The Pennsylvania State University

The Graduate School

College of Engineering

RECLAIMING FOUNDRY WASTE GREEN SAND AND BAGHOUSE DUST VIA ULTRASONIC IRRADIATION, ADVANCED OXIDATION, INDUCED CAVITATION AND DISCRETE PARTICLE SETTLING

A Thesis in

Environmental Engineering

by

John Thomas Fox

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science

May 2009

The thesis of John Thomas Fox was reviewed and approved* by the following:

Frederick S. Cannon
Professor of Environmental Engineering
Thesis Advisor

William D. Burgos
Associate Professor of Environmental Engineering
Graduate Officer

Robert C. Voigt
Professor of Industrial Engineering

*Signatures are on file in the Graduate School

ABSTRACT

The wet reclamation of a waste foundry green sand or baghouse dust has been demonstrated with applied ultrasonics, cavitation, settling (UCS) and advanced oxidants (AO). This technique reclaims sand, clay and coal from waste green sand or a bag house dust system while operating at near ambient temperature. The research presented herein evaluated a pilot-scale system that reclaimed waste green sand and a full-scale system that processed baghouse dust. This UCS process was developed to reclaim waste green sand, yet this same UCS system can be modified to serve as a replacement for blackwater clarifiers. AO treatments have been established as an effective way to diminish VOC emissions during mold cooling and shakeout.

Pilot-scale trials were conducted using waste green sand that initially contained 7.9% methylene blue (MB) clay and 3.8% loss on ignition (LOI). The pilot scale reclamation unit generated recycled silica sand with only a small residual 0.4-1.0% LOI and 0.4-0.6% MB clay. This reclaimed sand can be used as make-up sand for a green sand system or as a replacement for new sand in the core room. Foundry cores made from 60% reclaimed sand, 40% new sand, and 1.1% phenolic urethane binder, yielded a 120 psi tensile strength, well above the 70-80 psi tensile strength that is often specified at this foundry.

For the full-scale baghouse dust processing, a UCS system was integrated with the existing AO – Clearwater (AO-CW) system on Neenah Foundry's Plant 3 sand return system. In this configuration, AO-treated baghouse dust experienced the UCS treatment; and the ultrasonics-cavitation was designed to remove the coating of carbonaceous pyrolytic residue from the surfaces of the clays and silica fines in this baghouse dust, and thus render the treated clays and organic matter for reuse in the green sand system. Over a one year start-up period, the baghouse dust concentration in the AO slurry was increased from 0.25 lbs dust/gal AO water to 0.75 lbs dust/gal. Pouring, cooling and shakeout VOC emissions were about a third as much as when only the AO - Clearwater system was operating without any added baghouse dust. With the UCS system operating in conjunction with AO, the bond consumption was 11% less than when AO was operating with no baghouse-UCS components. Also, as this UCS system stabilized, the proportion of MB clay, LOI and silica fines increased within the baghouse dust, while there was a decrease in amount of silica grains larger than #140 mesh that ended up in the bag house dust.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

I would like to thank Dr. Fred Cannon for his guidance, insight, effort and vision during this research. I would also like to thank Fred for his effort and wisdom extended to me beyond this project. I would like to also thank Dr. Voigt and Dr. Burgos for their time, effort, insight and tutelage during this research effort. A very special thank you to Frank Headington, Steve Lewallen, Paul Smith, Jeff Goudzwaard, Matt Wosoba, Harvey Luebben and the personnel at Neenah Foundry for opening their operations, personal expertise and facilities during this research. I would also like to thank Jim Furness and Dave Paulsen of Furness-Newburge INC., for their effort, guidance and input during this project.

This research was supported by the National Science Foundation and Neenah Foundry, Neenah, WI.

"Do not rebuke a mocker or he will hate you;
rebuke a wise man and he will love you.

Instruct a wise man and he will be wiser still;
teach a righteous man and he will add to his learning."

- Proverbs 9:8 and 9

1 Introduction

1.1 Waste Green Sand Reclamation

High production green sand foundries "consume" large quantities of new sand each year both as the aggregate in core making and for green sand system additions to maintain sand system performance. For example, just in the green sand system alone, a relatively large foundry that melts 0.2-0.3 million tons of iron/year will waste and replace roughly 50,000 tons/year of silica sand (200 rail cars) as well as 20,000 tons/year clay, and 6,000 tons/year of coal as green sand system additives [**1,2**]. The metal casting process is shown in Figure 1.1, which demonstrates how the green sand mixture is shaped so that molten metal solidifies into the desired product.

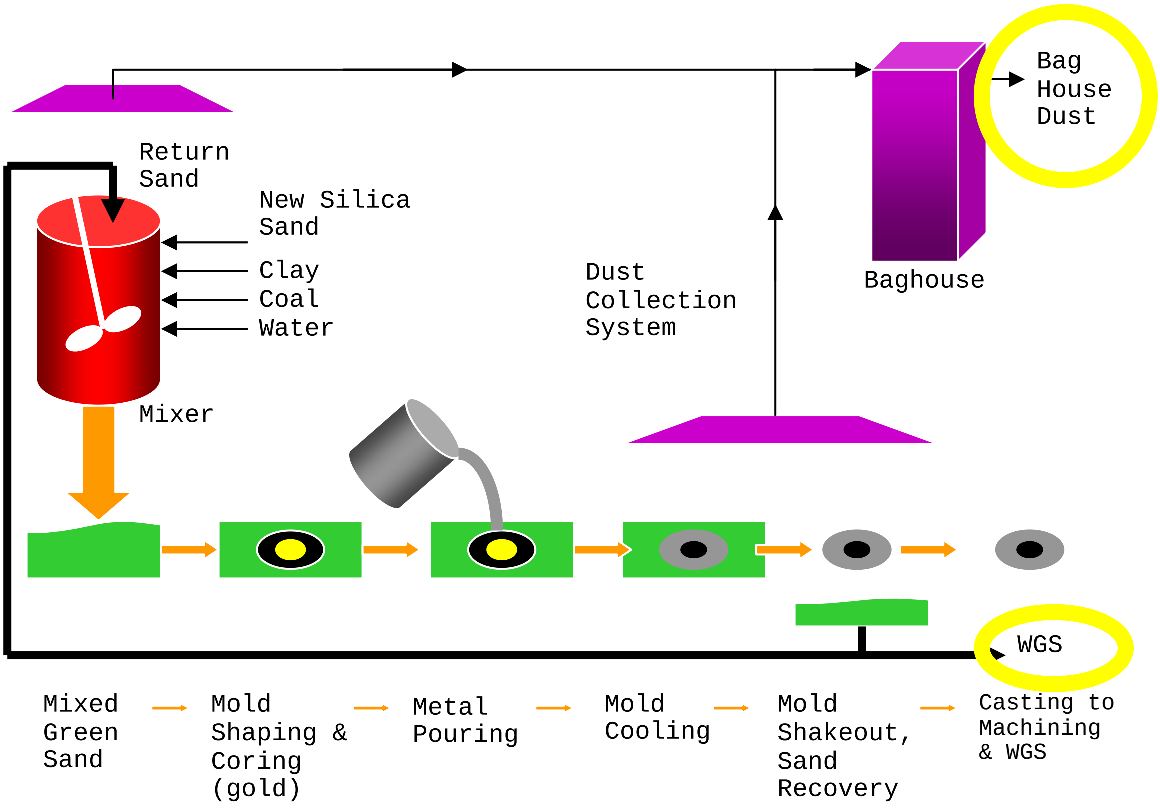

Figure 1.1. The Metal Casting Process, showing introduction of new silica sand to the mixer. Gold circles indicate the source for reclamation; baghouse dust from the baghouse and waste green sand (WGS) from the molding process.

In order to diminish such high consumptions of green sand materials, reclamation offers a means to reduce materials usage. While sand reclamation is not a new concept; existing technologies include: mechanical, wet and thermal reclamation systems [**3-5**], each with their own advantages and disadvantages. Mechanical systems use abrasion to physically remove the residual material off of the surface of the silica grains [**3-5**]. The clay coating, dust and silica fractures from the mechanical or pneumatic system are removed by the dust collection system [**3,5**]. Thermal reclamation systems heat sand to between 930^{o}F and 1475^{o}F [**3**], where organic coatings on the core sand and coal from the green sand system are removed via combustion. The resultant calcined clay layer on the sand surface is then removed mechanically. However, calcium bentonite and sodium bentonite are destroyed at 850^{o}F and 1150^{o}F, respectively [**6**]. This means that thermal reclamation removes organic residues but destroys valuable active clays in the process. Also, thermal reclamation requires much energy. Simple wet reclamation techniques have been used to attempt to remove the clays from the waste green sand and return the sand to the core room, but has been deemed unfavorable due to high water volumes that must be treated, inadequate sand quality – specifically high MB clay residual, and excessive floor space requirements [**3,5**]. These systems all offer conceptual means for sand and sand additive reclamation, but none offer simultaneous sand, clay, and coal recovery.

A novel wet reclamation process has been developed for recycling spent green sand that uses induced particle collisions, cavitation, discretionary settling, ultrasonics, and ozone/hydrogen peroxide. The ultrasonic-cavitation system was developed by Furness-Newburge (Versailles, KY) and is named Pneu-Col™. This concept was pilot-tested at Neenah Foundry, WI and the results reported herein suggest that this cleaning process will successfully reclaim silica sand, active clay and seacoal from spent green sand. The treated sand can be used as both green sand make-up and as core sand. The treated coals and clays are returned to the sand system as a "black water" slurry.

A number of the concepts in this novel ultrasonic-cavitation process have built on the previously-developed advanced oxidation-blackwater (AO-BW) systems, which have reduced clay and coal consumption in foundries by 20-35% [**1,2,7,8**]. The ability to reduce clay and coal consumption with an AO-BW system occurs because advanced oxidants can remove organic coatings from clay platelet surfaces. As molten metal is poured into a green sand mold, coal additives pyrolize, forming a hydrophobic carbon coating, or "raincoat" on the clay and sand. This carbon raincoat formation on sand and bentonite clay prevents the clay and sand from bonding to one another [**3,9,10**]. But if the waste green sand could be treated with advanced oxidation coupled with ultrasonic-cavitation, the carbon coating could be removed, and the sand could be reclaimed.

The ultrasonic-cavitation process herein has a relatively small footprint, and the process requires relatively little energy. Moreover, this process segregates the active clay and coal back to a green sand system with a blackwater clarification system. This means that the process can reclaim not only the sand, but also the clay, coal and carbon colloids. While, the ultrasonic-cavitation mechanisms that are used for reclamation involve fundamentally complex unit operations, they are uniquely designed into an industrial system that offers simple operation, Fig. 1.1.2. The system operates by circulating a slurry that is comprised of waste green sand and tap water. As the slurry continuously circulates, the waste green sand is exposed to induced particle collisions, ultrasonics, cavitation, and advanced oxidants. After adequate exposure to the cleaning mechanisms, settling begins. Vertical settling pipes are opened and closed via diaphragm valves at the top of the pipes which controls both the processing time and settling conditions. Thus, during the wash cycle, the valves are closed to achieve continuous circulation. Once the wash cycle is over, the top valves open and the settling cycle begins. The bottom valves remain closed and the pipes fill with silica grains as they separate during settling. The proto-type unit that was evaluated herein had only two settling pipes, whereas a full-scale system would have multiple settling pipes so as to increase the system throughput. When the settling pipes reach their filled capacity during the settling cycle, the top valve closes and the bottom valve opens. The recovered wet sand is pneumatically forced out of the settling pipe, to yield sand that is ready for green sand system reuse. Alternatively, the recovered wet sand can be dried for core sand use. Additionally, the effluent blackwater that has been circulated during the green sand washing cycle is high in clay, coal, and the carbon colloids that have been removed from the sand grains. This effluent blackwater can be re-circulated to an AO blackwater clarifier system, where it can provide make-up water to the muller and sand cooler. This will diminish the need for make-up clay and coal in the green sand system.

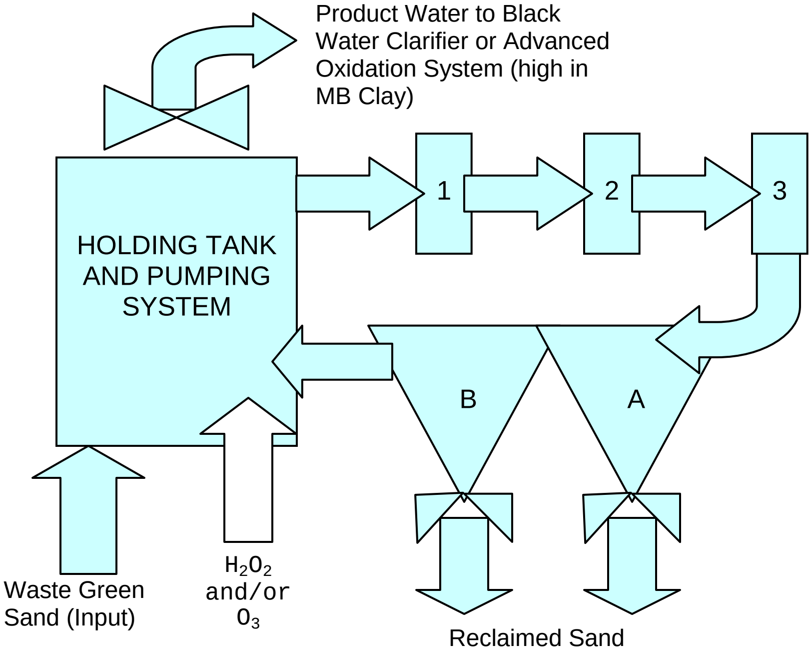

Figure 1.1.2. Flow schematic of an ultrasonic-cavitation system (1) Induced particle collision, (2) Cavitation (3) Ultrasonic Treatment (A) First settling pipe (Tube A) (B) Second settling pipe (Tube B) in series

Ultrasonics are widely used for surface cleaning and have been used in foundry labs. The use of ultrasonics in a foundry green sand lab is commonly practiced for preparing clay samples for methylene blue titrations. Furthermore, Farmer et al. [**11**] observed that localized ultrasound forces remove iron oxide and clay coatings from sand surfaces. Cavitation bubbles generate hydroxyl radical products as their collapse ‘tears’ water apart [**12, 13**]. The developers of the system herein built on this prior science to design a sand reclamation process that couples ultrasonics, cavitation, advanced oxidation, induced shearing, and discretionary settling.

Though not investigated in this study, another anticipated benefit of this system, beyond sand, clay and coal reclamation pertain to sand cooling and improved casting tolerances. A high-volume foundry will rapidly re-circulate sand; and this causes sand systems to rise in temperature. Temperatures that rise above 120-130°F cause poor sand properties [**6, 14, 15, 16**]. Thus, when wet cool sand (70-80°F) from the ultrasonic-cavitation process is added to the green sand prior to mixing; the reclaimed sand will cushion the rise in temperatures and promote stable operation.

