catalytic reactor, UV photo-catalysis and air phase wet oxidation with Clean Water AND Black Water AAOP systems.

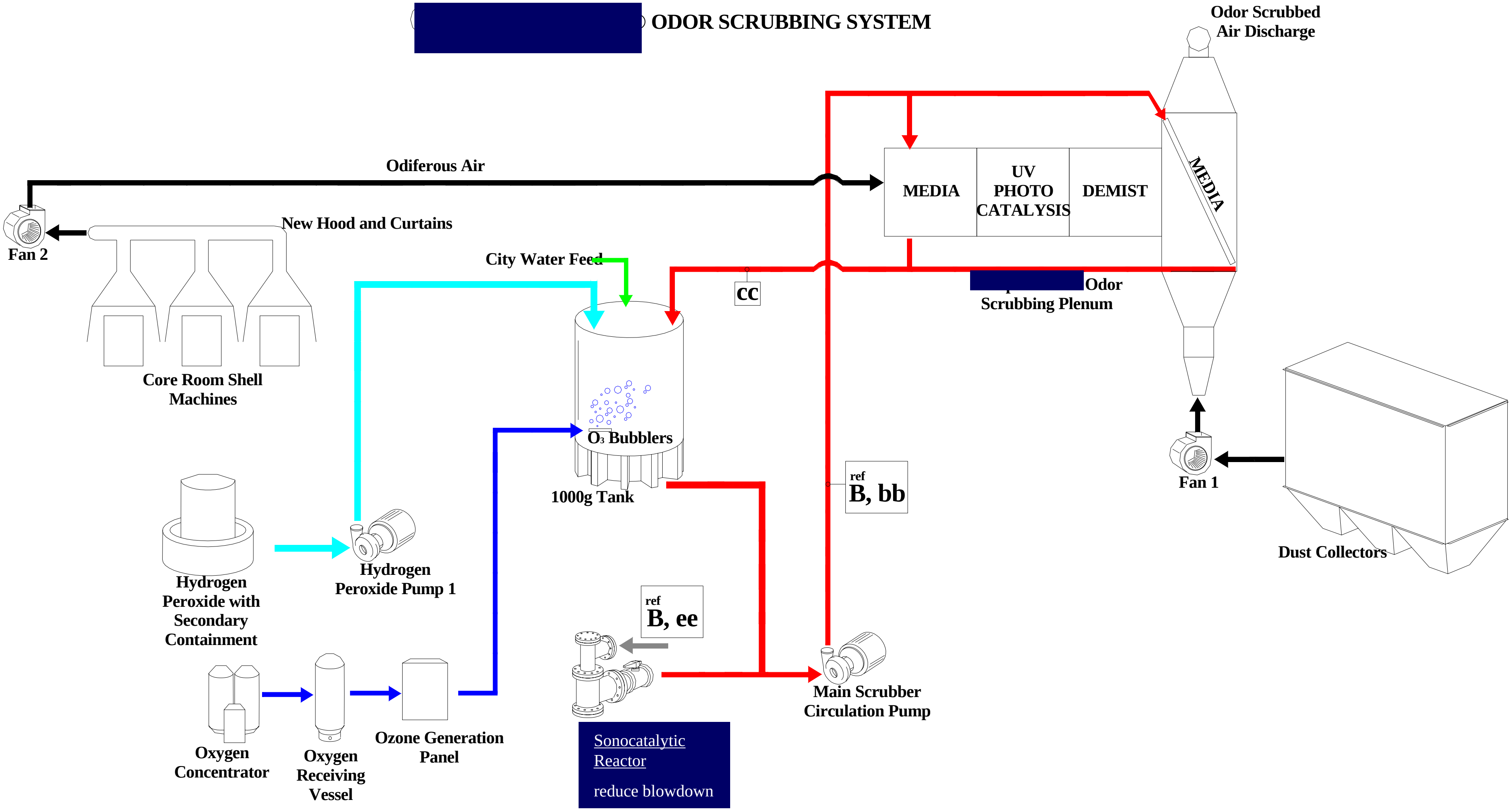
[redacted] BLACKWATER SYSTEM



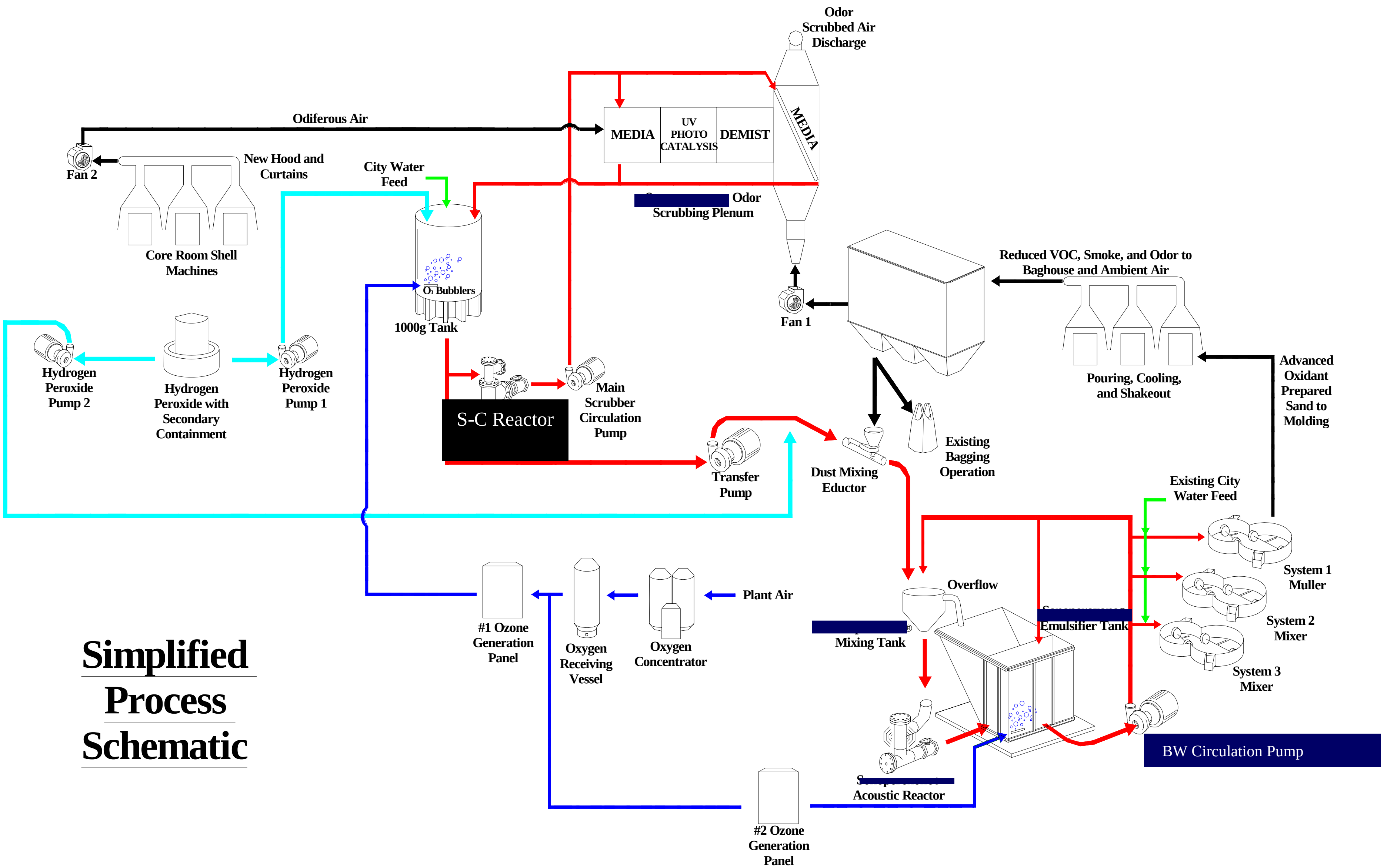
(B) WATER TRANSFER AND DUST FEED SYSTEM



[redacted] ODOR SCRUBBING SYSTEM



Simplified Process Schematic



In addition to foundry use, customized versions of the foundry industry developed clean-water AAOPs are destroying PCBs in landfill leachate and ground water, cleaning natural gas storage wells, stimulating oil well production and destroying odors from agricultural wastes.

AAOP System

History

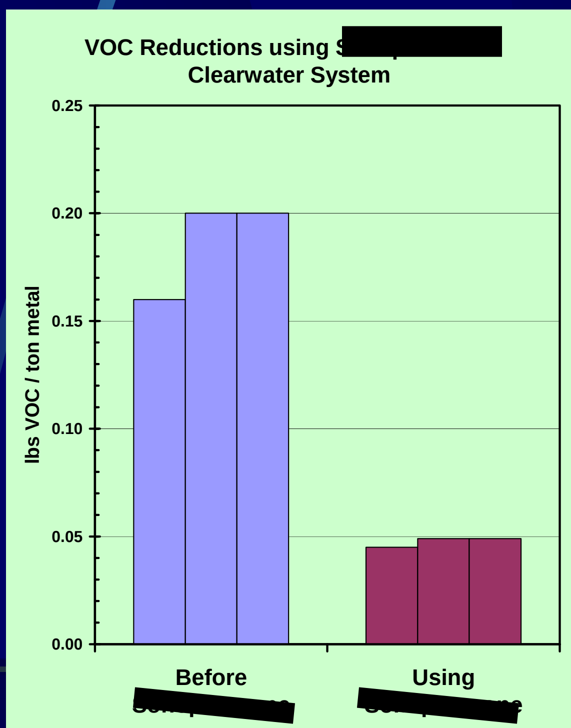
- First Clean water installation: Dec. 1994
- First Blackwater installation: May 1997
- First Dry Dust to Blackwater: Jan. 2000
- First Brass Foundry: May 2002
- First Core Room Odor Scrubber integrated into Dry Dust to Blackwater: July 2003
- Currently ten systems in seven foundries are operating in the U.S. and Canada (6 clean water, 3 blackwater, 1 core room odor scrubber)
- 5 more Blackwater systems are presently being installed or engineered in the U.S.