1.2 Baghouse Dust Processing

Iron foundries are continually pressed to seek alternative methods and environmental solutions to meet ever more stringent emission regulations. Among the technologies developed in the last decade that reduce green sand system emissions are Advanced-Oxidant (AO) systems. In AO systems, the tap-water used for sand cooling and pre-blending is treated with hydrogen peroxide (H_2O_2), ozone (O_3) and ultrasonics to produce highly oxidative species, including the hydroxyl radical ($OH^{\bullet}$) [**17**]. This water with a high advanced oxidant concentration can be used to 'condition' the sand during pre-blending or sand cooling. This process has been identified as AO-clearwater (AO-CW) in previous papers, and has been operating at Neenah Foundry's Plant 3 for the past eight years. In the next generation AO system, the advanced oxidant water can be blended with baghouse dust, and then this slurry applied to provide the make-up water for green-sand. This process has been identified as AO-blackwater (AO-BW) in previous papers.

The work herein appraises a yet further modification of this concept, called the Pneu-Col™ (by Furness-Newburge, Versailles, KY). In this system, ultrasonics, cavitation, and settling (UCS) is applied to an AO-treated slurry of the bag house dust (subsequently identified as the UCS system—see schematic, Figure 1.2). This system processes baghouse dust at the supporting foundry, Neenah Foundry, Neenah, WI. During related pilot-scale studies, when the UCS processed waste green sand, the treatment system removed the hydrophobic surface coating from waste green sand [**21,22**]. The set-up for waste green sand processing and for baghouse dust is very similar. For the system modified to process baghouse dust, an AO-CW system had been converted to an AO-UCS system. The high concentration AO water from the former AO-CW has been added to the ultrasonic-cavitation-settling device where it has mixed with baghouse dust that is then exposed to ultrasonic mechanisms.

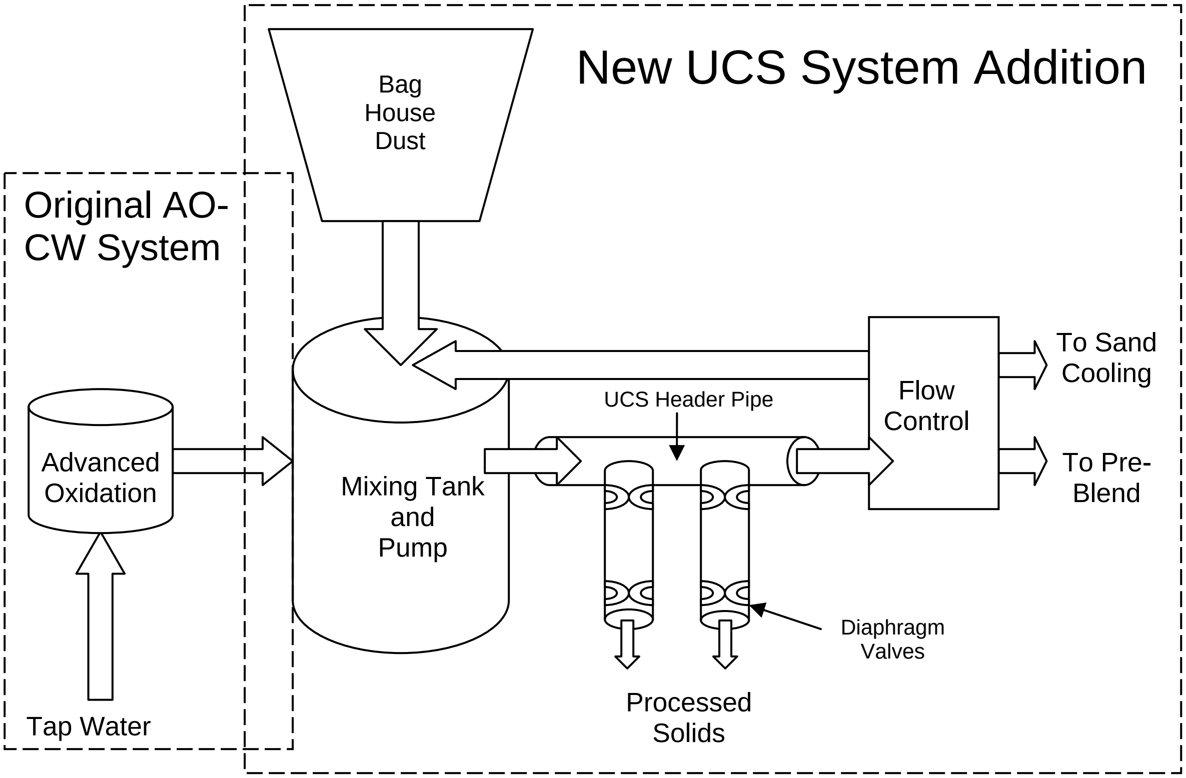

Figure1.3. Ultrasonic-Cavitation-Settling device integrated into an existing Advanced Oxidation system.

AO technology has been established as a method which significantly reduces emissions during mold cooling and shake-out [**7,8**]. Emission reduction has been reported that ranges from 20% to 75% for AO-BW systems [**1,2,7,8**]. Also, when AO-BW is employed, substantial material reductions have also been reported. For instance, sand system clay consumption has been reduced by up to 20-35%, when comparing AO-BW clarifier applications to conventional operations [**1,2,7**].

The mechanisms that enable material and emission reductions pertain to the cleaning and recycling of residues from clay and sand particles. Specifically, the clay-rich baghouse dust accumulates a hydrophobic carbon coating from the casting process; and this coating inhibits the clay bonding mechanism for direct baghouse dust reuse [**8,9**]. This carbon coating prevents the necessary electrostatic forces which bond sand and clay with water [**19,20**]. The ultrasonic – AO processing removes this carbon coating; and this enables the successful transformation of inactive clay to active clay [**8,9**].

Neenah Foundry (Neenah, WI) has two production lines where an advanced oxidation system has been used. The first, Plant 2, transitioned from conventional operations to an advanced oxidation-dust-to-blackwater clarifier (AO-BW) using a conventional clarifier during 2000-2001. This transition resulted in a 21% drop in sand system bond consumption [**2**]. Subsequent gradual reductions in bond consumption have been observed on this line since then. In this AO-BW system, the baghouse dust has been conditioned with advanced oxidants and then settled in a clarifier. On the Plant 3 line, Neenah transitioned from conventional operations to an advanced oxidation – clearwater (AO-CW) system in the late 1990's. Then from July 2006 through July 2007, this Plant 3 line installed a companying – ultrasonics-cavitation-setting (UCS) system, in which the UCS system (without the need for a separate blackwater clarifier) cleans carbonaceous pyrolysis residues off the surface of the dust grains, and then segregating larger grains (which settle) from smaller grains, which get carried along in the blackwater. Whereas the Plant 2 blackwater clarifier occupies 450 square feet of floor space, the Plant 3 UCS system only requires 90 square feet of floor space, in that it is primarily comprised of 6” diameter pipes, valves and fittings. Also, the ultrasonic-cavitation-settling system costs about 20-30% as much as a conventional blackwater clarifier.

2 Objectives

The **objectives** of this research were:

(a) Evaluate the AO-ultrasonic-cavitation system could reclaim waste green sand in a manner that rendered it suitable for reuse in green sand systems or as a core sand. For these trials, the success of segregating sand and shearing carbon was inferred by measuring the loss on ignition (LOI) and methylene blue (MB) clay of the USC processed sand. Lower LOI and MB clay indicate a greater potential for sand reclamation.

(b) Test whether the AO-UCS could process baghouse dust during full-scale implementation in a manner similar to a conventional AO-BW Clarifier Tank. For the trials herein, the success of UCS baghouse dust processing was measured by reduction in sand system clay consumption and pouring, cooling and shakeout VOC emission reductions. Other USC processed sand properties surveyed such as LOI, sieve distribution and MB Clay was measured as secondary indicators of UCS effectiveness.

3 Literature Review

Industrial and hazardous wastes are often processed as water-solid slurries; thus, both the liquid constituents and the solid components must be considered. Water chemistry and water treatment techniques have been widely studied and can offer useful methods when considering the solid content in slurries or solid surface interactions. Ultrasonic mechanical cleaning is often harnessed for removing surface contaminants from solid particles, which can be enhanced with chemical cleaning processes such as advanced oxidation. These methods can be applied for the removal of surface coatings for purification (i.e. sands used in glass making), removal of coatings to develop desired surface properties, or to remove surface compounds which inhibit the attachment of other desired compounds [**11**]. Ultrasonic cleaning has been attributed to three forces; chemical reactions between the soluble impurities and the cleaning agents in water, dissolution of the impurities from the surfaces into solution, and the ultrasonic cavitation removing the insoluble impurities from the surface [**23**]. The chemical degradation of compounds due to ultrasonic irradiation is attributed to: oxidation by hydroxyl radicals, pyrolytic decomposition and supercritical water oxidation [**24**].

One ultrasonic mechanism of interest is cavitation which creates the ultrasonic surface cleaning force. Cavitation occurs when the negative pressure of ultrasonics pull liquid molecules apart and develop cavities [**11,18**]. Gas trapped in the liquid enhances the ability of ultrasonics to develop cavities from the negative pressure. The cavitation bubbles formed from the negative pressure can either; expand and contract (oscillate), continually increase in size, or the bubble can grow rapidly and not compress during the positive pressure [**18**]. Once, a cavitation bubble has reached a critical point it can no longer absorb energy, at this point the bubble is unstable and liquid rapidly fills the cavity as it explodes [**18**]. These explosions are extremely violent, with internal bubble temperatures and pressures estimated at over 5000 K and 500 atmospheres [**18**] to 1000 atmospheres [**11**].

Additionally, the mechanisms associated with particle removal due to ultrasonics include acoustic streaming, microstreaming, microstreamers and microjets [**25**]. Acoustic streaming is the transfer of acoustic energy into a fluid where the shear stresses imparted by the fluid enable the removal of loosely attached and readily dissolved surfaces [**25**]. Microstreaming is when the bubbles oscillate in size and cause fluid movement fluctuations in both magnitude and direction. Microstreamers are cavitation bubbles that form at nucleation sites and travel 10x faster than the average fluid velocity. Microjets are formed during the collapse of a cavitation bubble; during the collapse the bubble wall accelerates the greatest on the side opposite the solid surface creating a very strong water jet. Other mechanisms attributed to cleaning are the vibrations, shock waves from the collapse of cavitation bubbles and the chemical interactions from radicals produced [**25**].

As previously mentioned, radicals can be produced during the cavitation activity during ultrasonic treatment of aqueous solutions. More specifically, hydroxyl radicals, ozone and hydrogen peroxide offer high oxidizing potentials for carbonaceous materials. These organic ‘scavengers’ are interconnected through a series of decomposition and generation reactions outlined by Hart and Henglein [**26**]. Hart and Henglein found that the presence of ozone during sonolysis, allows H_2O_2 to experience a six-fold increase in hydrogen peroxide production in the presence of ozone as compared to the presence of oxygenated water.

An examination of the reactions controlling radical and hydrogen peroxide production from ozone is detailed below (As per Hart and Henglein [**26**]):

Ozone degradation occurs from two reactions:

$$O_3 \rightarrow O_2 + O$$

And,

$$O + O_3 \rightarrow 2O_2$$

Water is decomposed by the reaction:

$$H_2O \rightarrow H + OH$$

When oxygen is present:

$$H + O_2 \rightarrow HO_2 \rightarrow OH + O$$

When oxygen is present, hydrogen peroxide is produced via:

$$O + H_2O \rightarrow 2OH^{\bullet}$$

$$2OH^{\bullet} \rightarrow H_2O_2$$

$$2HO_2 \rightarrow H_2O_2 + O_2$$

Thus, from Hart and Henglein's study it can be confirmed that as hydrogen peroxide and ozone are introduced, the linkage between ultrasonics and advanced oxidants increases the aqueous solution concentrations of radicals and hydrogen peroxide – overall, increasing the oxidation potential of the system. The mechanisms enabling these phenomena are that with an increasing oxygen concentration more hydrogen atoms are scavenged. However, since Hart and Henglein could not measure an appreciable amount of ozone and concluded that ozone degradation occurs during cavitation. Yet the overall increase in H_2O_2 does occur and ozone and H_2O_2 are interlinked during ultrasonic irradiation [**26**].

There are multiple examples in the literature where ultrasonics and advanced oxidants have been harnessed for diverse applications in water-solid slurries. These examples demonstrate the power of ultrasonics and can better develop the phenomenon during irradiation.

The effect of ultrasound on the surface cleaning of silica particles has been examined by Farmer et al. [**11,27**]. Iron levels found in silica sands that are used in glass making have stringent requirements for table ware, where the sand must contain less than 0.015% iron. Farmer was capable of reducing the typical silica sand with 0.025-0.03% Fe_2O_3 content to >0.015% Fe_2O_3 using a 20 kHz sonicator in a water bath. It was also found that in this particular case the addition of either sodium hydroxide (0.03%) or sodium carbonate (0.02%) enhanced the removal. These results indicate that the removal of iron from sand is strongly time-dependent. Also, the level of ultrasonic power applied was in direct correlation to the amount of iron removed. Farmer suggested that energy required to remove small particles increases between a flat surface and a sphere in accordance with Derjaguins approximations – thus the enhanced removal at a higher level of power input is within expected limits. Also, Farmer suggests that ultrasound enables the electrostatic separation of materials, which is enhanced with sodium bicarbonate due to the increased sodium concentration at the grain surface [**11,27**] .

Ultrasonic irradiation has been experimentally proven by Rege et al.[**28**] to enable the aqueous desorption of contaminants on granular activated carbon and polymeric resins. Phenol desorption, occurred much faster at 40 kHz frequency than at 1.44 MHz. Additionally aerated water improved the desorption, which is supported by the findings of Suslick [**18**] as previously discussed. Additionally, the desorption followed first order kinetics. However, from this study it was found that the intensity of the ultrasonics pulverized the activated carbon at 1.44 MHz.. However, Rege [**28**] does not discuss the sonochemical interactions taking place during irradiation and the desorption process is linked to the physical phenomenon which occur during ultrasonic activity. Rege [**28**] states that the desorption of phenol from the resin was pore-diffusion limited and that desorption was limited by the surface reaction. Furthermore, it was asserted that mechanism of acoustic microstreaming within pores enhanced diffusion transport which was also attributed to the lowering of the activation energy with an increase in ultrasonic power [**28**].

Natural Organic Matter (NOM) fouling of membranes is of particular concern in water treatment. Recently, Chen et al. [**9**] have found that NOM fouling can be significantly reduced by the use of a 20 kHz ultrasonic stinger in laboratory tests. From this study it was found that high pH enhanced foulant removal, however the presence of Ca^{2+} decreased the effectiveness of ultrasonics [**9**]. Lamminen et al. also studied ceramic membranes and investigated the mechanisms behind ultrasonic de-fouling [**25**]. Their results suggested the mechanisms were attributed to: detachment and loosening of particles by microstreamers and the transport away from the surface with acoustic streaming [**25**]. The NOM fouling is removed through ultrasonics mechanisms that are physical-based phenomena.