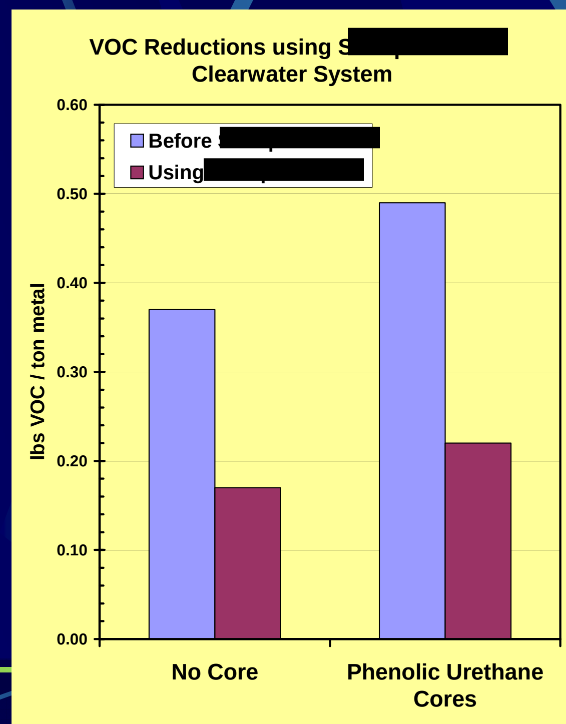
Several government agencies have supported research at Penn State into the Furness-Newburge AAOP systems via grants from the DOE-CMC (1998-2001), DOE-NICE3 (2001-August 2004), NSF-EPA (2001-present)

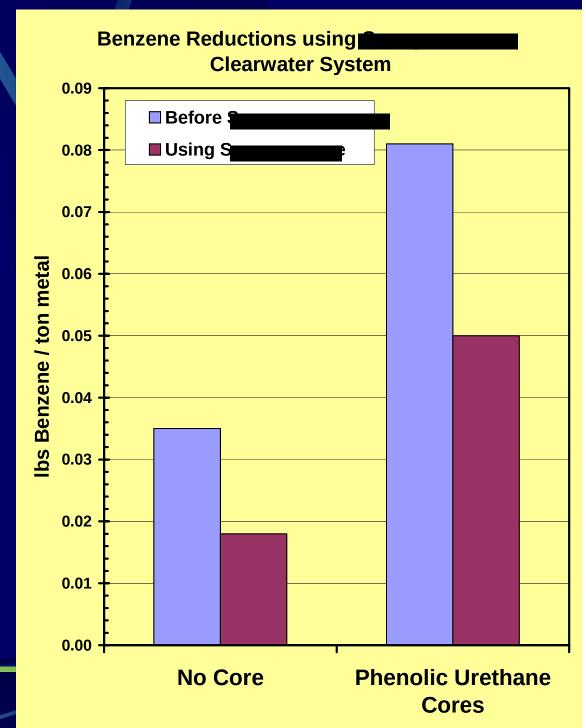
AAOP System

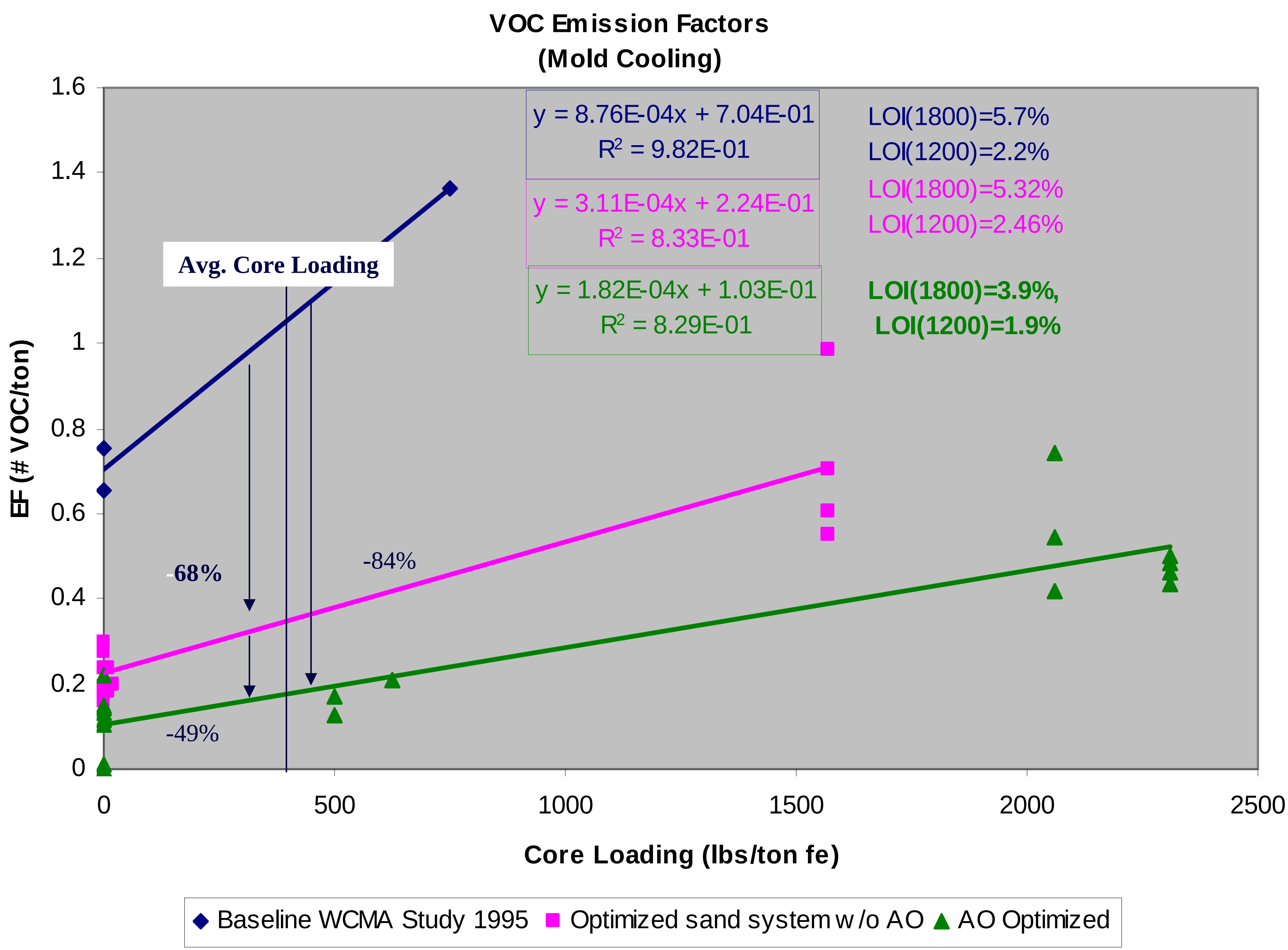
Emission Reduction Results

Emission reductions vary with coal and organic content of green sand mixture and with core size and type – just as a foundry's emissions will vary.







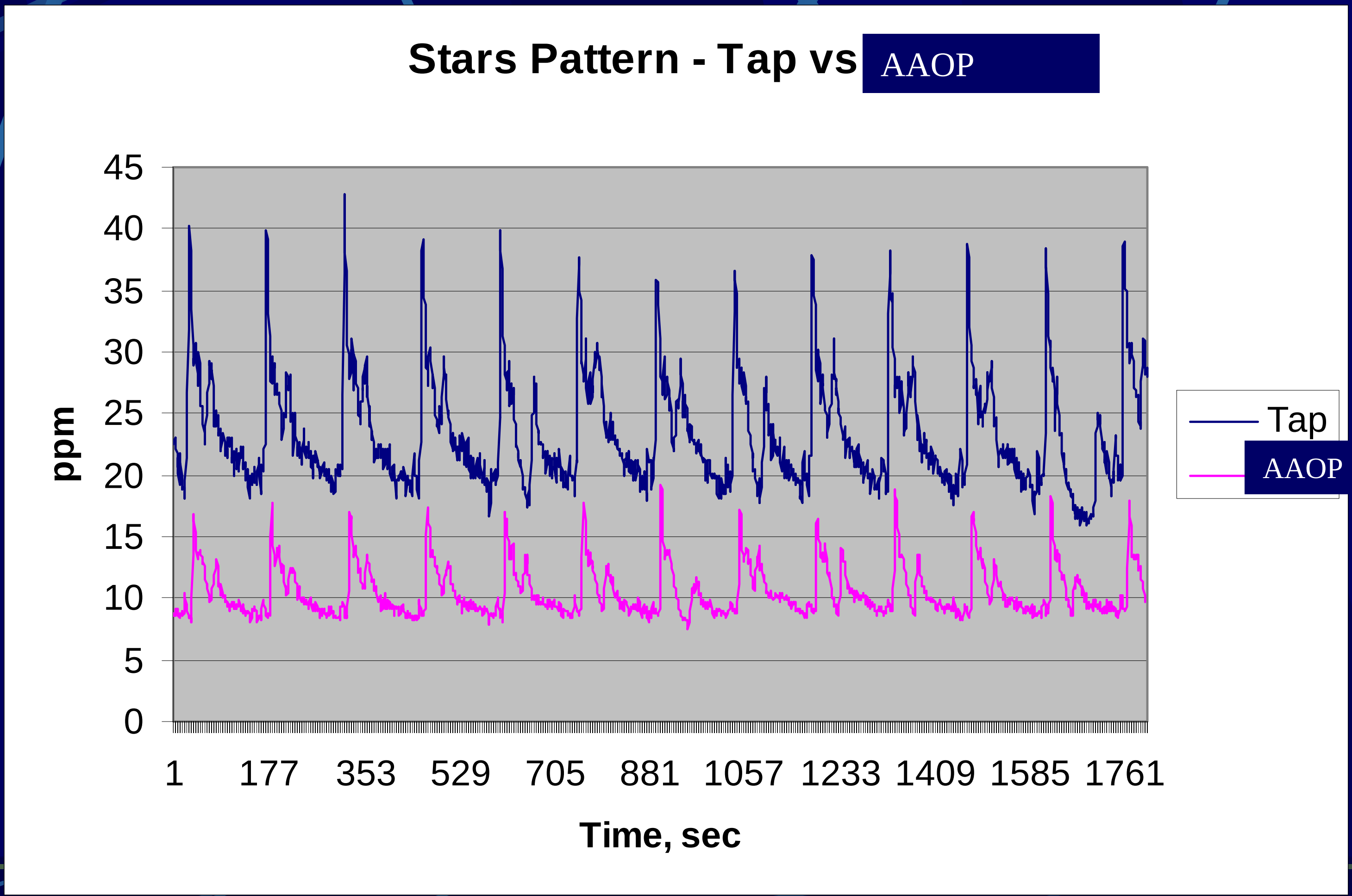

VOC Emission Factors
(Mold Cooling)
y = 8.76E-04x + 7.04E-01
R2 = 9.82E-01
y = 3.11E-04x + 2.24E-01
R2 = 8.33E-01
y = 1.82E-04x + 1.03E-01
R2 = 8.29E-01
LOI(1800)=5.7%
LOI(1200)=2.2%
LOI(1800)=5.32%
LOI(1200)=2.46%
LOI(1800)=3.9%,
LOI(1200)=1.9%
Avg. Core Loading
-68%
-84%
-49%
EF (# VOC/ton)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
500
1000
1500
2000
2500
Core Loading (lbs/ton fe)
Baseline WCMA Study 1995
Optimized sand system w/o AO
AO Optimized

How does this compare to the published proposed new source MACT Standard of <u>20 ppmv</u> <u>VOCs</u> for a sand system?

<u>After AAOP and optimization:</u>

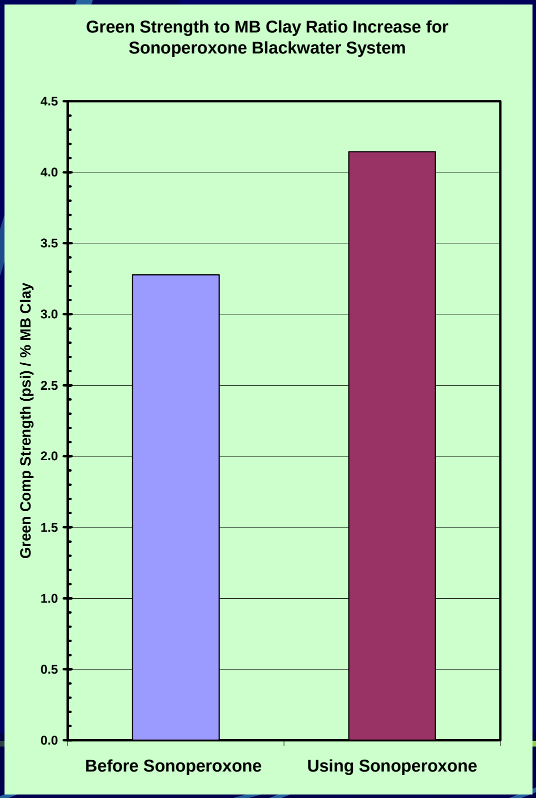
- A Wisconsin foundry has tested 1-18 ppmv on last certified stack test (EPA method 18 as propane) (Extremely heavy cored)
- A Wisconsin foundry has tested 4-10 ppmv with heavy core load (WI Occupational Health Lab)
- A Pennsylvania foundry has tested .8 to 3 ppmv after AAOP but before optimization is complete (EPA method 18 as hexane)
- A heavily shell cored California foundry tested less than 6 ppmv.
- A federally funded California research foundry has tested 14-16 ppmv via real-time FID (EPA method 25) of heavily cored engine block tests, lower on high surface area no-core. See graph provided.

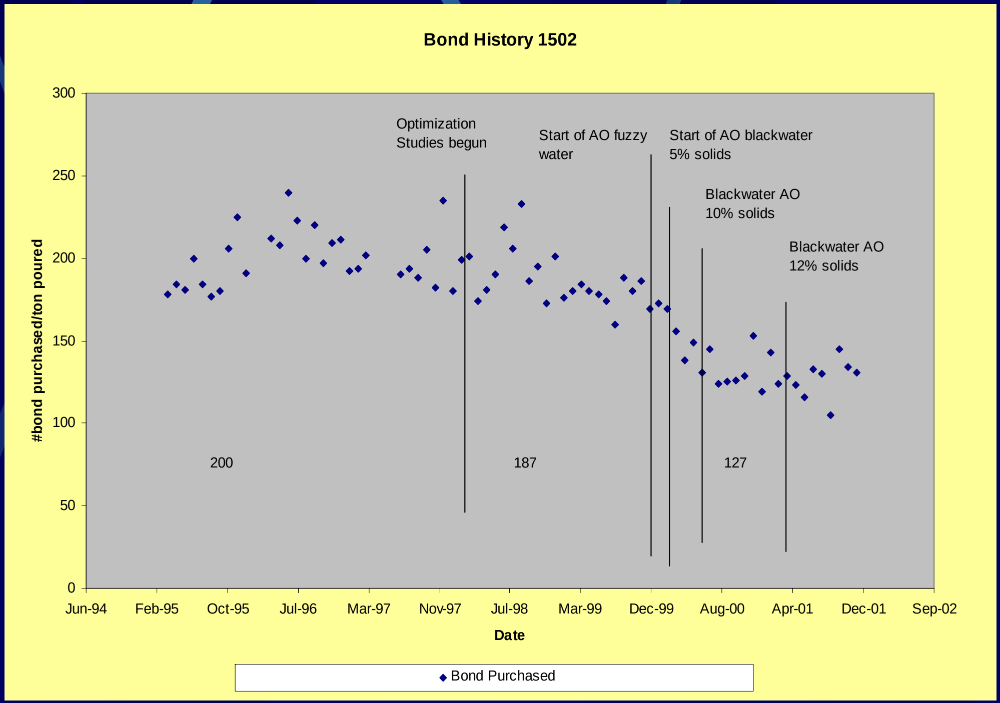
AAOP
Real Time Test Results
Pouring, Cooling & Shakeout in Production Foundry



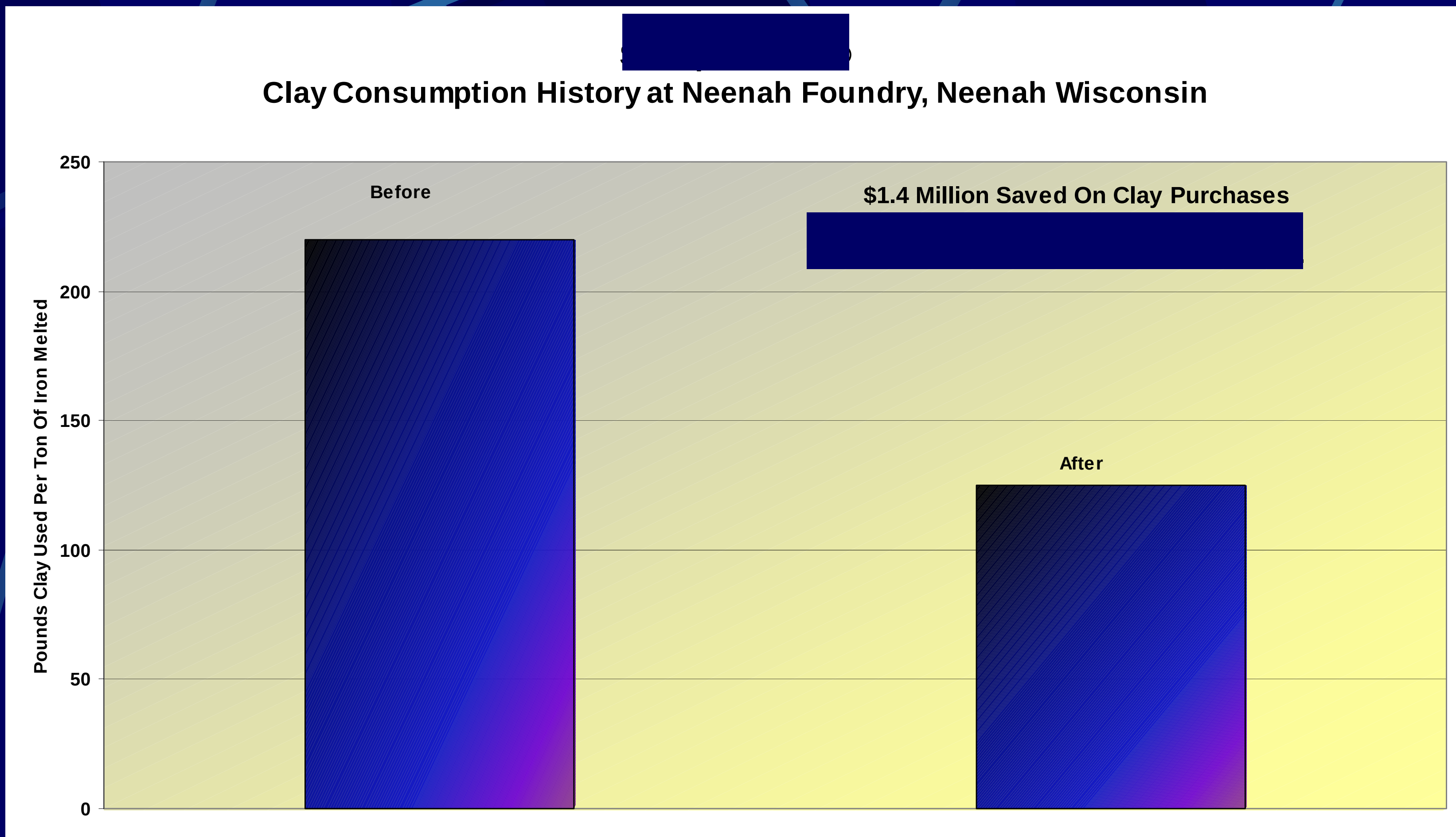
AAOP System
Sand Property Changes

AAOP system implementation reduces the need for coal and clay and can improve sand strength





Foundry Industry - AAOP Greensand Clay/Coal Recycle Systems



Neenah Foundry received one Wisconsin, two National and one International award for the AAOP System.

AAOP

How does it do what it does?