Another application of ultrasonic technology pertaining to water-solid slurries has been applied within foundries. Specifically, the use of ultrasonics and advanced oxidants has been quite beneficial for the use within a foundry's green sand system. A system (AO-BW) that recycles bag-house dust, which is generally a waste product of ferrous foundries, is able to remove the valuable bentonite clay from a waste-slurry through ultrasonic and advanced oxidation treatment [**8**]. In addition to removing the hydrophobic carbon coating in sand and reactivating the valuable clay, the system reduces air pollution by over 70% [**8**]. Wang et al.[**9**] was able to attribute the success of these systems to the ultrasonic mechanisms ability to remove the carbon from the clay which restored the clay's MB uptake, thus significantly reducing the required clay addition within a foundry. Since advanced oxidants are used in addition to ultrasonics – it is likely that this process relies on both chemical and physical mechanisms of ultrasonic irradiation to remove the carbonaceous coating and to reactivate the clay.

Koparal et al., has also examined ultrasonic removal of tar from sand. A 40 kHz frequency was used to irradiate the sand in a column which was compared to that of mechanical agitation. The wash-out from the sands was compared for tar, and it was found that ultrasound was more effective at the removal of tar from the contaminated sand. Additionally, it was observed that the ultrasonic removal mechanism closely fit a first order reaction [**30**]. The removal of tar by both mechanical and ultrasonic methods produced fines which were washed out and analyzed. The fines produced from ultrasonic irradiation contained an average particle size of 5mm, where the particles produced from mechanical agitation had an average particle size between 9 and 10 mm. Additionally, the particles from the ultrasonic agitation contained 7% tar, or about 35 times more than the original tar composition, whereas the fine particles from mechanical agitation contained just 3% tar. Koparal et al. suggest that the ultrasound treatment enables a thin surface layer to be removed via microjet cavitation and mechanical agitation requires larger particles or chunks to be removed, yet is less effective at removing the tar surface coating [**30**].

Another study examined pertains to copper removal from granular pieces of brick which was used to simulate a contaminated soil. From the study ultrasonically irradiated samples, the fines removed contained 96% of the mass removed, 3% copper was removed on the pieces larger than 20 mesh and about 1% was in the soluble form [**31**]. Meanwhile, mechanical agitation removed 31% of the copper on pieces of brick over 20 mesh, while only 68% of copper was removed via fines and 1% was soluble [**31**]. While not stated by Newman et al., the fact that only 1% remained soluble in both mechanical and ultrasonic agitation suggests that there is limited or no chemical interaction from ultrasonics and copper solubility. Overall, the removal from ultrasonics increase the total mass fraction removed to 41% from just 14% when mechanically agitated for identical time periods of 30 minutes [**31**].

Building upon the size fractionation that may occur during ultrasonic irradiation – particle size reduction of silica and alumina particles of different size classifications was also examined. After treating the particles with ultrasonics at 20 kHz for a predetermined time period, the diameter of the particles were then measured. For alumina particles with a D_o = 130 μm, the decrease in particle size was determined to be a first order reaction [**32**]. From Lu et al., it was also determined that size reduction rate is faster for larger particles than for smaller particles. Interestingly, it was attributed that the size reduction for alumina is greater for particles with a larger surface area. The mechanisms behind the size reduction were attributed to microstreaming and particle collisions [**32**].

Overall, the chemical production of hydrogen peroxide and radical scavengers coupled with the physical phenomona of cavitation produced microjets, acoustic streaming and microstreatming from ultrasonic irradiation offers accelerated reaction kinetics which is favorable to remove a vast array of surface contaminants from solid particles in an aqueous environment. While most work has found that the removal via irradiation is strongly time dependent – ultrasonics most often accelerate the desired reaction or contaminant removal. While the chemical reactions encountered in ultrasonics can be favorable and tend to be enhanced with the presence of oxygen and ozone [**26**] – most surface removal phenomena examined herein are dependent upon the physical mechanisms. These physical mechanisms are powerful and can pulverize GAC [**28**] and redistribute the size classification of the sample being irradiated. Furthermore, a greater number of fines generated will often contain the greatest amount of contaminant during the removal process is very effective way to shear-off a small layer of the surface along with the contaminant.

4 Materials and Methods

4.1 Waste Green Sand Materials and Methods

Pilot-scale experiments were conducted while processing the supporting foundry's waste green sand. The pilot-scale ultrasonic-caviation system was varied over a range of operating variables as the authors tracked the USC reclaimed sand properties to establish reclamation feasibility. Reclamation potential of the reclaimed sand was quantified through laboratory measurement of percent volatiles, loss on ignition (LOI), methylene blue (MB) Clay and AFS Washed Sieve Analsysis. The experimental protocol used for the laboratory testing was identical to that of Neenah Foundry, Neenah WI, except where noted.

4.1.1 Waste Green Sand

Before embarking on these pilot-scale trials, the authors collected twenty 55-gallon barrels of waste green sand from foundry operations at one time. This uniform green sand source was used for all pilot-scale trials herein. During each batch run, the waste green sand was evaluated relative to LOI, MB clay etc. On average, this waste green sand contained 7.92% MB clay, 3.81% LOI, 3.63% fines, and a grain fineness number (AFS washed GFN) of 67.7; and there was very little variability on this waste green sand's properties from one run to another.

4.1.2 Operation Overview

Experiments evaluated the ultrasonic-cavitation system for green sand and core sand recovery. While multiple parameters were examined, the general protocol for system operation remained consistent through the evaluation. The ultrasonic-cavitation system in was operated in batch experiments so as to most effectively control and evaluate the system parameters. Three trial runs were operated for each set of conditions. Each run employed a discrete batch of water and waste green sand, which was circulated as a slurry around the USC loop during the entire run. This was a closed loop with the exception of (a) the product sand that settled, and (b) the bleed of blackwater effluent that transferred to the blackwater clarifier. Operations included two distinct cycles - a wash cycle and a settling cycle. The wash cycle of the system was defined as the time period that ALL sand was circulated to promote exposure to the cleaning mechanisms. During the wash cycle there was no settling. After this, the settling cycle commenced when the top valves opened into the settling pipes. This allowed the USC treated sand grains to settle. It should be noted that during the settling cycle, the circulating sand that had not yet settled was still exposed to the cleaning mechanisms-and there was no distinct termination of the wash cycle during this batch operation. The settle time used was 10 minutes and remained constant for all tests; and the wash time varied, with listed times of 5, 7, 7.5 and 10 minutes.

4.1.3 System Start-up

The ultrasonic-cavitation system was operated with a total water volume of 65 gallons. All tests were operated at a ratio of 1 pound of sand to 1 gallon of water (1 pound sand to 8 pounds water). To start, 65 gallons of water were added to the system and the pump was turned on. Then, 65 pounds of waste green sand was gradually added to the system. Once the sand was added, the ultrasonics were turned-on and the slurry was exposed to the cleaning mechanisms for the beginning of the ‘wash cycle’, hence the batch run commenced. Trials that used ozone addition were exposed to ozone by sparging ozone into the holding tank. For trials that employed hydrogen peroxide, the

30% hydrogen peroxide solution was added to the holding tank, which was subsequently mixed throughout the slurry via diffusion and advection.

4.1.4 Sampling

The sand that was discharged from the settling pipes (Tube A or B) has been referred to as reclaimed sand herein, and this is the sand that has been deemed suitable for reuse within the foundry. The product sand from each tube had the water content removed and measured, then the dried sand was weighed. After being weighed, the sand was thoroughly mixed to ensure uniformity and a grab sample was removed for testing (Samples were dried in a 220^{o}F oven for test preparation).

4.1.5 Methylene Blue Clay Titration

All sand property tests were conducted in accordance with the American Foundrymen's Society Mold and Core Test Handbook (1988) [**34**], except as noted for minor distinctions herein. The Methylene Blue Clay titrations were conducted with 5.00 ± 0.05 g of dried reclaimed sand, which were weighed into a stainless steel beaker. Then, 50 mL of 2% tetrasodium pyrophosphate solution was poured into the beaker. The sample was ultrasonically scrubbed for 10 minutes (versus 7 minutes per AFS), and stirred to ensure that the sample was not adhering to the beaker. Approximately 90% of the anticipated total methylene blue solution was added and rapidly stirred for 4 minutes. The sample was manually stirred with a glass rod and then placed one drop of the stirred solution on #50 Whatman filter paper. The formation of an acceptable halo indicated that the titration end point had been reached, while a subsequent blow-out (i.e. outward bleed) of the blue color verified the final result. If no halo formed, then more methylene blue solution was added, until the formation of an acceptable halo appeared. The methylene blue forms electrostatic bonds with the clay molecules in solution, when there is an excess amount of methylene blue in solution, it forms a blow-out on filter paper, indicating the end of the titration. This test was performed in triplicate for each sample.

4.1.6 Standardizing Methylene Blue Clay Measurements at Low Levels

Typical MB Clay measurements at foundries are at least one order of magnitude higher than the MB Clay levels in the reclaimed sand. For this reason, a standardization curve showing percent MB clay as measured in Neenah Foundry's sand lab, versus percent standard clay with prescribed clay levels that were mixed in with silica sand. Specifically, American Colloid Company (ACC) provided five standards that contained 0.25, 0.50, 0.75, 1.00 and 2.00 percent MB clay by weight. As shown in Figure 4.1.6, the measured percent MB clay was 0.1% higher than actual at MB clay levels of less than 0.7%. This means that the silica sand itself sorbed this 0.1% of the methylene blue dye. The authors note that the MB Clay values reported are the measured values, they have not been corrected for silica sand sorbtion.

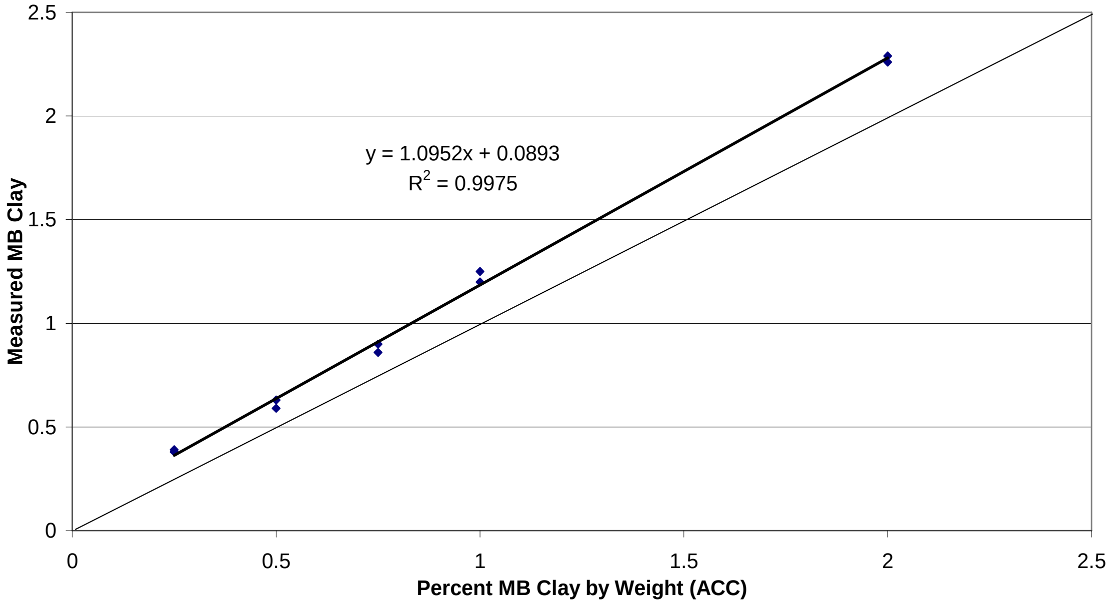

Figure 4.1.6. Percent MB Clay by Weight (standards provided by American Colloid Company) versus the Measured MB Clay through titration – and the resulting deviation from idealized conditions.

4.1.7 Percent Volatiles at 1200°F

From the dried reclaimed sand sample, 50 ±1.00 g was weighed out in a ceramic crucible, and the exact mass was recorded. The crucible was placed in an oven (preheated to 1200°F) and covered with a ceramic crucible lid so as to limit (but not eliminate) exposure to oxygen. After 1 hour in the muffle furnace, the sample was removed and allowed to cool for approximately 5 minutes, then weighed. Percent Volatiles was performed in duplicate for each sample.

4.1.8 Loss on Ignition at 1800°F

Following the percent volatiles test, the same sample was used for the Loss on Ignition measurement. This sample was again placed in a muffle furnace which this time was preheated to 1800°F. The sample was exposed to ambient air, with no crucible lid, for 1 hour in the muffle furnace at 1800°F. Then, the sample was cooled for approximately five minutes before being weighed. Each sample was tested in duplicate for loss on ignition (LOI).

4.1.9 AFS Clay Wash and Sand Sieve Analysis

Samples were washed, sieved, and weighed in accordance with the AFS Standard cited above in order to monitor the sand sieve size distribution. Specifically, 50±1.00 g of dried sand and approximately 500 mL of water were added into a 1000 mL beaker. The sample was placed on the rapid sand washer for at least 5 minutes. When the rapid sand washer was removed, the washer was sprayed to rinse sand adhering to the mixer, back into the sample. The beaker was then placed on an automatic siphon, after the beaker was drained the first time, 25 ml of 2% tetra sodium pyrophosphate was poured in the beaker. The automatic siphon was operated until the water was clear. The contents of the beaker were passed through a 25 micron sieve basket. Rinsing of the beaker helped transfer sand particles that adhered to the side of the beaker. The basket was placed over a heat lamp for 45 minutes to dry. After the sample was dry, the contents of the basket were transferred to the sand sieves. The sieves were shaken, and each sieve was brushed to transfer the contents, which were weighed and recorded. This washing protocol removed the clay and coal so as to not confound the sand size classification. A washed sieve analysis was performed in duplicate for each sample.

4.1.10 Core Tensile Strength Through Dog Bone Production

Core tensile strength was evaluated using the procedure specified by AFS 3301-00-S. Dog bone shaped test samples were made with reclaimed Tube A product sand that had been processed through the pilot-scale unit while using a 7 minute wash time, 1000 ppm H_2O_2, and intense cavitation. For comparison, the authors also produced dog bone samples from a composite of tube A and B sand, while using a 10 minute wash time and no hydrogen peroxide. For both cases, the product sand was dried to achieve less than 0.1% moisture. For the case of the sand products that included H_2O_2, dust was dissipated from the sand samples by pouring the reclaimed sand from on container into another, repeated 4-8 times, until the dust was no longer visible. This dust removal was not practiced with the non-H_2O_2 reclaimed sand. Then, virgin sand and reclaimed sand were weighed to achieve the desired percentage by weight for testing. Both the virgin sand and reclaimed sand were poured into a full-scale mixer (minimum batch size 200 pounds) and mixed with 1.1% of a two-part phenolic-urethane polymer. A sample was removed from the full-scale mixer to mold several dog bones which were cured with dimethylethylamine (DMEA). Dog Bones were tested for tensile strength, following 15 minutes of curing (unless otherwise specified); and the tensile strengths were monitored in quadruplicate.