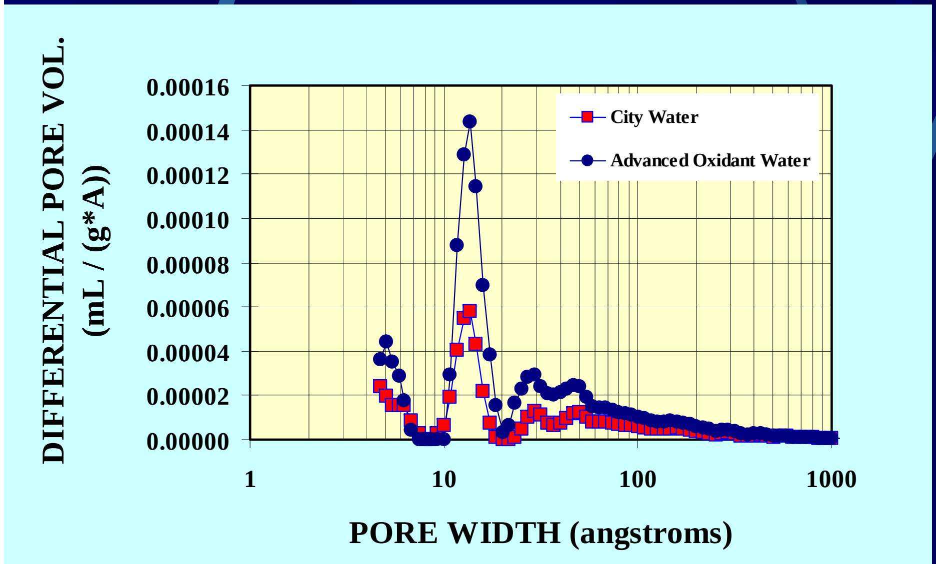
- In production we observe
  - Reduced organic pollutants
  - Higher GCS/MB Clay
  - Lower bond consumption
- Advanced oxidation accomplishes much of this by:
  - Generating greater porosity in the sand system so pollutants are adsorbed instead of released
  - Catalytic, ambient and elevated temperature Advanced Oxidation of adsorbed VOCs
  - Altering the surface charge of the clay
  - Better hydration of the clay

Following are a series of slides showing ongoing DOE, EPA and NSF funded research at Penn State

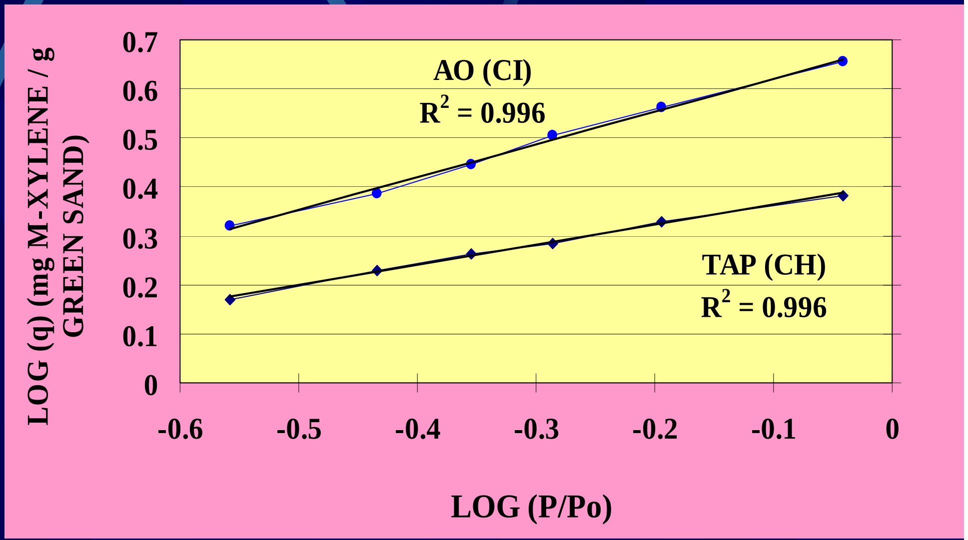
AAOP System

How does it do what it does?

Pore Structure via Argon Adsorption



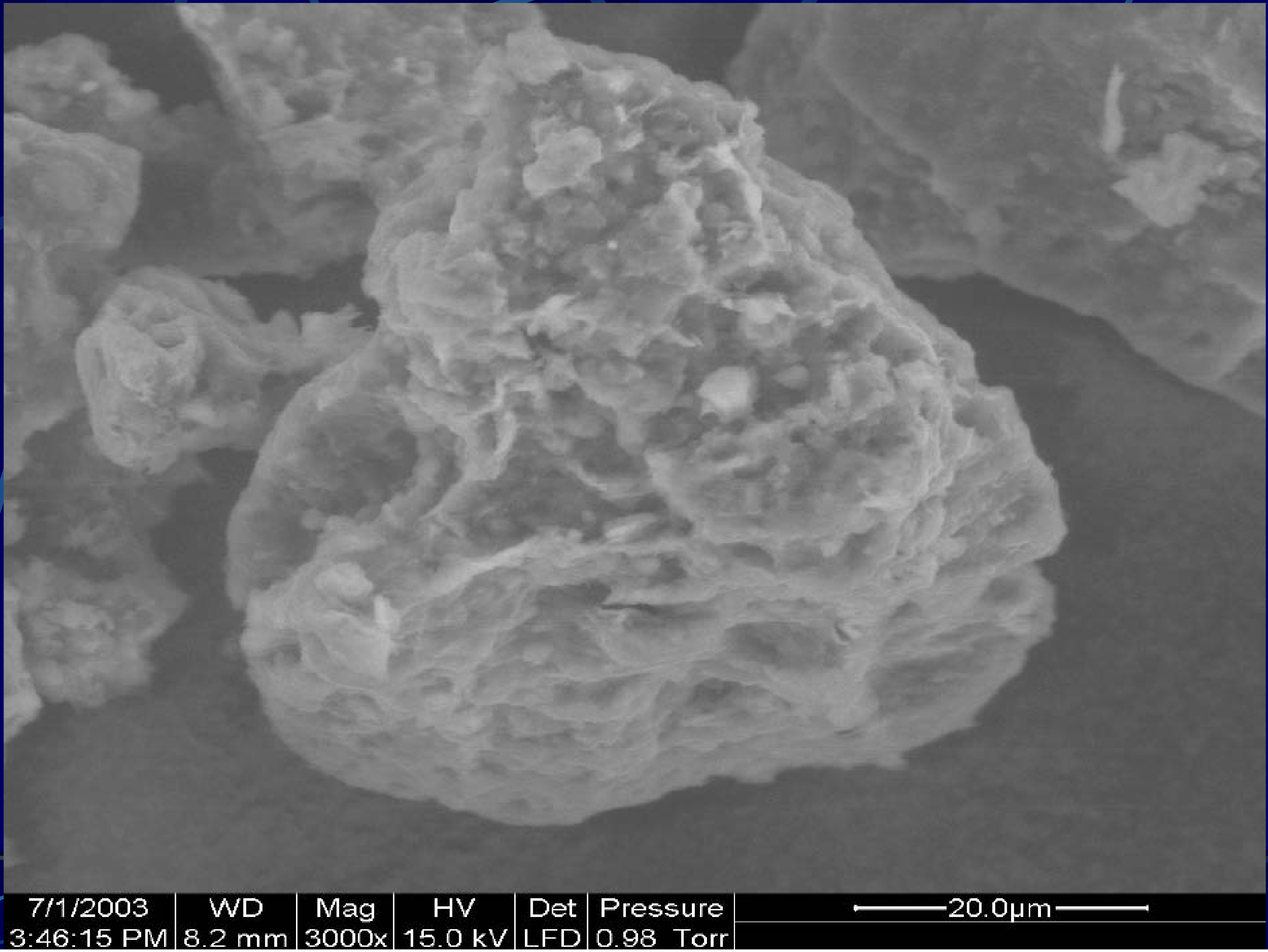
m-Xylene Adsorption



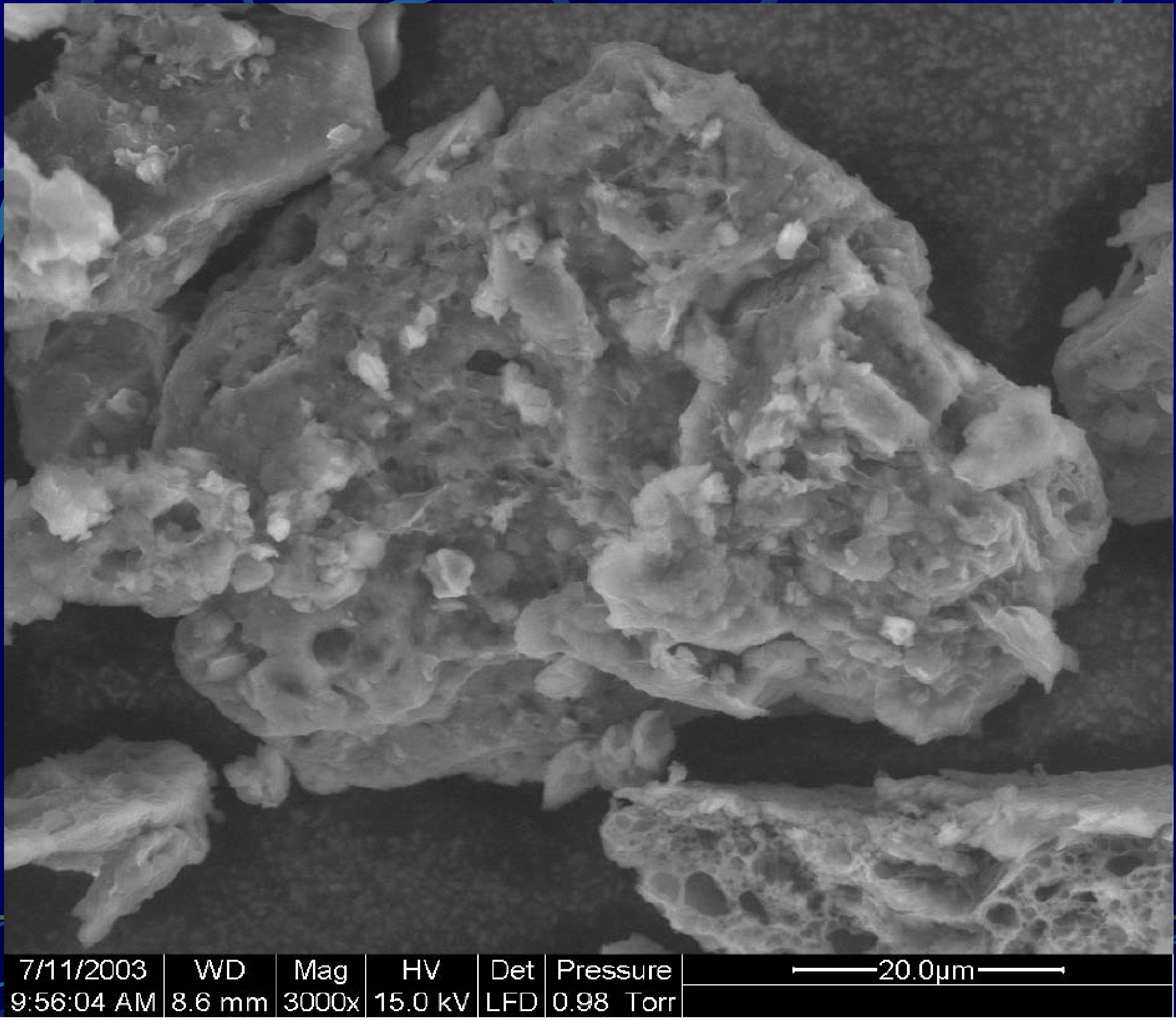
A simplified explanation of these tests is available

Following are a series of PSU "WET SEM" photographs illustrating clay pore structure during simulated conditions encountered during various baghouse clay recycle scenarios.

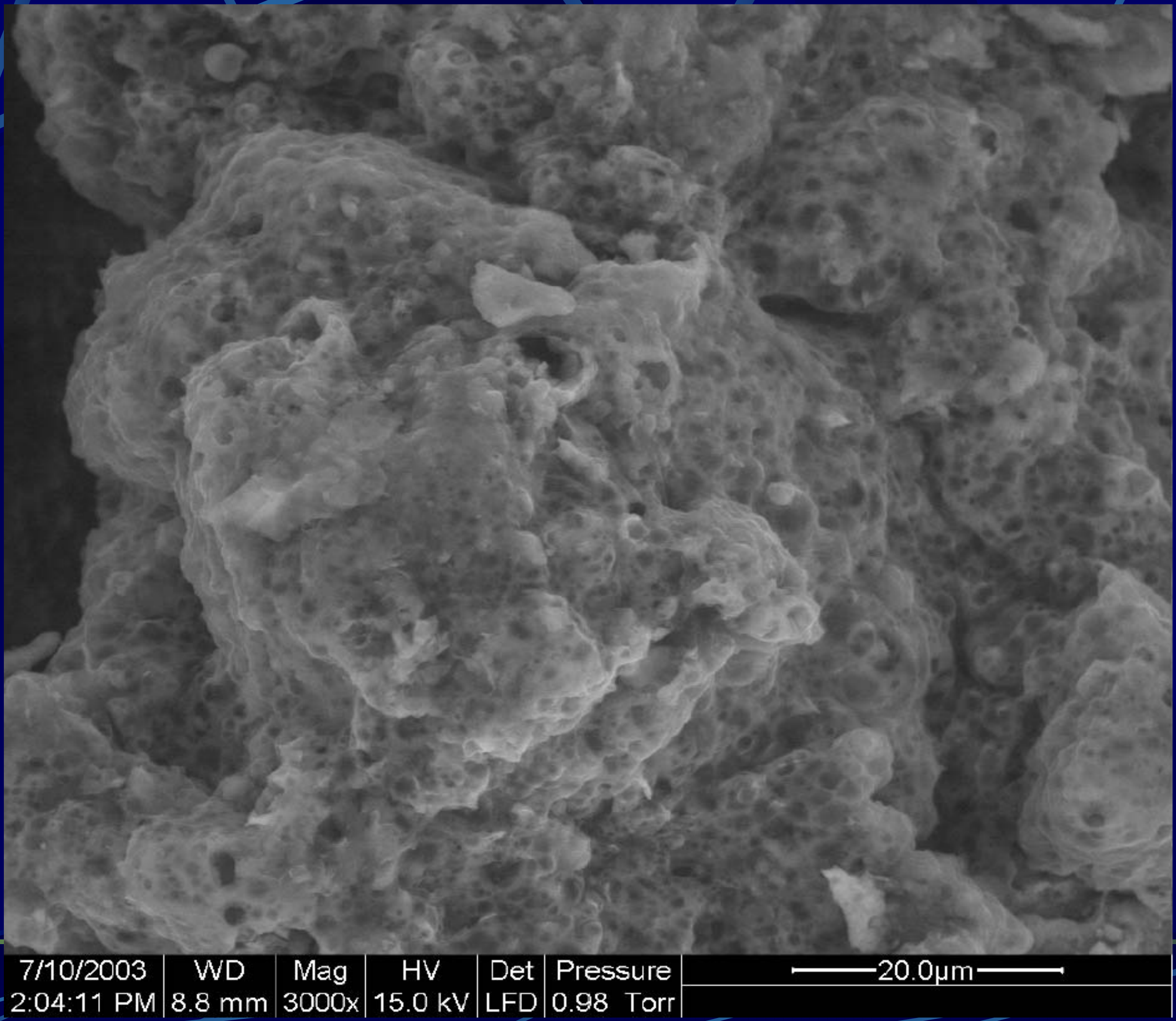
Raw dust stirred in city water to simulate "conventional" blackwater systems



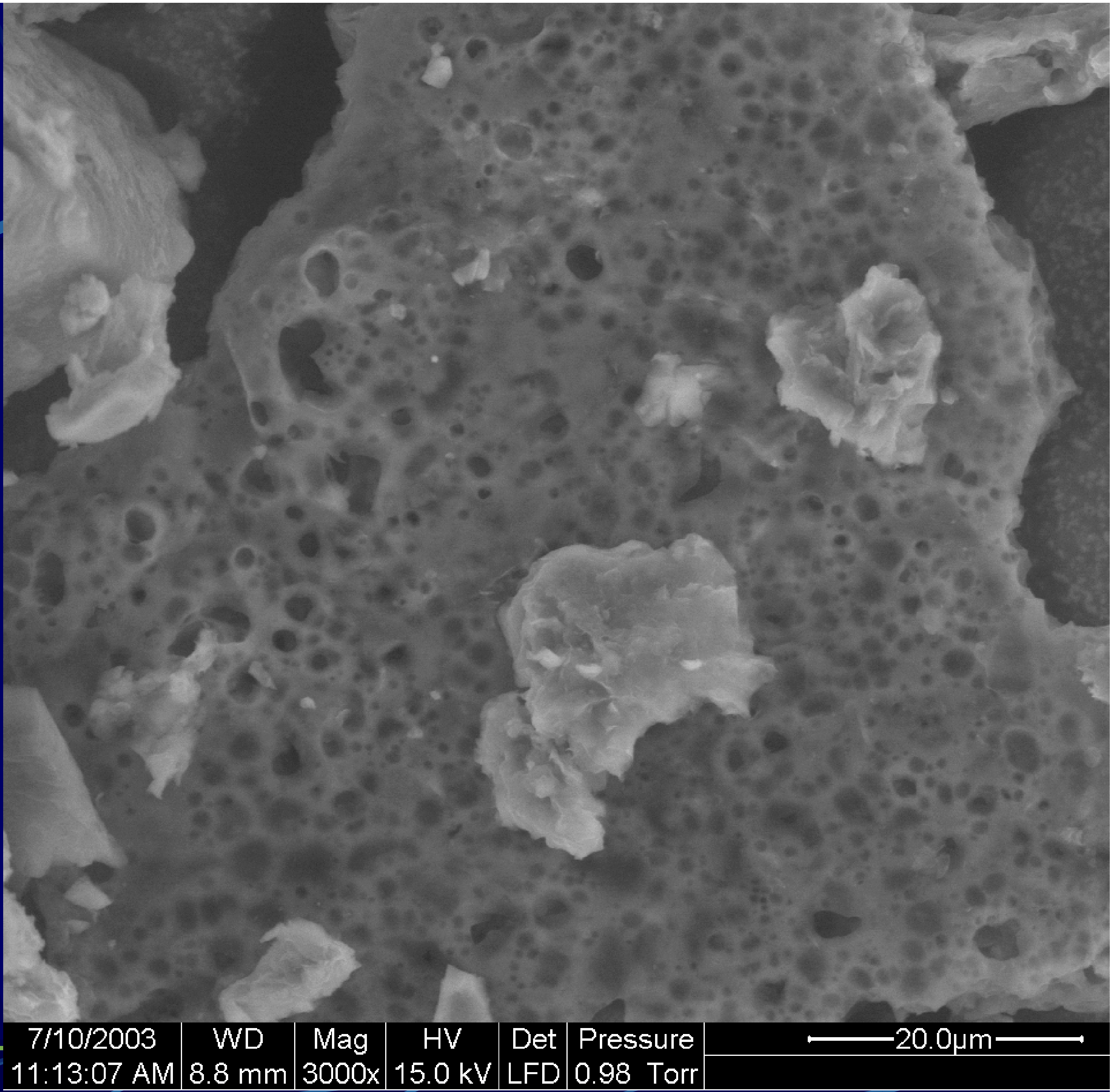
Dust that is ozone treated only - simulating peroxide and acoustic system failure