4.1.11 Thermal Gravimetric Analysis (TGA)

Samples of reclaimed sand, waste green sand and phenolic-urethane bound reclaimed sand were dried prior to analysis at 110^{o}C for at least 24 hours. A clean and dry quartz basket was tared in the TGA (CAHN TG-131). A 1.00 g sample was then placed in the quartz basket. The samples were heated under nitrogen gas to simulate the oxygen deprived conditions experienced at the molten metal interface. Samples were heated at 20^{o}C/min until 1000^{o}C, and then held for 10 minutes at 1000^{o}C.

4.1.12 Scanning Electron Microscopy (SEM)

Reclaimed sand, waste green sand and phenolic-urethane bound sand samples were dried prior to analysis at 110^{o}C for at least 24 hours. Uncoated samples were then placed on carbon tape. Samples were not coated in gold. Samples were analyzed under high-vac mode, with voltage at 20.0 kV, and a spot size near 4. Various magnifications were used ranging from 50x to nearly 10,000x. Once a particle or point of interest was in focus a digital photograph was taken to document the image.

4.1.13 G Value Calculation

G values are commonly used in water treatment practices to determine the appropriate mixing required. That same principles can be applied to this work to quantify the amount of mixing or agitation experienced by the sand grains. The general equation for G is:

$$G = (P/V\ \mu)^{\wedge 1/2} \text{ (Linsley, 1992)}$$

Where, G is the mean velocity gradient ($\sec^{-1}$), P is the power requirement (Watts), m is the dhynamic viscosity ($N\ s/m^2$) and V is the total volume (m^3). Also, for this application, P can be calculated for pipes and channels:

$$P = \rho Qgh \text{ (Bache, 2007)}$$

Where, P is the power requirement (Watts), ρ is the fluid density (kg/m^3), Q is the flow rate (m^3/sec), g is the gravitational coefficient (m/sec^2) and h is the headloss through the system (m).

Furthermore, the flow rate is dependent upon the degree of cavitation. The appropriate temperature used was 30^oC for the dynamic viscosity value. Additionally, total head loss across the entire system was assumed to be 30m, which is the output of the pump, and then the system returns to zero head once flow enters the holding tank. Lastly, Gt values, were the G values multiplied by the time of mixing in seconds.

4.2 Baghouse Dust Processing Materials and Methods

4.2.1 System Operation

For the AO-UCS system, the Neenah Foundry, (Neenah, WI) Plant 3 water continues to be treated as before via the AO-CW system. This AO-laden water is mixed with baghouse dust that is fed via a screw auger; and the combined slurry feeds into the ultrasonic-cavitation-settling device. Slurry concentrations have progressed from an initial 0.25 to the current 0.75 lbs baghouse dust/gallon of AO-tempered water. The slurry is circulated continuously via a circulation pump. As the slurry circulates through the UCS header pipe, some of the larger and denser solids settle down the 6" diameter down pipes; and all such solids are discharged as sludge. However, since February 2007, there have been virtually no solids discharged from the settling chamber.

4.2.2 Sampling

Baghouse dust was removed from the input line that fed the UCS header pipe. Samples were removed via buckets from the 4 discharge tubes. Samples were completely mixed and dried at 240^{o}F prior to testing.

4.2.3 Testing

Testing was performed in accordance with the AFS sand testing protocol, except as specifically noted below. However, as time progressed, it was noticed that the AFS protocols, that have been developed for green sand testing, were in some cases not well suited for bag house dust testing; therefore some MB Clay and LOI tests were performed both according to the AFS protocols, and according to revised protocols developed for baghouse dust evaluation.

4.2.4 Sieve Analysis

AFS Clay wash sieve analysis was performed on baghouse dust samples throughout the duration of analysis, using standard AFS protocols as described previously in section 4.1.10.

4.2.5 Loss On Ignition

The AFS protocol for monitoring loss on ignition (LOI) of green sand is to burn 50 g of the sand in a crucible at 1800^{o}F (982^{o}C). The authors have modified this protocol for ashing baghouse dust. Initial testing indicated that the very fine grains of the baghouse dust precluded air from penetrating down to the lower portion of this crucible, as manifest by this region remaining black (i.e. carbon-laden) after ashing 50 g. However, when 15 g of baghouse dust was ashed, there was no black residual near the bottom, indicating that the full depth of the sample had indeed been ashed within the crucible. For this reason, the authors propose that the 15 g sample more properly reflects actual LOI; and when this sample size had not been initially used (as in the earlier analyses), the authors computed the equivalent LOI's. The LOI analyses were conducted in duplicate for a given grab sample.

Table 4.2.5. Baghouse Dust loss on ignition variation with respect to sample weight.

Sample Size	LOI Average	Standard Deviation
50 g	11.90	0.58
15 g	15.48	0.50

4.2.6 MB Clay

The standard protocol for monitoring the MB Clay of green sand involves sonicating a sample for 7 minutes. In this study, the AFS MB Clay protocol was used for the baghouse dust samples, except a 10 minute rather than 7 minute sonication time was used. This longer 10 minute time is consistent with the sonication duration routinely used by Neenah Foundry for monitoring green sand MB Clay levels on a day-to-day basis [**21,22**]. Also, AFS protocol requires a 5 gram sample for green sand, while the authors herein used a 1 g baghouse dust sample for testing.

It was noticed that the measured MB Clay value of a green sand will not continue to significantly increase when sonication time is extended beyond ten minutes. However, in contrast, when baghouse dust samples were sonicated for longer than 10 minutes, their apparent MB Clay measurements continued to increase, even after 60 minutes of sonication time, as shown in Figure 5.2.3. For this reason, the authors have reported the MB Clay following both 10 and 60 minutes sonication time. During this research it was noticed that as sonication time increases, the opportunity for dislodging the pyrolysis carbonaceous residue from the clay and silica fines surfaces may also increase [**10**]; and this represented a confounding issue.

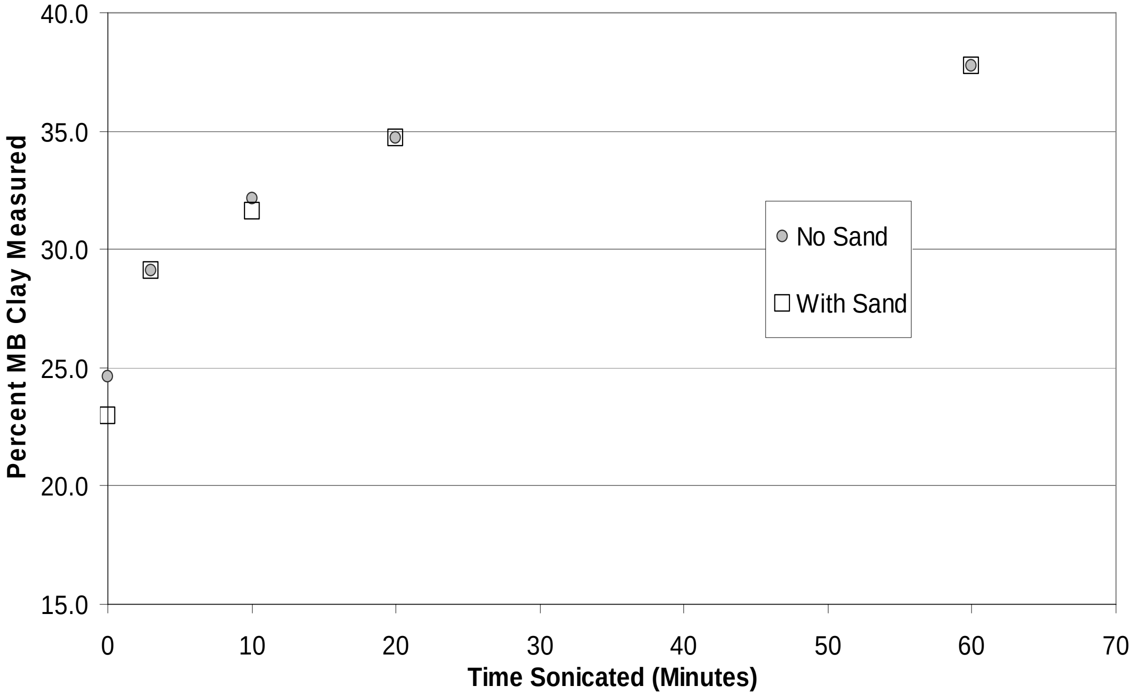

Figure 4.2.6 Percent MB Clay measured with respect to time sonicated prior to titration when processing 1g of baghouse dust, with no sand make-up (circles); and when 4 g sand is added to sand make-up to 1 g baghouse dus (squares), so as to test the 5 g sample as per AFS protocol for testing waste green sand.

4.2.7 VOC Emissions

All emission samples were conducted by Neenah Foundry's personnel, with slip stream capture methods, where samples were pumped from mold cooling or shakeout exhaust ducts. The emission samples were sorbed onto activated carbon tubes for VOC analysis. Further discussion regarding the VOC emissions protocol used herein has been presented in Goudzwaard et al., 2003 [**8**].

5 Results

5.1 Waste Green Sand

5.1.1 Cavitation Effect on Performance

The overall flowrate through the USC system was measured and simple calculations were performed to estimate velocity. The induced cavitation significantly reduced the overall flow rate through the system and subsequently reduced the velocity over the settling pipes. Table 5.1.1 tabulates the degree of cavitation and flow rate. The degree of cavitation and flow rate was then used to calculate G and subsequently G*t. The percent LOI in the reclaimed sand from Tube B, appears to be strongly dependent on G (Figure 5.1.1.A), as an increased G corresponds to a decrease in LOI. However, an identical relationship occurs between Flow rate and percent LOI in the reclaimed sand from Tube B. Thus, the amount of LOI recovered in Tube B is dependent upon Flow Rate if the relationship is dependent on settling. However, if the amount of LOI recovered in the reclaimed sand in Tube B is dependent upon G*t, then the relationship is dependent upon the exposure to the cleaning mechanisms within the system. It must be noted that the LOI in Tube A (Figure 5.1.1.C) is not dependent upon G*t, thus it would suggest that the flow rate is the variable which controls the LOI obtained in Tube B, thus settling characteristics of organics at lower flow rates are the reason for the higher LOI.

Differences in flow rate over the settling pipes affected the ability for sand grains to settle, as seen in Figure 5.1.1A. Specifically, cavitation influenced the balance between LOI and percent 140 screen (i.e. per AFS designation, the fraction that is #100<size<#140 mesh). The data in Figure 5.1.1D depicts a range of cavitation intensities, while employing no hydrogen peroxide. As shown, attaining reclaimed sand with over 10% 140 screen grains was only achievable under Intense or Very Intense Cavitation. This must be highlighted, as the percent #140 is a critical element of a green sand system and is typically maintained between 10-19% [**14**] so as to achieve a proper casting surface quality. With less 140 screen sand and fines, the molten metal can penetrate into the mold, causing casting defects. With too much 140 screen sand and fines, gas cannot permeate into the mold, and blow defects will be observed. Tube B consistently retained over 10% 140 screen sand grains with intense cavitation (i.e. velocity 0.45 ft/sec), but this 140 screen retention could not be achieved with low or moderate cavitation. As the percent 140 screen increased, the LOI likewise increased for Tube B product sand.

In comparison, the Tube A product sand generally contained 0.4-0.6% LOI following intense or very intense cavitation; while its 140 screen fraction remained in the 4-6% range. Thus, the Tube B product was better suited to replace new sand addition in the green sand system, while the Tube A product was better suited for core sand. As a further interpretation, intense cavitation yielded as good a product sand (solid squares) as did very intense cavitation, either for Tube A or Tube B, yet the intense cavitation required less energy input then did very intense cavitation. Due to this, intense cavitation was employed during subsequent tests. Moreover, intense cavitation was employed for all runs that included ozone or hydrogen peroxide.

Table 5.1.1 Cavitation Intensity and Flowrate

Subjective Cavitation Degree	Flowrate (gpm)	Estimated Velocity passing through 6 inch diameter manifold above settling pipes (Ft/sec)
Low Cavitation	75.22	0.96
Moderate Cavitation	56.34	0.72
Intense Cavitation	35.22	0.45
Very Intense Cavitation	22.24	0.28

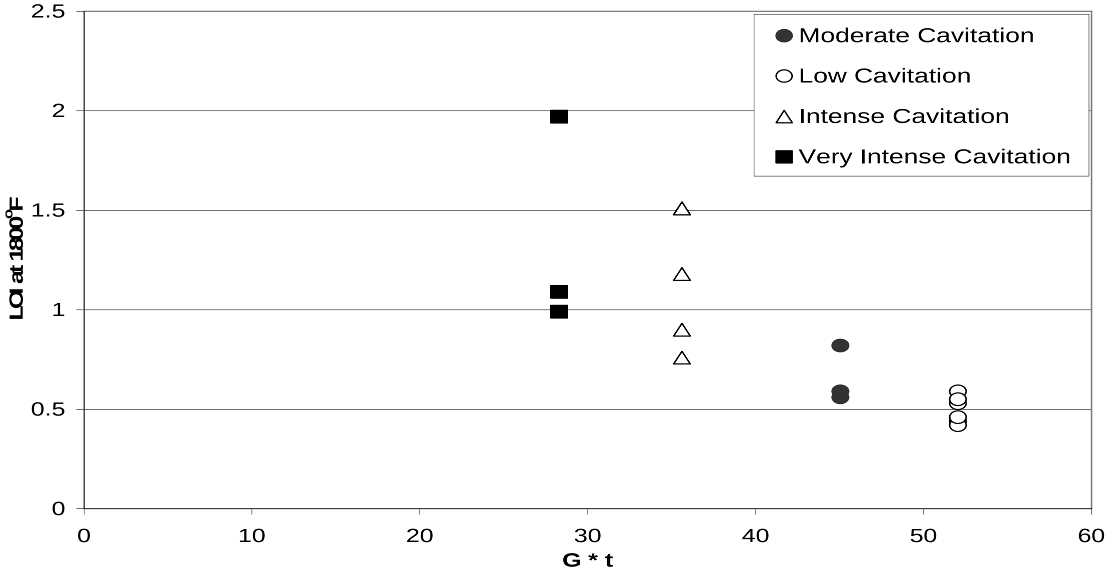

Figure 5.1.1A. The percent LOI at 1800°F, compared to the calculated G*t values, for each cavitational degree, using a 10 minute wash time and 1 lb sand to 1 gal water, for Tube B.