Peroxone treated to simulate acoustic system failure

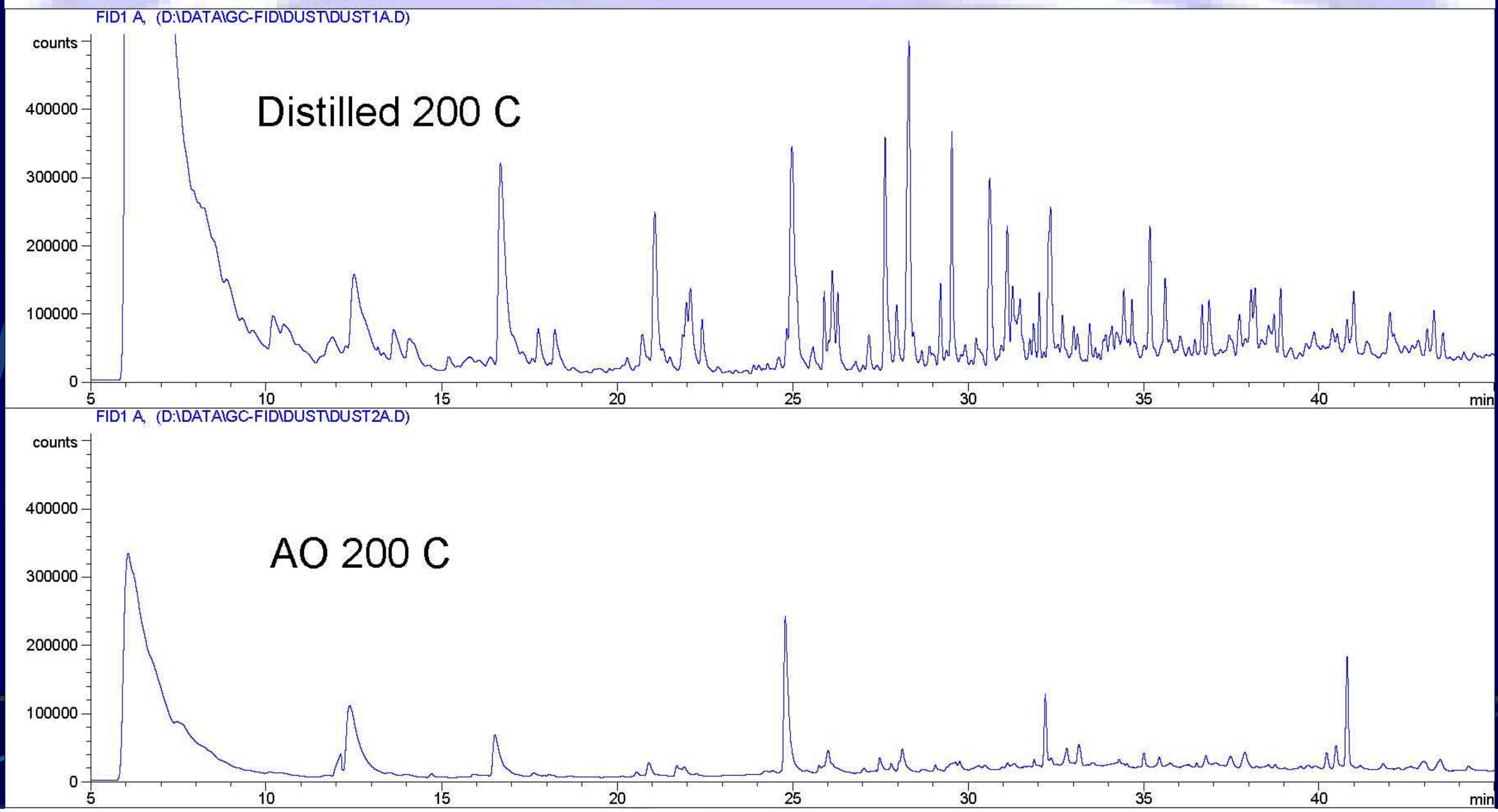


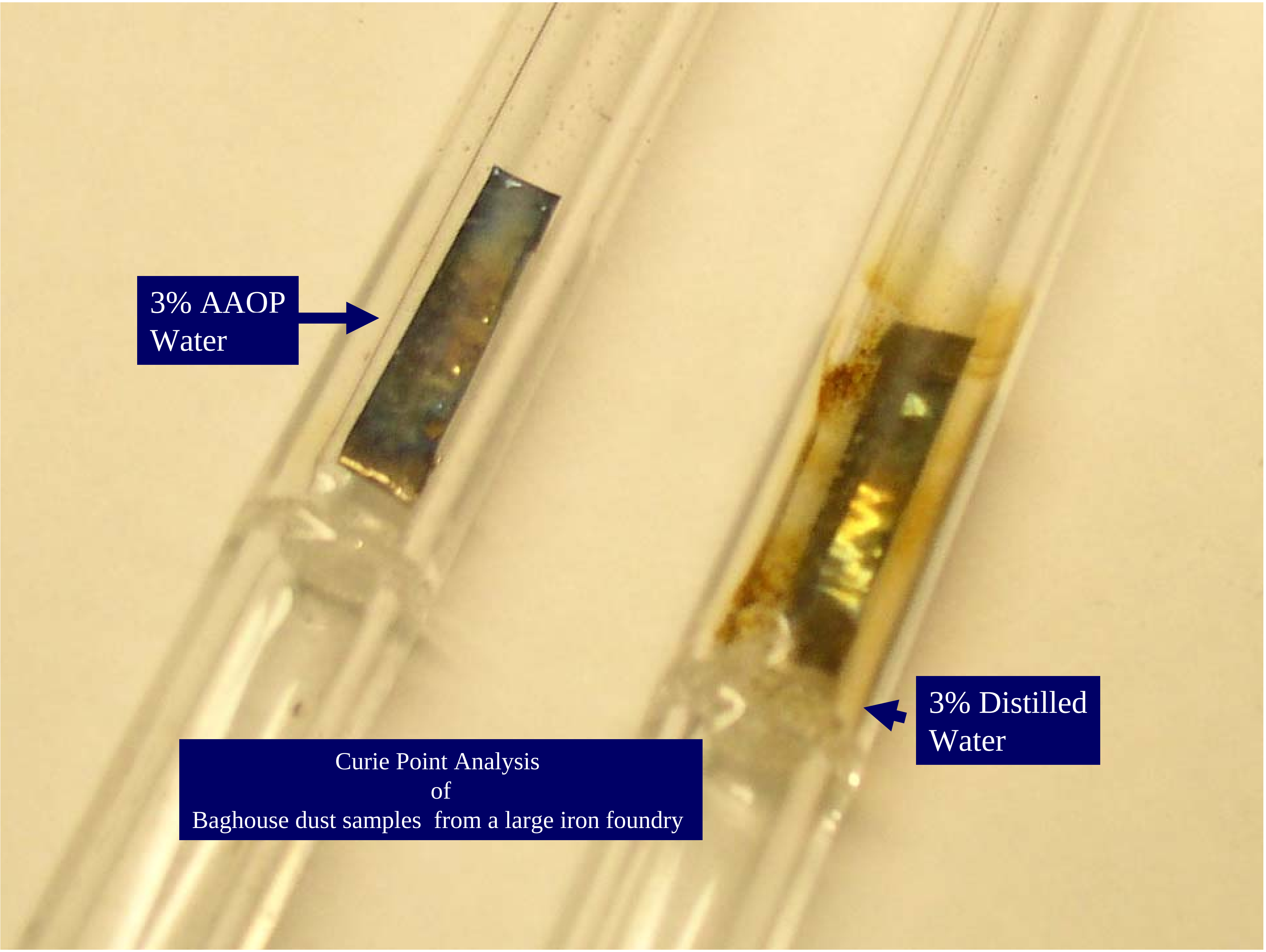
After
AAOP
or
sono + peroxone
treatment



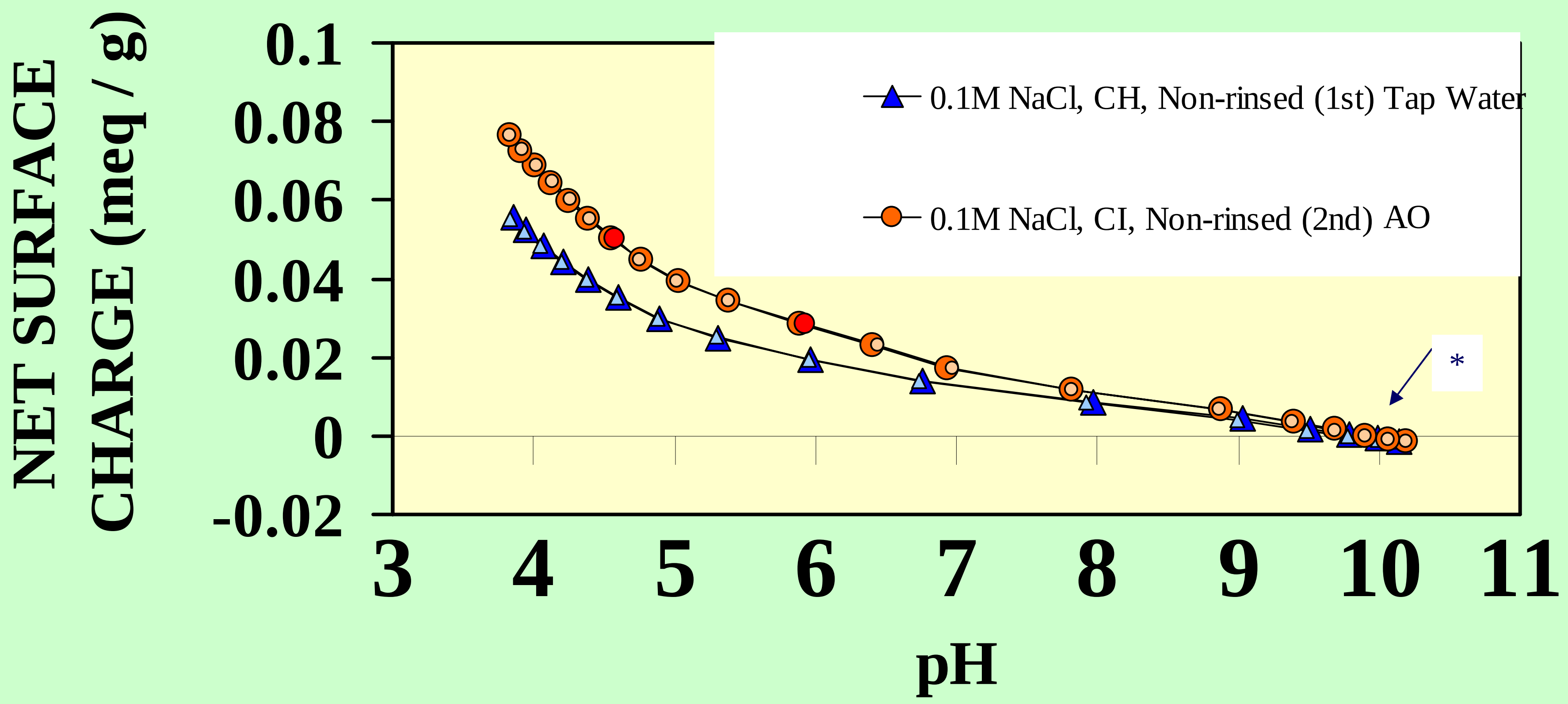
Gas Chromatograms of Curie Point Pyrolizer EPA/NSF funded research at Penn State of a large iron foundry sand system dust sample.

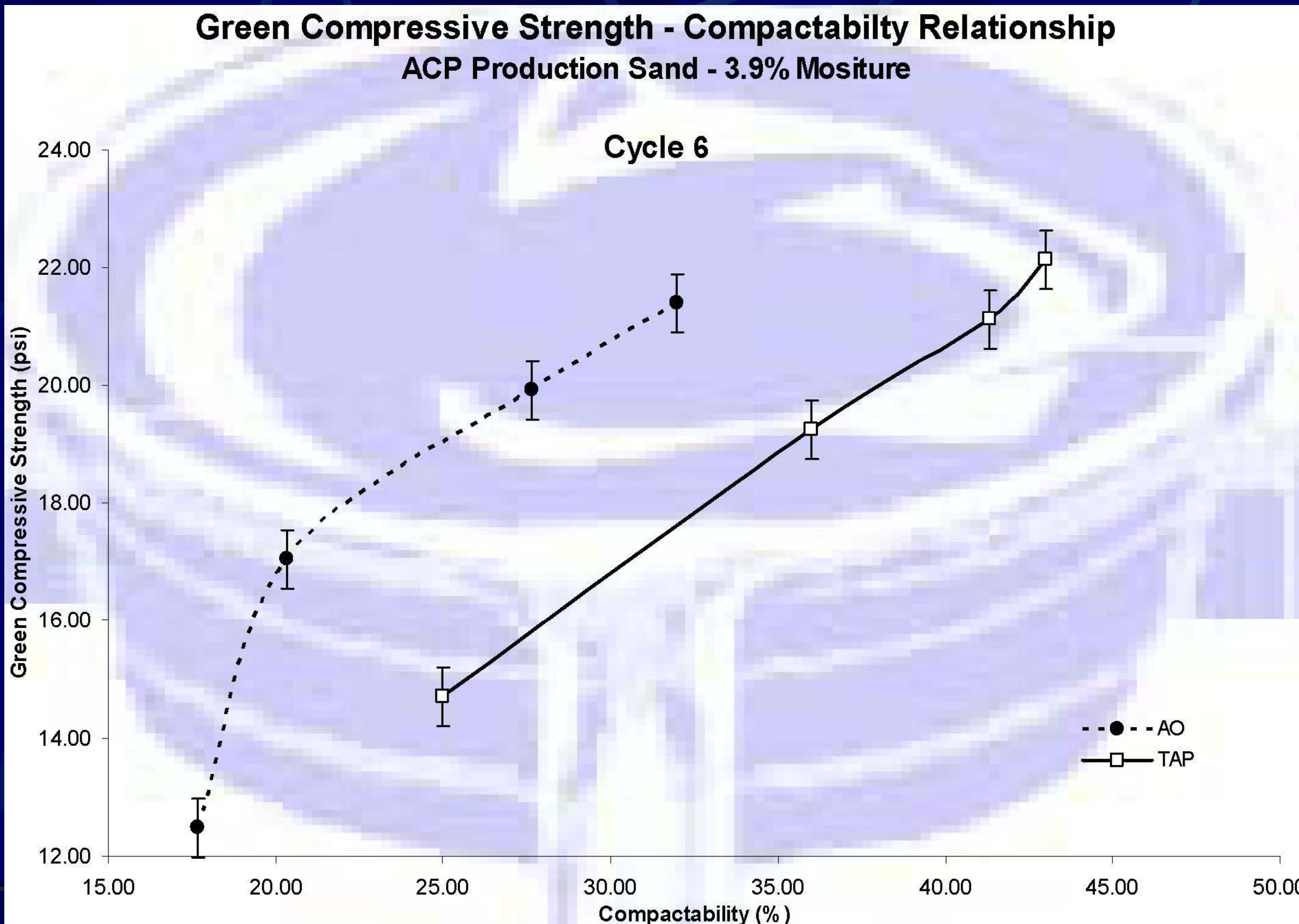
~3% distilled and AAOP water was added to dust. The samples were dried at 200C then flash pyrolized up to ~750 C in ~.5sec. Emissions were captured and analyzed with GC.




3% AAOP Water
3% Distilled Water
Curie Point Analysis
of
Baghouse dust samples from a large iron foundry

Consistent clay surface charge changes with AAOP




Green Compressive Strength - Compactabilty Relationship
ACP Production Sand - 3.9% Mositure
Cycle 6
Green Compressive Strength (psi)
24.00
22.00
20.00
18.00
16.00
14.00
12.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
Compactability (%)
AO
TAP

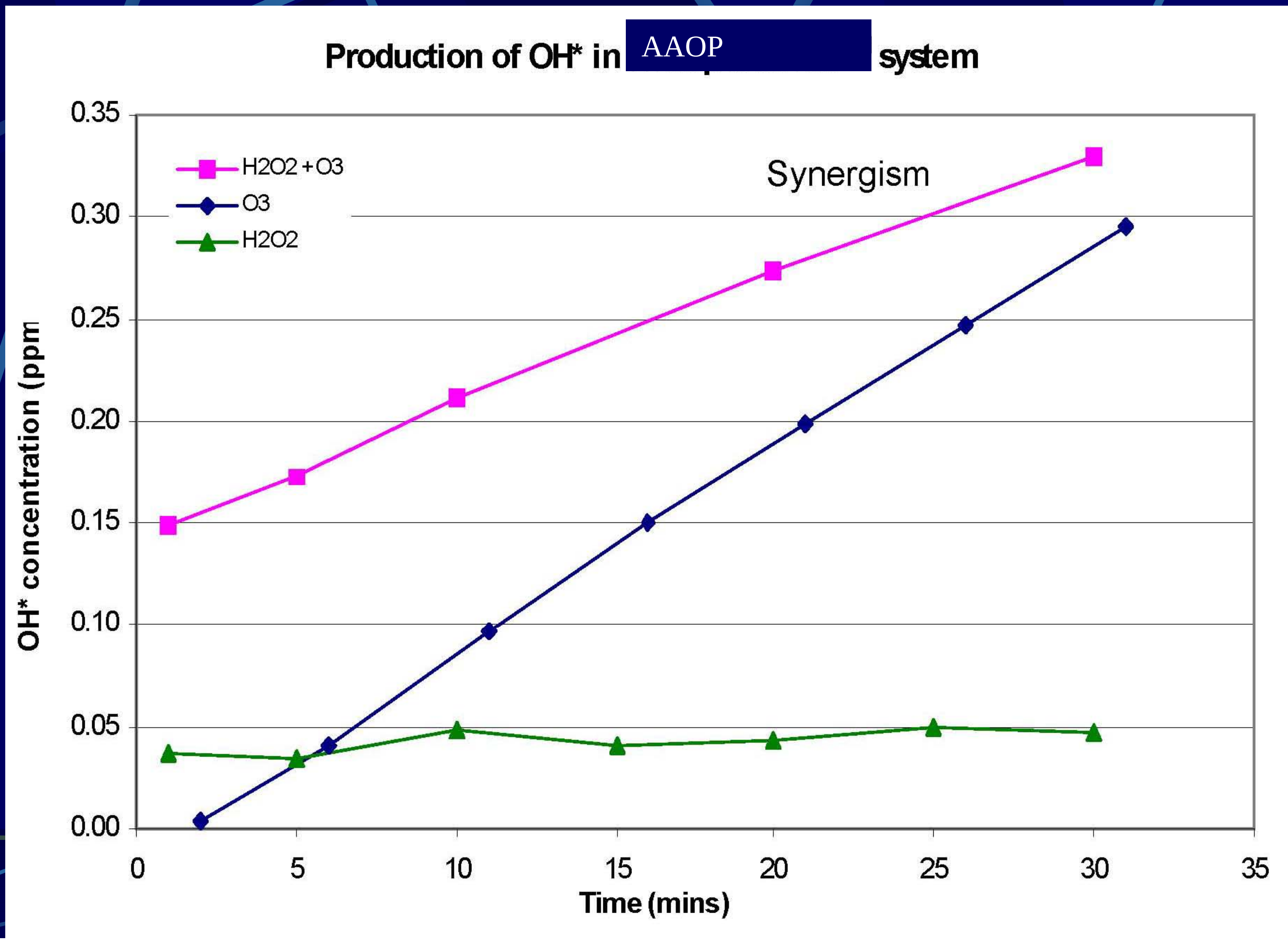
Summary of clay and coal pore structure ongoing DOE, EPA and NSF funded research – What we know and *think* we know.