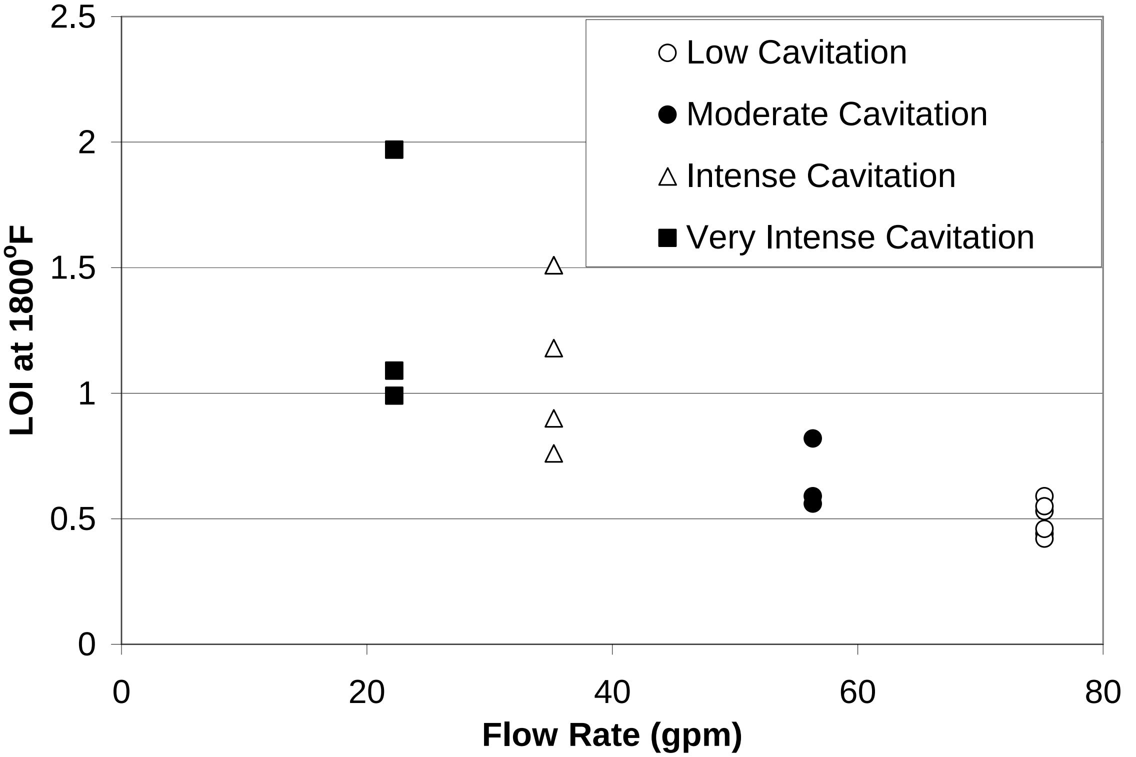

Figure 5.1.1B. The percent LOI at 1800°F, compared to the flow rate (gpm) for each degree of cavitation, using a 10 minute wash time and 1 lb sand to 1 gal water, for Tube B.

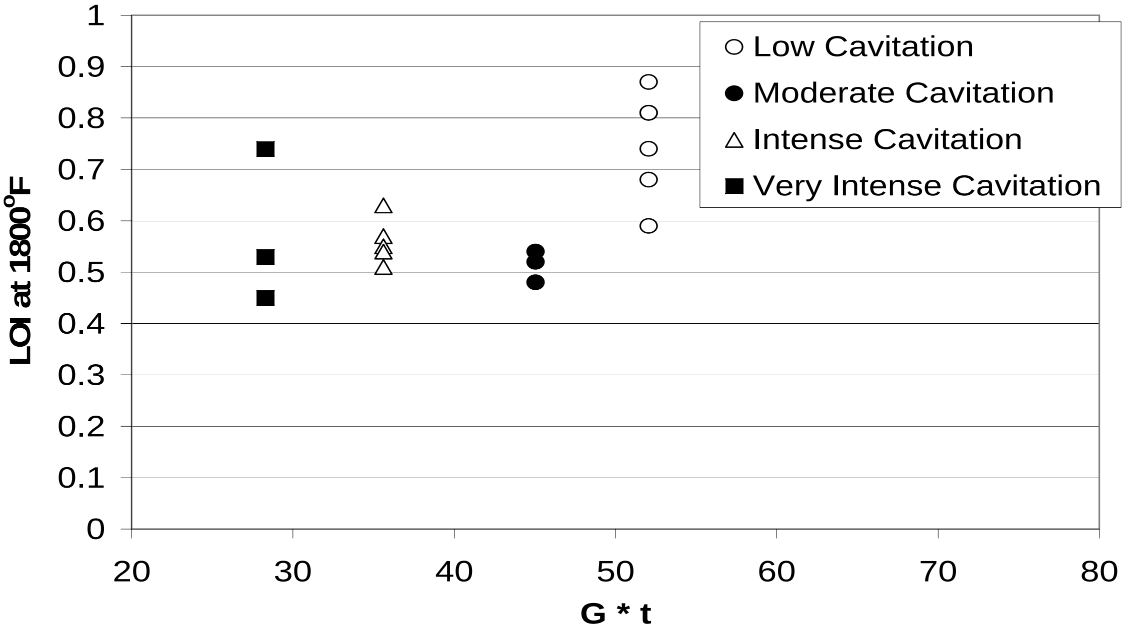

Figure 5.1.1.C. The percent LOI at 1800°F, compared to the calculated Gt values, for each cavitational degree, using a 10 minute wash time and 1 lb sand to 1 gal water, for Tube A.

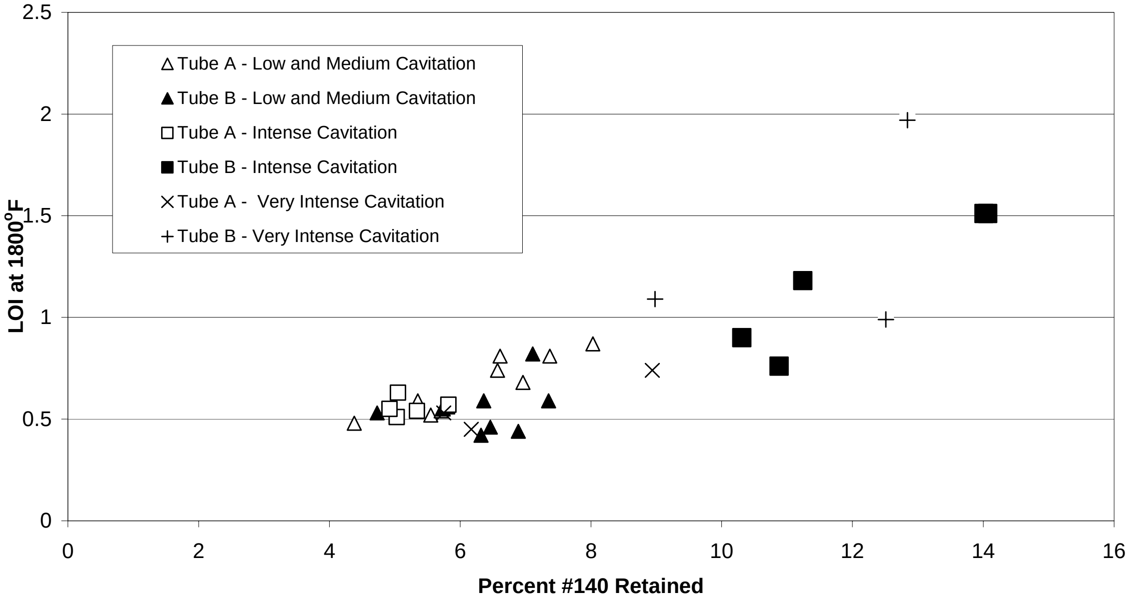

Figure 5.1.1.D. Percent 140 screen retained vs. 1800°F LOI, as a function of the Degree of Cavitation and the settling pipe location (Tube A or B), when using 10 minute wash and no Hydrogen Peroxide or Ozone addition.

Regardless of cavitation intensity, all product sand samples contained 0.4 to 0.6% MB clay (Figure 5.1.1B). The MB clay increased with respect to percent 140 screen retained. As shown in Figure 5.1.1B, the MB clay remained between 0.4-0.6% for all conditions, and it varied less with cavitation intensity than did the LOI or percent 140 screen. This means that it required less energy to segregate MB clay from sand grains than it did to scour the carbonaceous LOI off the sand grains. Interestingly, it was found that removal and subsequent recovery was enhanced by rinsing the product sand. It was found that rinsing product sand removed half of the clay, and then measured MB clay levels were reduced as low as 0.2 to 0.25%.

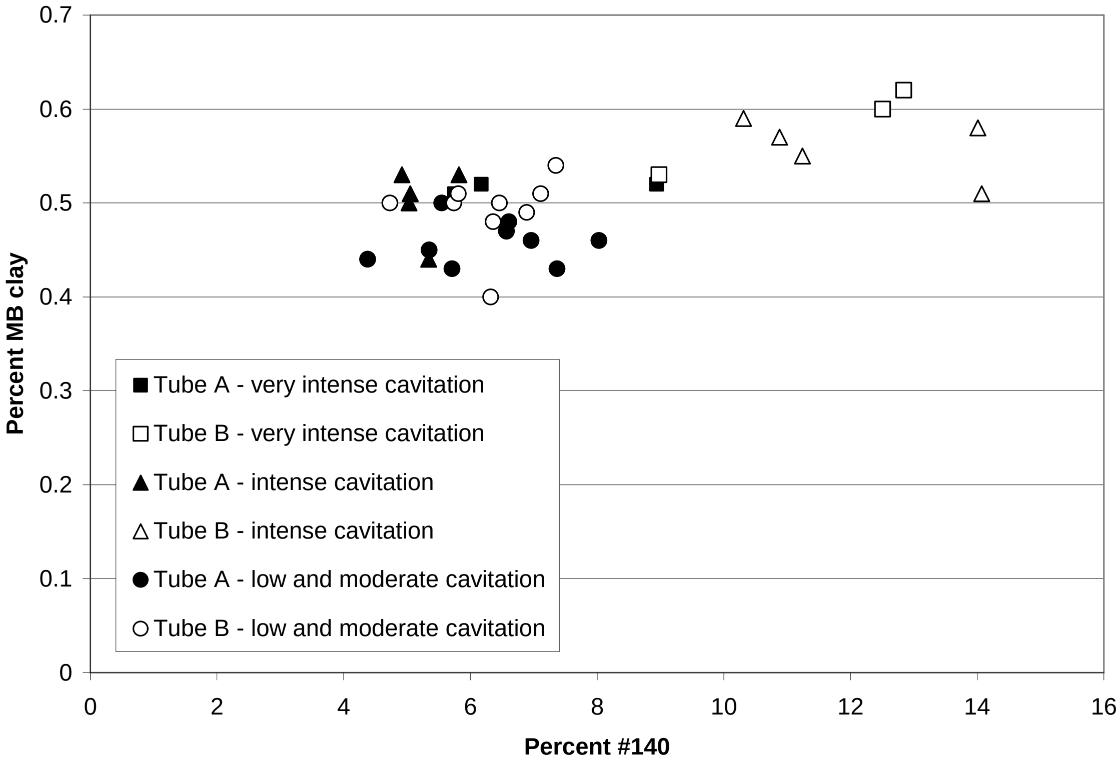

Figure 5.1.1.E. Percent 140 screen retained vs. MB clay, as a function of the Degree of Cavitation and the settling pipe, when using 10 minute wash and no Hydrogen Peroxide or Ozone addition.

5.1.2 Wash Time Effect When Using No Hydrogen Peroxide or Ozone

The effect of wash time was monitored, which varied as 5, 7.5 and 10 minutes. These experiments employed intense cavitation and no advanced oxidation. Figure 5.1.3A shows that as the wash time increased, from 5 to 7.5 minutes, the LOI decreased; and then the 10 minute wash time achieved no lower LOI than did 7.5 minutes. Thus, 7.5 minutes was optimum for these conditions in the pilot-scale unit when neither hydrogen peroxide or ozone were added.

5.1.3 Wash Time Effect When Using 1000 ppm H_2O_2

Wash time was appraised to quantify how LOI was affected when hydrogen peroxide accompanied the unit operations during intense cavitation. In this case, the 5-

minute wash time achieved lower and more consistent LOI's (0.8-1.0%) than did 7 or 10 minutes (Figure 5.1.3B).

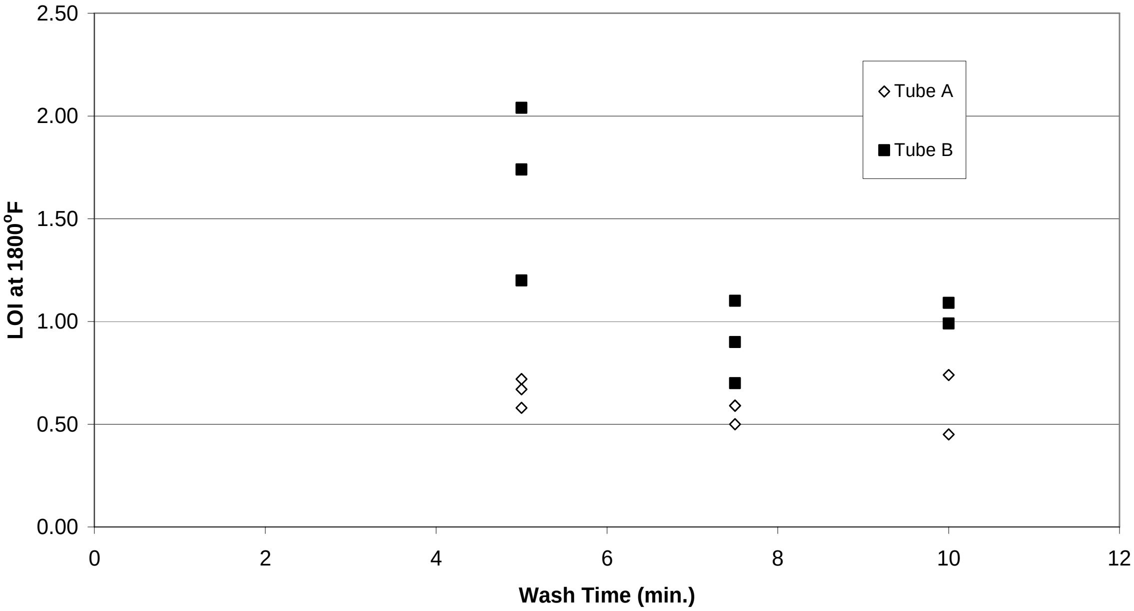

Figure 5.1.3A Wash Time (5, 7.5 and 10 minutes) plotted against the Tube A and B product sand LOI, with system conditions set for intense cavitation, no Hydrogen Peroxide or Ozone.

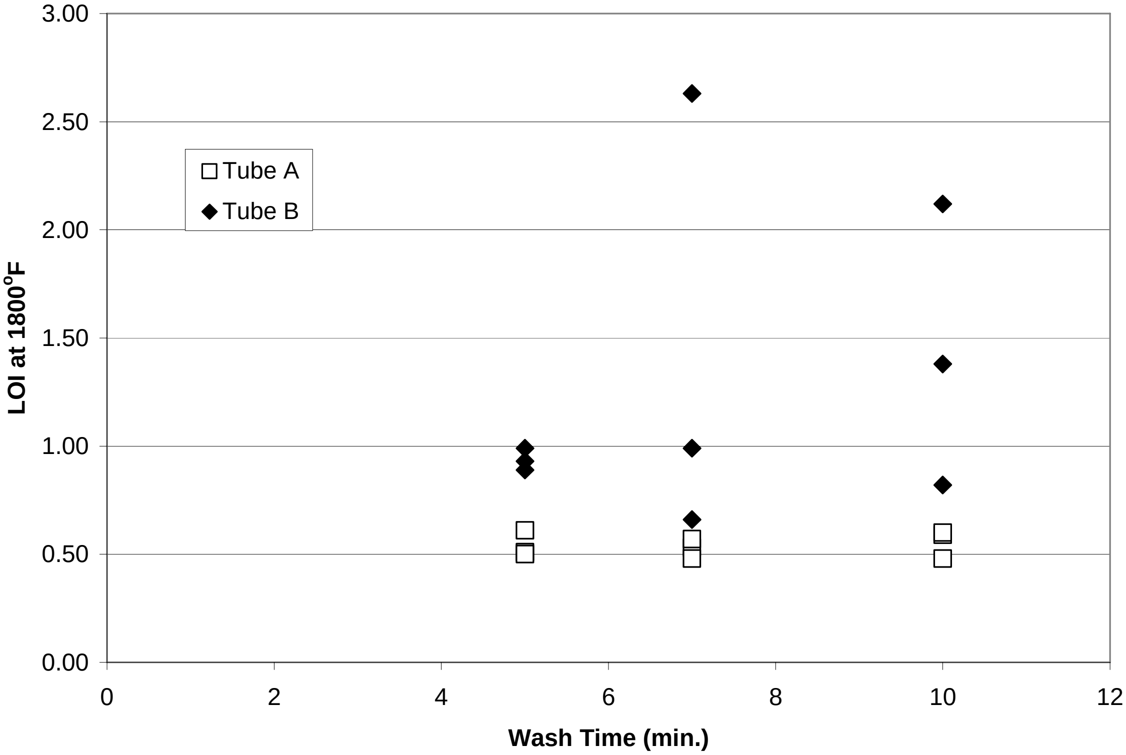

Figure 5.1.3B. Wash time (min.) versus the LOI at 1800°F, when 1000 ppm H_2O_2 is added during intense cavitation

5.1.4 Effect of Hydrogen Peroxide Dose

Next, the effect of hydrogen peroxide dose was examined. Trials compared H_2O_2 doses of 0, 500, 750 and 1000 ppm while employing a 5 minute wash time. As shown in Figure 5.1.4, the Tube B sand LOI was lower (0.8-1.0%) and more consistent when dosing 1000 ppm H_2O_2; then when dosing 0-750 ppm H_2O_2. These results indicated that hydrogen peroxide accelerated the degradation and/or shearing of carbonaceous material.

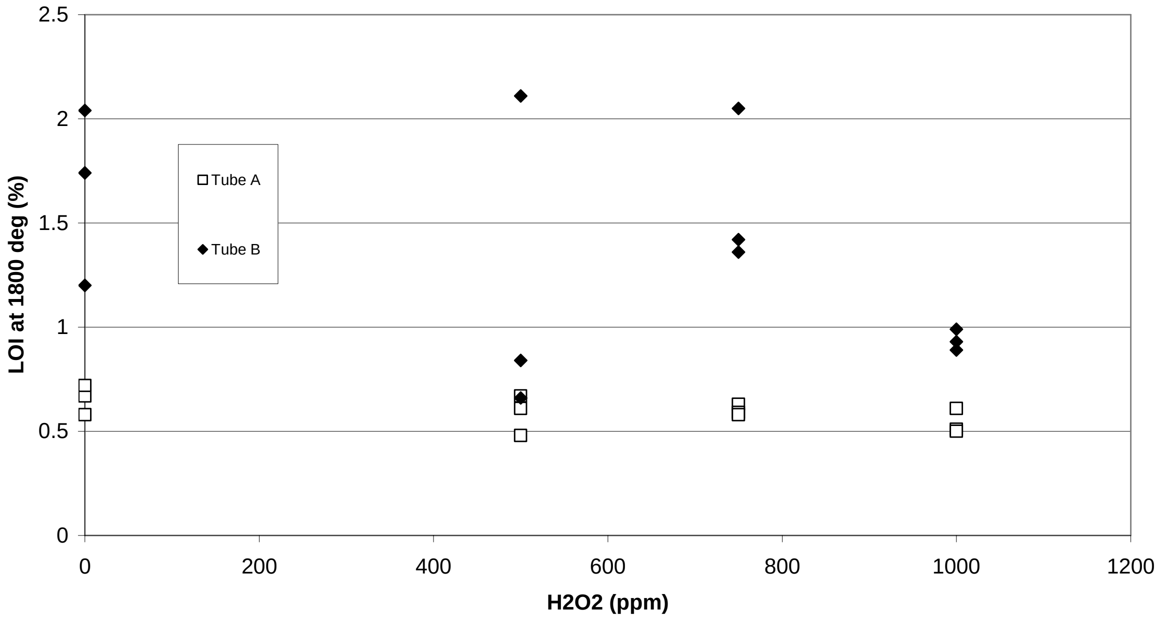

Figure 5.1.4. The LOI at 1800°F for various Hydrogen Peroxide (ppm) dosages, when system operation was 5 minute wash time and intense cavitation.

5.1.5 Ozone Treated Sand

This research appraised how ozone additions influenced sand properties. For these trials ozone was generated with an ozone generator, and was present in the slurry at supersaturated ozone levels [**17**] As shown in Table 5.1.5, these conditions achieved acceptable sand segregation, with most of the LOI and MB clay removed from the product sand. This also provided insights regarding how the sands classified into Tube A as compared to Tube B. Tube A product sand was coarser (61.29 GFN), had lower LOI (0.56%) and lower MB clay (0.44%) than the Tube B reclaimed sand. Tube B retained mesh # 140 (US Mesh sieve size) sand at nearly 13%, but was higher in LOI (0.91%) and MB clay (0.58%). Parenthetically, these trends for Tube A and B were generally true when operating with intense cavitation for a range of other variables. Both tubes produced sand that was very favorable compared to the waste green sand used which had a MB clay of (7.92%), LOI of (3.81%) and 3.3% fines.

Table 5.1.5. Waste Green Sand (Input Sand to Ultrasonic-Cavitation System) and Results of Ozone Treated Sand.

	Waste Sand In	New Green Sand	Ozone Treated	
Parameter	Value	Value	Tube – A	Tube - B
% Methylene Blue Clay	7.9 ± 0.2	0.3 ± 0.1	0.4 ± 0.0	0.6 ± 0.0
% Percent Volatiles	1.72 ± 0.12	0.00	0.43 ± 0.07	0.71 ± 0.30
% Loss on Ignition	3.81 ± 0.21	0.00	0.56 ± 0.09	0.91 ± 0.46
Percent #140 Retained	12.1 ± 1.5	10.0 – 16.0	7.6 ± 0.4	12.7 ± 2.2
Percent Fines (<#140)	3.6 ± 1.0	1.0 – 4.0	1.1 ± 0.1	1.7 ± 0.3
Grain Fineness Number	68 ± 3	68.0	61 ± 1	67 ± 1

This research monitored the AFS-washed sand size distributions during the trials that included ozone, as presented in Figure 5.1.5. Tube A, the first in series, tended to accumulate more of the larger grains, as evidenced by higher proportions of #40, 50, and 70 in Tube A than in the initial waste green sand, and less #40, 50 and 70 in Tube B than in the initial waste green sand. Concurrently, Tube B accumulated proportionally more 100 screen and 140 screen than was present in the waste green sand, while Tube A accumulated less of the #100 and #140. Notably, both Tube A and Tube B accumulated less #200, #270 and pan fines than were present in the waste green sand. This means that the wash cycling rinsed these fines away and generally that is favorable. The same trends that have been illustrated for the ozone trials (Figure 5.1.5) were also observed for many of the other batch conditions.

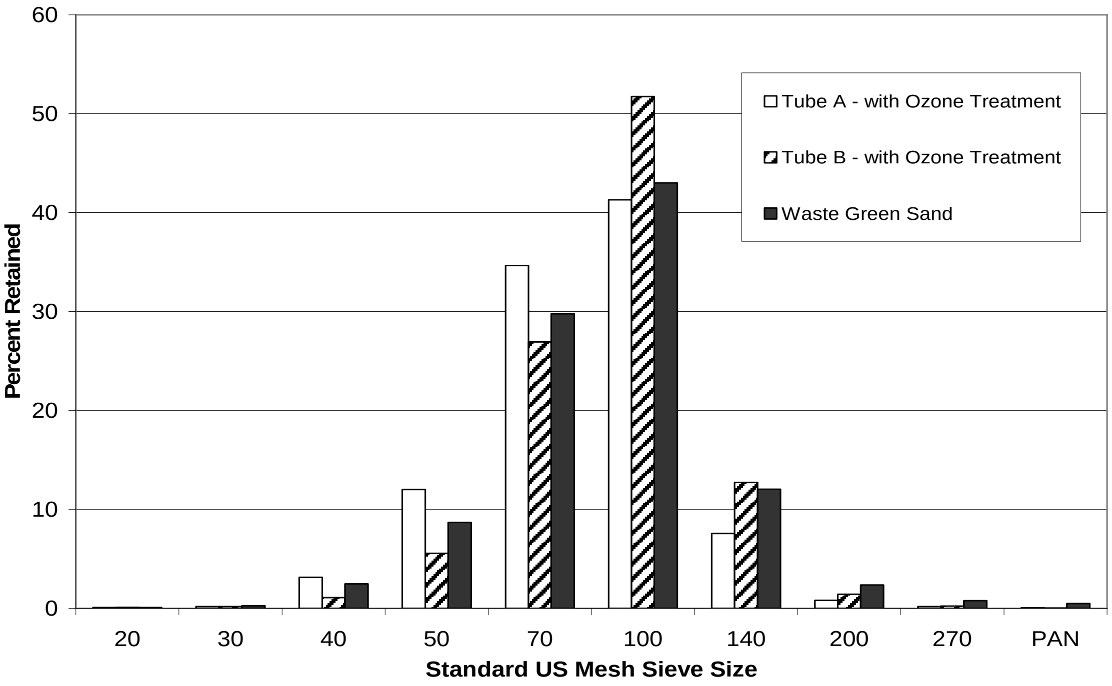

Figure 5.1.5. Sieve Distribution for Initial Waste Green Sand, Tube A product sand and Tube B product sand when treated by Ozone

5.1.6 Effect of Ozone or Hydrogen Peroxide on LOI, Percent #140 and MB Clay

As a general trend, additions of ozone and 1000 ppm hydrogen peroxide achieved more consistently low LOI's for a given percent 140 screen sand than was achieved without O_3 or H_2O_2. The results showed this for both Tube A reclaimed sand (Figure 5.1.6A) and Tube B reclaimed sand (Figure 5.1.6B). The Figure 5.1.6A data also depicts the Tube A H_2O_2 reclaimed sand that was used for core tensile strength tests ("dog-bone" tests, discussed later).

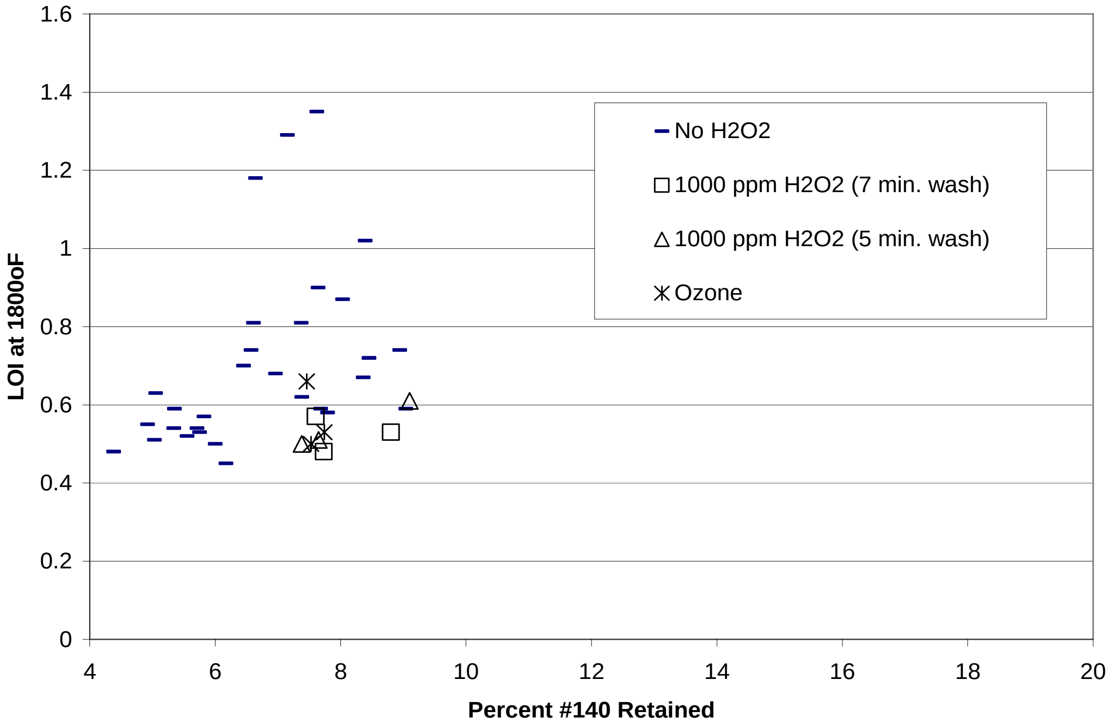

Figure 5.1.6A Percent #140 retained and LOI at 1800°F of Tube A only, when using intense cavitation with 1000 ppm H_2O_2 (7 min. wash), 1000 ppm H_2O_2 (5 min. wash) and Ozone (7 min. wash), when considering Tube A with No H_2O_2 under various cavitation conditions.