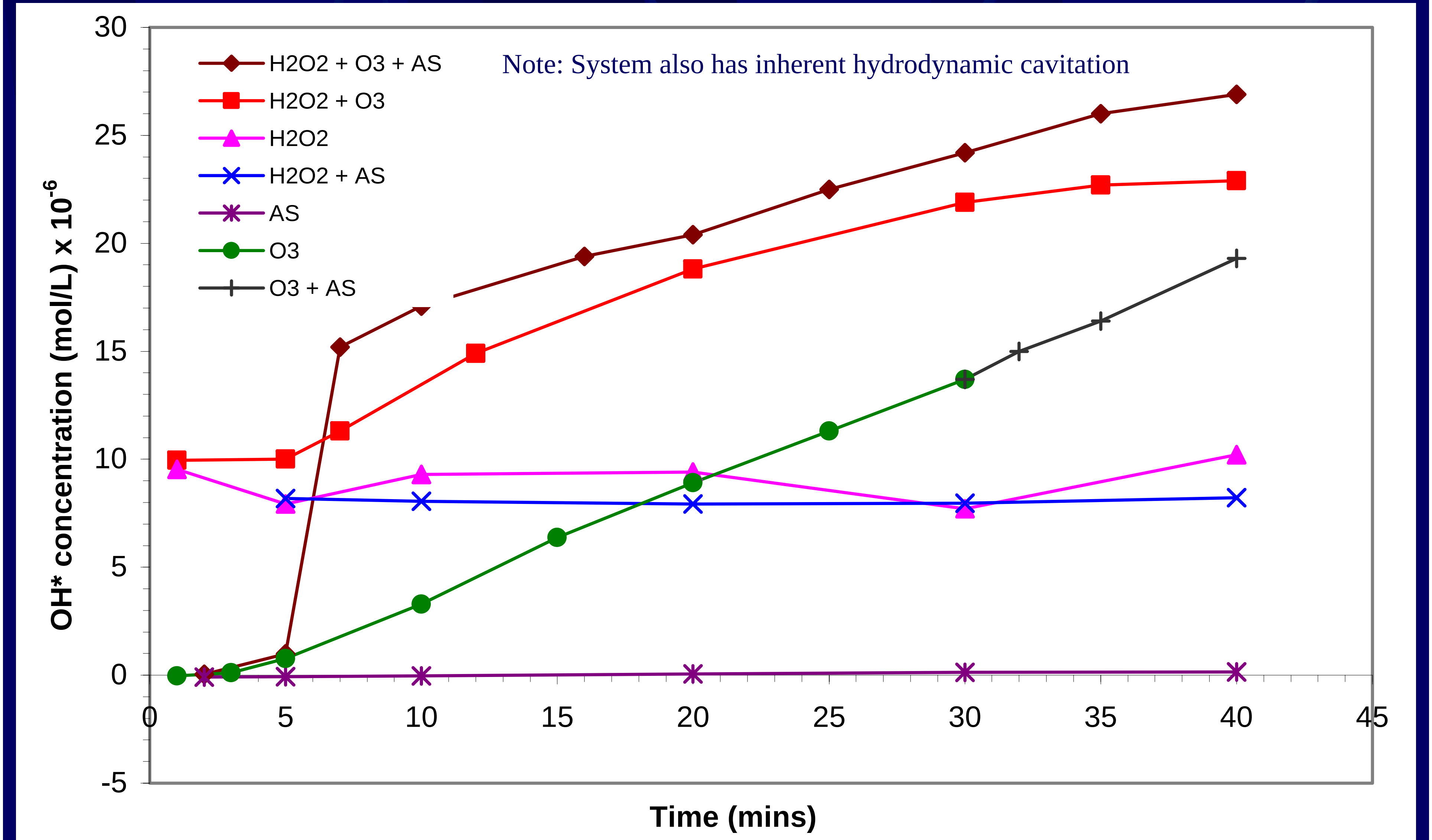
- Pore structure of foundry sand changes with AAOP use.
- AAOP changes the pore structure of foundry clay recycled from APC systems more than standard AOP methods.
- AAOP Blackwater systems argon and m-xylene adsorption studies indicate the system is acting as if 10% of the clay and coal is a high quality virgin activated carbon that is continuously regenerated by the acoustic AO process.
- The pore structure is not available in non-AO systems. It may be organic coated or not created or some combination of both.

Summary… (continued)

- Complex and most likely ***catalytic*** ambient and elevated temperature AAOP reactions with the "concentrated" organic compounds are indicated.
- Pore structure availability to the foundry's mixer/mullers is believed to be the primary reason for the improvement in speed of "activation" of the bentonite in foundry sand systems.
- The ratio of AFS clay to Mb clay changes.
- The ratio of compactability to moisture in the bentonite and sand system changes.
- We ***KNOW*** more research is needed.

System component interaction studies using a **m**ethod developed at Penn State for measuring OH radical production. (**terephthalate)**

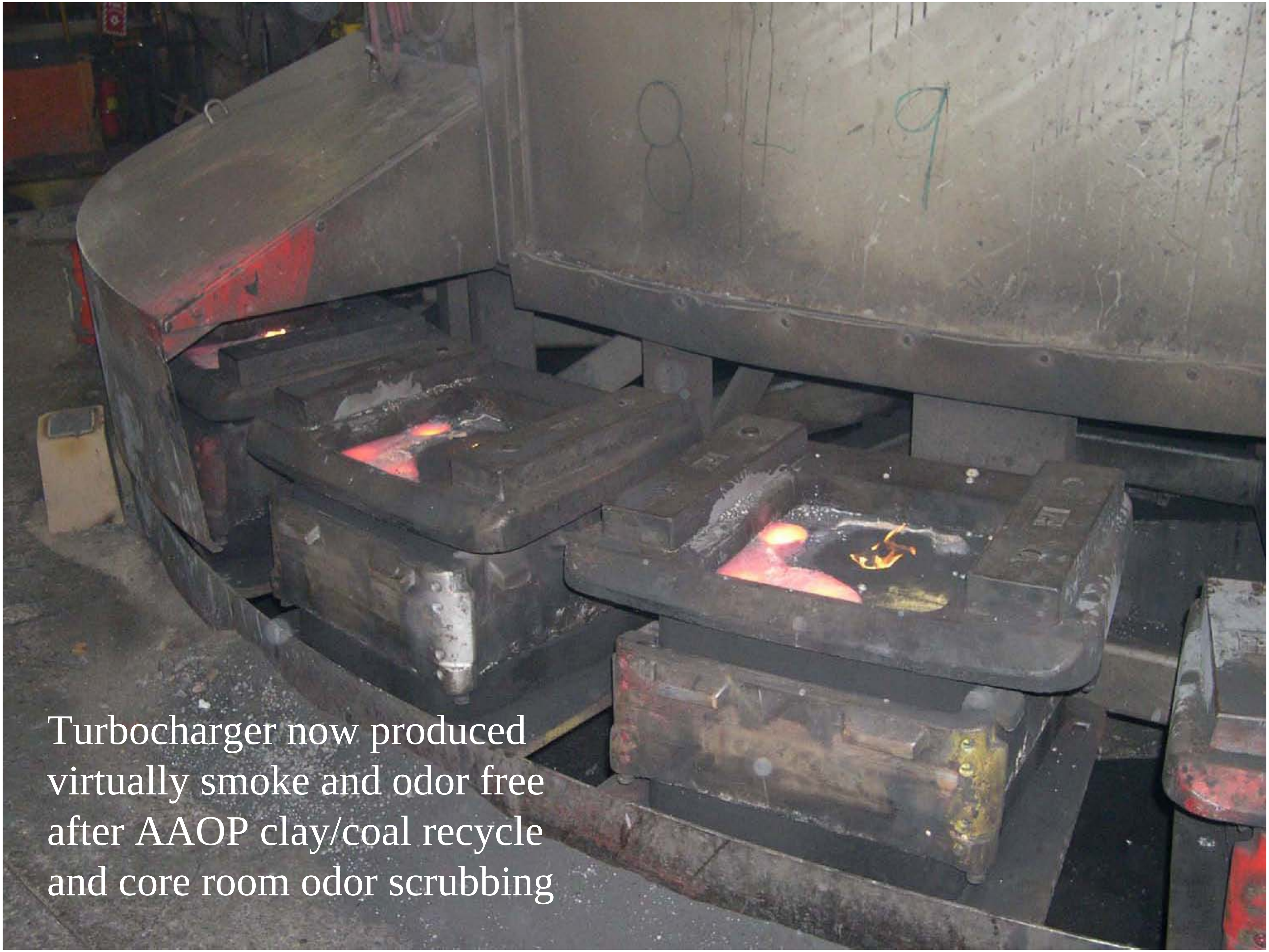




Cumulative production of OH* radicals in AAOP system with and without acoustic system. Initial concentration of H_2O_2 = 170 mg/L

(for brown data: H_2O_2 added after 5 min)

This turbocharger core package generated many smoke and odor complaints.


Turbocharger now produced
virtually smoke and odor free
after AAOP clay/coal recycle
and core room odor scrubbing

AAOP Components operational parameters that are presently monitored or interlocked

- Ozone Generator- minimum oxygen flow safety interlock, plasma voltage and plasma current.
- Ultrasonic Power Supply – adjustable minimum wattage and multiple internal faults.
- Hydrogen Peroxide – minimum consumption via weight or tank level monitoring.

The team of Furness-Newburge, Inc. and the Neenah Foundry Group, including Dalton Corporation, is recognized as a world leader in pollution prevention technology implementation. In addition to the state, national and international awards the team has won for this technology, the Swedish Foundry Association sent a delegation of leading industry experts to Neenah Foundry to learn how it successfully reduced both cost and pollution.

A multi-nation technical delegation from the European Union charged with the task of reducing foundry emissions also visited Neenah Foundry. It studied the team's innovations and asked for advice on implementation of the technology. As a direct result of these visits, multiple systems are now being designed for installations in several European countries.

In Closing

Acoustic AOP modified greensand casting works synergistically with other pollution prevention strategies including solid waste recycle, low emission core binders, sand system optimization and coal substitutes. Additionally, research at operating foundries, FNI, Penn State and CERP has provided the in-sight to implement substantial additional pollution reduction opportunities through continuous improvement of both process and equipment.

It's only just beginning…

Acoustic based advanced oxidation research is continuing at Penn State, Furness-Newburge, Neenah Foundry Group and several other strategic partnerships around the world.

Acoustic science use is rapidly expanding within the foundry/metals industry into metallurgical, sand molding and environmental applications.

Acoustically enhanced processes are increasingly emerging in multiple scientific, environmental and manufacturing disciplines.

Questions ?

Pore Structure Tests

A gas sorption instrument analyzed the green sand samples for pore structure. In these tests:

A small green sand sample inside an analysis tube is inserted into the instrument.

Analysis tube is immersed in a liquid argon bath.

Analysis tube is evacuated to a pressure of 10-6 atmospheres

Analysis tube is slowly dosed with argon.

Instrument measures cumulative argon dose and relative pressure inside analysis tube to develop an argon adsorption curve.

The instrument’s analysis software applies density functional theory analysis to experimental adsorption curve in order to develop a pore size distribution for the sample material.

For reference, a benzene molecule is approximately 6 angstroms in diameter. Benzene family molecules (benzene, toluene, xylene, etc) preferentially adsorb into pores with sizes between 10 and 20 angstroms.

m-Xylene Adsorption Tests

A thermogravimetric analyzer (TGA) is used to collect m-xylene adsorption information. This TGA combines a furnace, sample environment control, and a sensitive microbalance (10-6 gram precision).

In these tests:

A small, dried green sand sample (100-1000 mg) sample is placed in TGA.

Continuous gas flow through test chamber controls gaseous environment.

m-Xylene vapor is introduced into a gas stream passing through sample through bubbling nitrogen gas flow through liquid m-xylene.

m-Xylene concentration is varied through dilution with pure nitrogen stream.

Furnace controls sample temperature.

Microbalance measures weight change in sample to measure the amount of m-xylene adsorbed for a given gaseous m-xylene concentration.

Mass adsorbed is normalized by dividing by the sample weight.

Gaseous concentration is normalized by dividing the vapor pressure of m-xylene. (The vapor pressure is the concentration at which m-xylene will condense on its own.)

A log-log graph of adsorbed mass vs. gas concentration is typically linear.