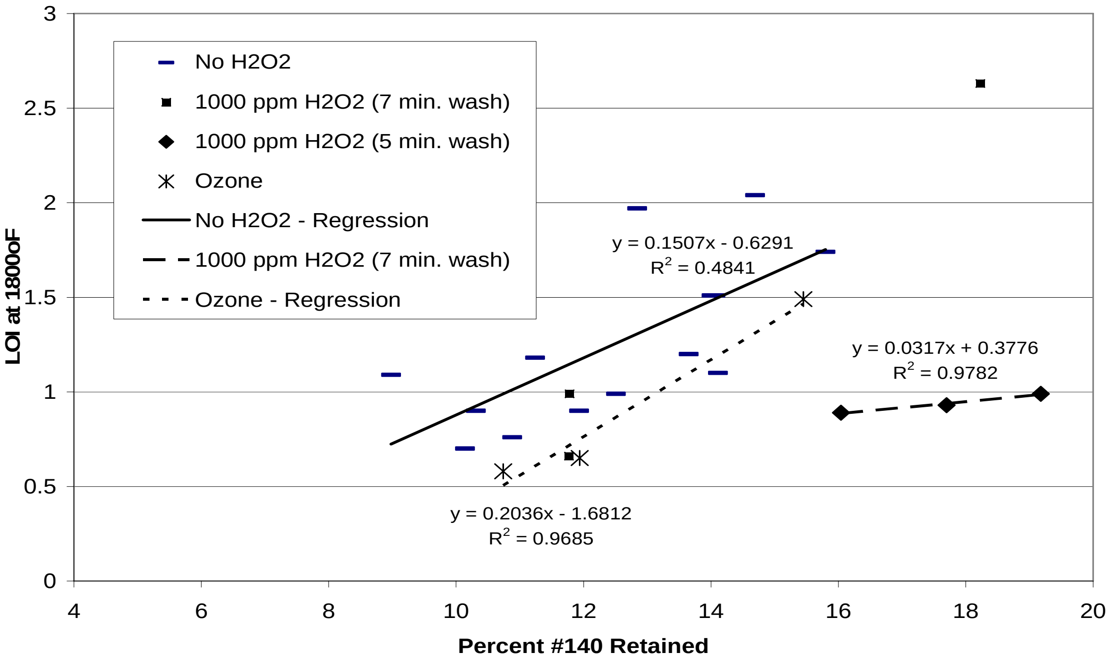

Figure 5.1.6B Percent 140 retained and LOI at 1800°F of Tube B only using intense cavitation with 1000 ppm H_2O_2, Ozone or No H_2O_2

As an indication of this the trend, several linear regressions were conducted of the Figure 5.1.6B data for Tube B results. The first regression was for all the runs that used no H_2O_2 or ozone while applying intense or very intense cavitation. The second was for all runs that included ozone with 7-minute wash and the third was for all runs that included 1000 ppm H_2O_2 with a 5-minute wash. As indicated, when the trials employed either hydrogen peroxide or ozone, the regressions showed a lower LOI (by about 0.5 percentage points) for a given percentage of #140 mesh sand than when the H_2O_2 or O_3 was not included. The 1000 ppm H_2O_2 with 5 minute wash achieved the lowest LOI (1%) while retaining the highest #140 mesh (16-19%). However, when ozone was included, the LOI was 0.5-1.5% while the #140 mesh sand remained 11-15%; and this would be a suitable reclaimed sand for make-up in green sand molds. This is particularly valid in light of the lower cost for ozone than for hydrogen peroxide. Subsequent trials will focus on including ozone while varying wash time, dose, etc.

The authors have also plotted percentage methylene blue clay versus percent #140 sand in Figure 5.1.6C. This data likewise depicts intense or very intense mixing conditions; and they appraise runs when hydrogen peroxide or ozone were included, compared to these without H_2O_2 or O_3. As shown, with no H_2O_2 or O_2, % MB clay ranged from 0.45-0.6%. With hydrogen peroxide or ozone, the MB clays ranged from 0.4 to 0.5. The MB clays with hydrogen peroxide or ozone were generally 0.05 to 0.1 percentage points lower than their non-O_3/H_2O_2 counterparts. All of these MB clays appeared in a reasonable range for reclaiming the sand for either green sand make-up or core sand.

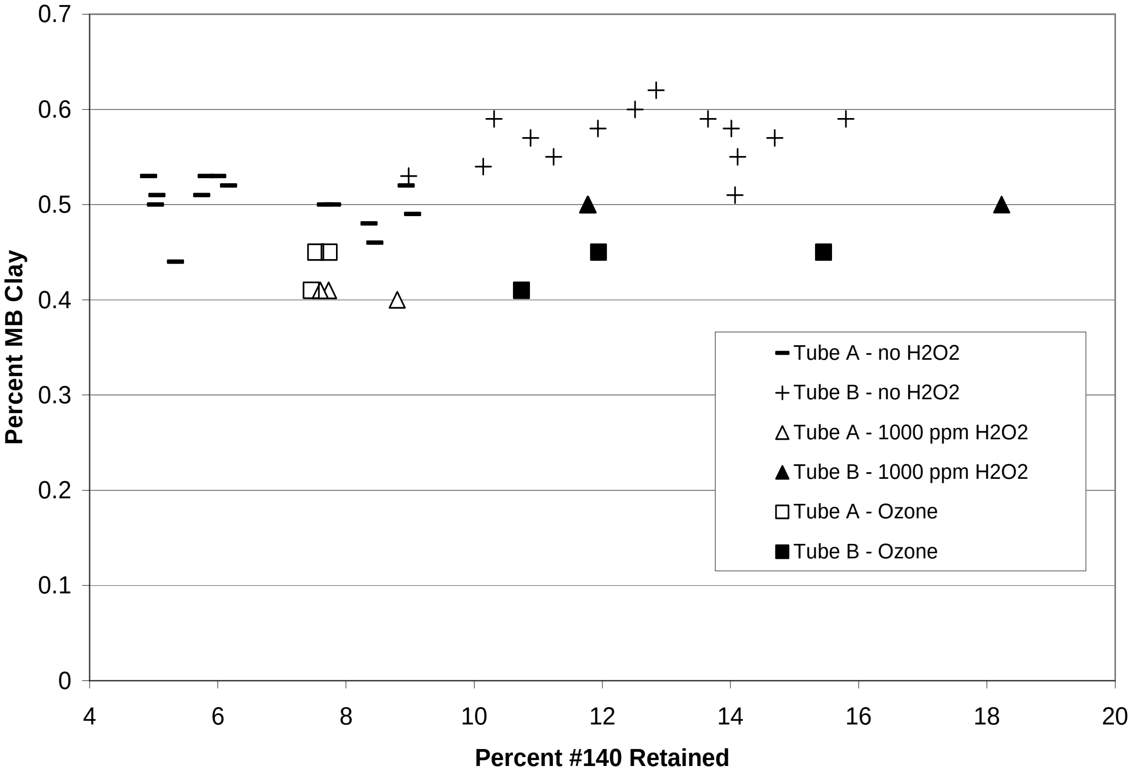

Figure 5.1.6C Effect of Ozone and Hydrogen Peroxide on Methylene Blue Clay and percent #140 retained; Tubes A and B. All results shown employed intense or very intense cavitation.

5.1.7 Comparison of Reclaimed Product Sand to Standard Specifications for Sand Used in Cores or Green Sand

The standard specification for sand that is used in cores is generally slightly coarser than for sand used in green sand. This is because when the core sand is recovered in the green sand system it will become finer as it is reprocessed. The sand in green sand should contain enough 140 screen sand to prevent molten metal from penetrating the mold. But there should not be so much #140 mesh and fines (<#140) that gases become trapped in the mold and cause blows. For this reason, the Neenah Foundry green sand specification calls for 10-16% #140 mesh sand and a grain fineness number (GFN) of 63-68 (Table 5.1.7). For the core sand, there are two conflicting constraints: on the one hand, larger sand grains require less core binder to set the core. However, on the other hand, any core sand that is used in a conventional iron foundry will be re-circulated with the green sand for multiple cycles, so whatever core sand is used should also be adaptable as a green sand. In balance of these considerations, the Neenah core sand specification calls for 15-19% 140 screen sand and a GFN of 67-71.

In comparison to these specifications, when 1000 ppm H_2O_2 augmented the sand reclamation system (with 7 minute wash), the Tube A product sand contained 8% #140 mesh sand and exhibited a GFN of 61 (Table 5.1.7). Moreover, the Tube B product sand contained 14% #140 mesh sand and a GFN of 68. Thus, the Tube A product sand was slightly coarser than the standard core sand specifications (i.e. Slightly more #40-70 than specified and slightly less #140). Moreover, the Tube B product sand slightly less #50 and slightly more #100 than specified for green sand. If a foundry preferred to remain rigidly constrained to a given set of specifications, then the balance between Tube A and B could be adjusted in a full-scale sand reclamation system. Indeed, a full-scale ultrasonic-cavitation system will have numerous distinctions from the pilot-scale unit. However, when a foundry is reclaiming 30-70% of its waste green sand and core sand, then the balances could be quite different from conventional operations; and under such circumstance, coarser core sand and finer green sand make-up is probably a good thing. Moreover, Tube A product sand generally has a lower LOI and MB Clay –it lends itself to higher core sand potential.

Table 5.1.7 Core Sand and Green Sand Specifications, compared to Tube A and Tube B product sand. The Tube A product sand was used for dog bone production

Standard US Mesh Size Retained on	Core Sand Spec		Tube A treated with 1000 ppm H_2O_2	Green Sand Specs.		Tube B treated with 1000 ppm H_2O_2
	Min	**max**	**Average**	**Min**	**max**	**Average**
20	0.0%	0.0%	0.1%	0.0%	0.0%	0.1%
30	0.0%	0.0%	0.1%	0.0%	0.0%	0.2%
40	0.0%	2.5%	3.2%	0.0%	4.0%	1.6%
50	4.0%	9.5%	11.6%	10.0%	17.0%	6.3%
70	25.0%	30.0%	34.8%	26.0%	34.0%	27.1%
100	37.0%	49.0%	41.1%	34.0%	42.0%	48.6%
140	15.0%	19.0%	8.0%	10.0%	16.0%	13.9%
200	0.0%	3.0%	0.8%	1.0%	3.5%	1.9%
270	0.0%	1.0%	0.2%	0.0%	0.5%	0.3%
Pan	0.0%	0.0%	0.0%	0.0%	0.0%	0.1%
GFN	67	71	61.5	63	68	68

5.1.8 Preparation of Core Samples and Tensile Strength Testing

Next, it was sought to determine whether this reclaimed sand could be used for core sand, and so the pilot unit processed the green sand through multiple batches under given prescribed operating conditions. Table 5.1.8 illustrates the properties of the two sands that were used to produce dog bones. The first sand was from Tube A only and was produced during a 7 minute wash cycle, utilizing 1000 ppm H_2O_2. This reclaimed sand contained a measured 0.40% MB Clay and 0.52% LOI, but was relatively coarse with a GFN of 61.5. The second set of sand was produced from Tube A and B; and made with intense cavitation but without hydrogen peroxide. This sand had similar MB Clay (0.40%), but was finer (GFN of 64.3) and had a higher LOI (0.98%).

Table 5.1.8. Characterization of the sand used to produce Dog Bones.

	Tube A only, 1000 ppm H_2O_2	**Tube A and B, no H_2O_2**
Parameter	**Average ± Std. Dev.**	**Average ± Std. Dev.**
% MB Clay	0.4 ± 0.0	0.4 ± 0.0
% Percent Volatiles	0.47 ± 0.03	0.68 ± 0.04
% Loss on Ignition	0.52 ± 0.05	0.98 ± 0.06
Percent 140 Mesh	8.0 ± 0.6	10.78 ± 0.58
Percent Fines (<140)	1.1 ± 0.3	1.8 ± 0.4
GFN	61 ± 1	64 ± 2

When trials appraised Tube A sand that had experienced hydrogen peroxide addition, the average tensile strength reached approximately 131 psi after 15 minutes curing for both 20 and 40 percent reclaimed sand (Figure 5.1.8). When 60% reclaimed sand was blended with 40% new sand, the tensile strength averaged 120 psi after 15 minutes curing. These values compare favorably to the 70-80 psi tensile strength regularly used by Neenah when producing cores that contain additives. It also should be considered that the tensile strengths are greater than that of most cores that contain additives.

The sand that came from Tube A and B while no H_2O_2 was employed exhibited an average tensile strength of 128 psi after 15 minutes curing, when using 33% reclaimed sand and 67% virgin sand. This favorable result was achieved even though this product sand contained 0.98% LOI. What this tells us, is that the sand requirements to produce dog bones in this tensile strength range are forgiving – and that the ultrasonic-cavitation system has flexibility in core sand production. The dog bones produced using mixed sand (Tube A and B), were also tested after curing for 5 hours, and gained 12% tensile strength during the additional curing time – to 144 psi.

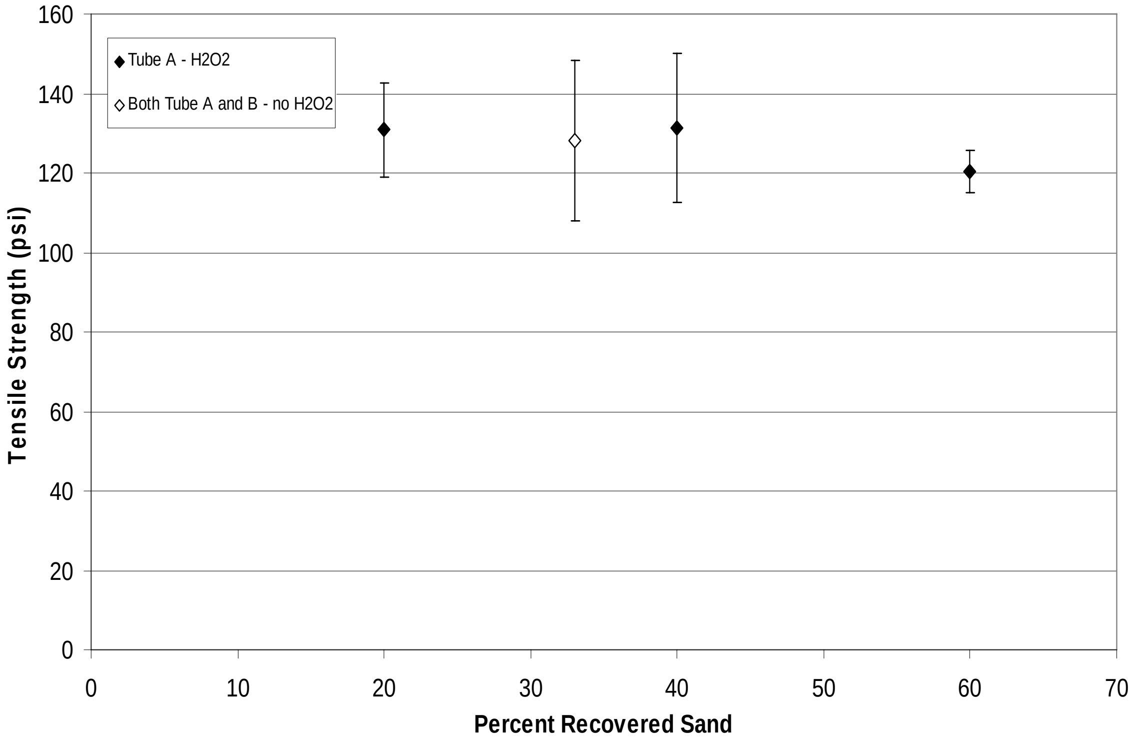

Figure 5.1.8. Percent Reclaimed Sand, which was mixed with new sand, plotted versus Dog Bone Tensile Strength. Results for two product sands (with one standard deviation bars shown)

5.1.9 Microscopic Photographs of Reclaimed Sand

Light microscope photographs were prepared of both the reclaimed sand grains and waste green sand grains. The reclaimed sand had experienced ozone addition and intense cavitation. As shown in Figure 5.1.9, the waste green sand grains hosted a heavy black-carbon coating, while the reclaimed sand that had experienced ultrasonic-cavitation-ozonation exhibited only scant residuals of this. It is this carbon coating that limits the extent to which sand can be re-ciriculated; and the photos show that the ultrasonic-cavitation process removed this carbon coating.

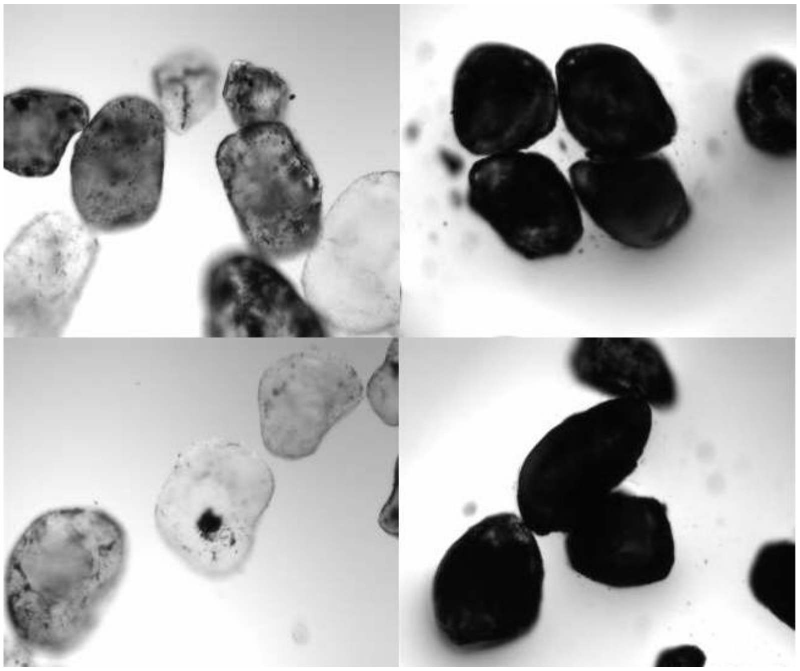

Figure 5.1.9. Tube A reclaimed sand, produced with intense cavitation and ozone addition (Top and Bottom Left), followed by waste green sand (Top and Bottom Right)

5.1.10 Thermal Gravimetric Analysis (TGA)

Results provided a thermal gravimetric fingerprint for analyzed samples. The samples which were analyzed were (1) waste green sand, from the Plant 2 at Neenah Foundry, (2) Phenolic-Urethane bonded reclaimed sand also called a 'dog bone'; and reclaimed sand (processed with one pound sand per gallon water, ozone, 7 minute wash time, 10 minute settle time) from (3) Tube A and (4) Tube B.

The waste green sand began mass loss at 350° C (Figure 5.1.10), the most significant mass loss began at 500° C. Mass loss proceeded at a constant rate until 725°C, where mass loss rate decreased but total mass loss realized 3.15%. This is less than the average LOI of 3.81%. Tube A reclaimed sand contained two mass loss zones. The first zone was from 550°C to 700°C, where the most mass loss occurred. The second zone of mass loss was between 750°C and 800°C, was a smaller fraction of the total mass loss. Tube B reclaimed sand had nearly an identical TGA 'fingerprint' as the Tube A sand as expected.

The reclaimed dog bone test realized the most significant early mass loss and over 3 thermal zones. The first mass loss zone began losing mass at 250°C to 500°C; this mass loss likely represents the loss of highly volatile organic compounds. The second mass loss zone is from 500°C to 650°C, which loses mass at a different rate than waste green sand, yet more similar to the rate experienced by the reclaimed sand. The final mass loss zone is from 700°C to 750°C, which was also experienced with Tube A and B samples.

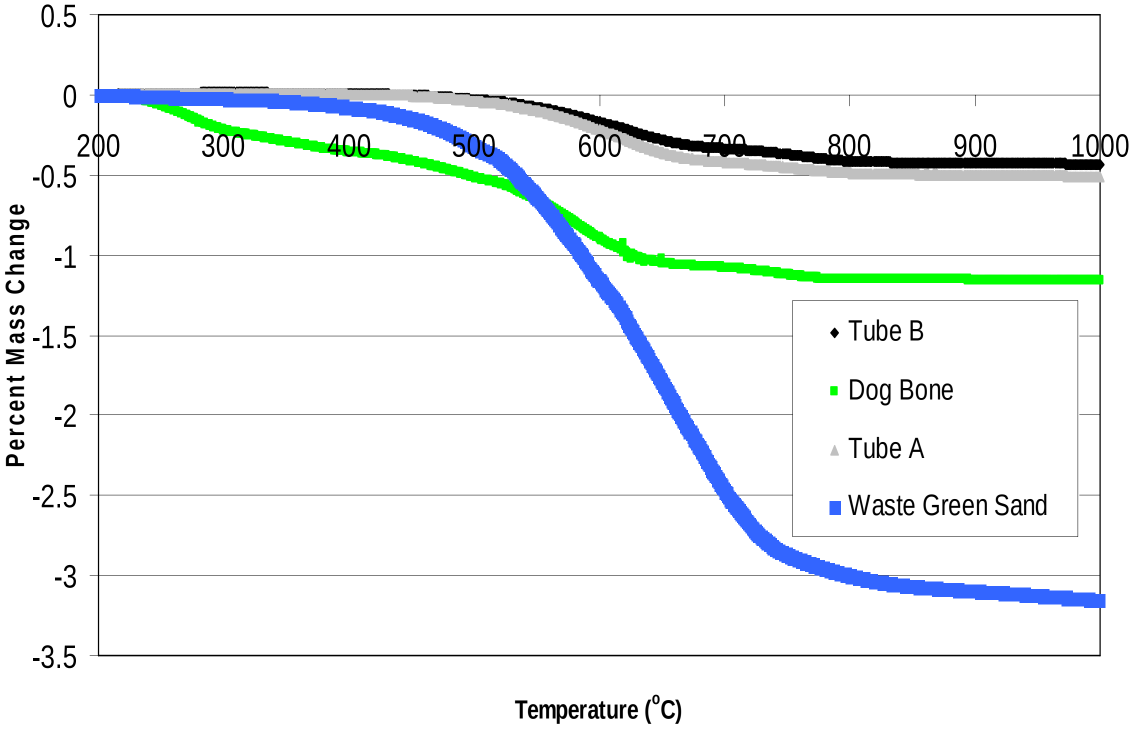

Figure 5.1.10. Thermal Gravimetric Analysis of Waste Green Sand, Tube A and Tube Samples as well as phenolic urethane bound dog bone.

5.1.11 Scanning Electron Microscopy

Scanning Electron Microscopy was useful in surface characterization of the unused sand, the waste green sand, reclaimed sand and the phenolic-urethane coated sand. Unused sand appears smooth under 100x magnification, however as magnification increases (up to 6000x) more surface characteristics are detected. In fact the relatively smooth sand has surface ridges that range from 2-15 micrometers in length, 1-5 micrometers in width and an estimated 2 micrometers in depth (Figures 5.1.11A, 5.1.11B). Waste green sand contains a ‘fuzzy’ appearance under SEM. This ‘fuzzy’ appearance is due to the dehydrated clay platelets and carbonaceous material on the sand grains. UCS reclaimed sand appears to be mostly smooth, however some sand grains still appear to be ‘fuzzy’ (Figures 5.1.11C, 5.1.11D). Additionally, some UCS reclaimed sand grains contain only small amounts of clay or carbon in fissures and small regions of a particular sand grain (Figures 5.1.11E, 5.1.11F, 5.1.11G, 5.1.11H, 5.1.11I). Lastly, phenolic-urethane bound sand was found to attach in an interesting manner. Between bound sand grains an approximately round binding site between sand grains forms. This binding site is approximately 10-30 micrometers in diameter, with a distance between sand grains of approximately 5 micrometers (Figures 5.1.11J, 5.1.11K). The failure sites of binding is readily detected by SEM with a discolored failure site of this approximate size located on the surface of previously bound sands.

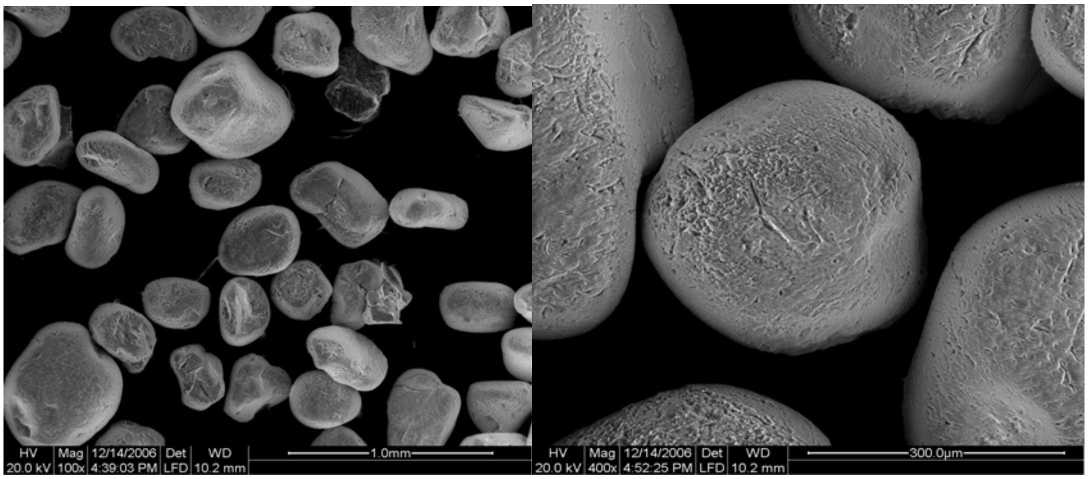

Figure 5.1.11A. SEM image of yet unused (virgin) Sand at 100x (left) and 400x (right)

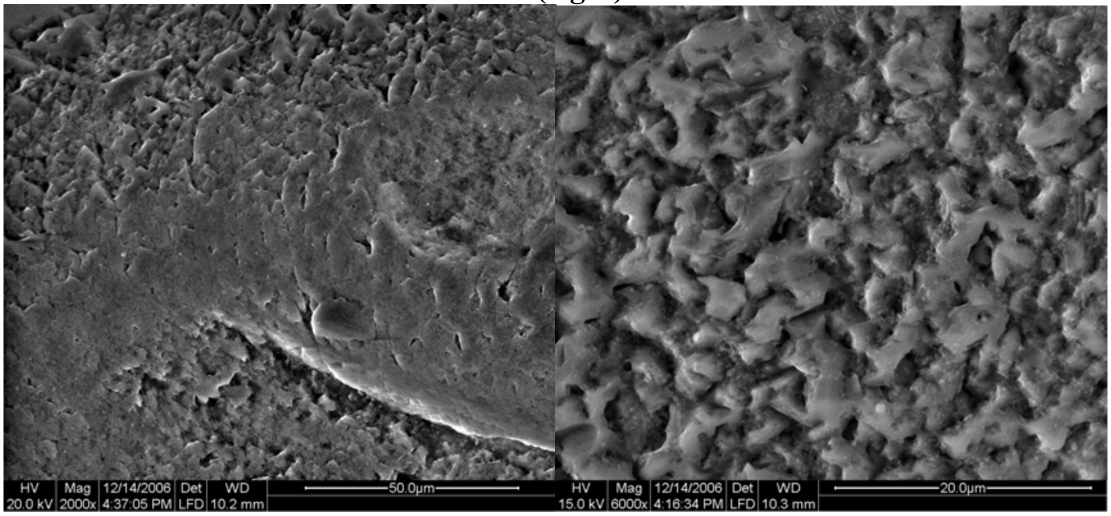

Figure 5.1.11B. SEM image of yet unused (virgin) sand at 2000x (left) and 6000x (right).

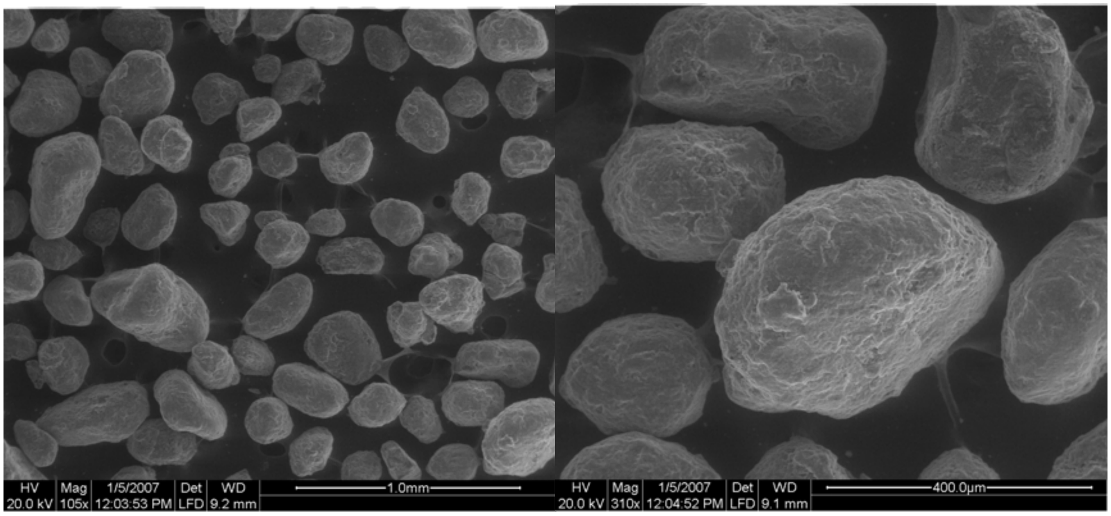

Figure 5.1.11C. SEM image of waste green sand 105x (left) and 310x (right).

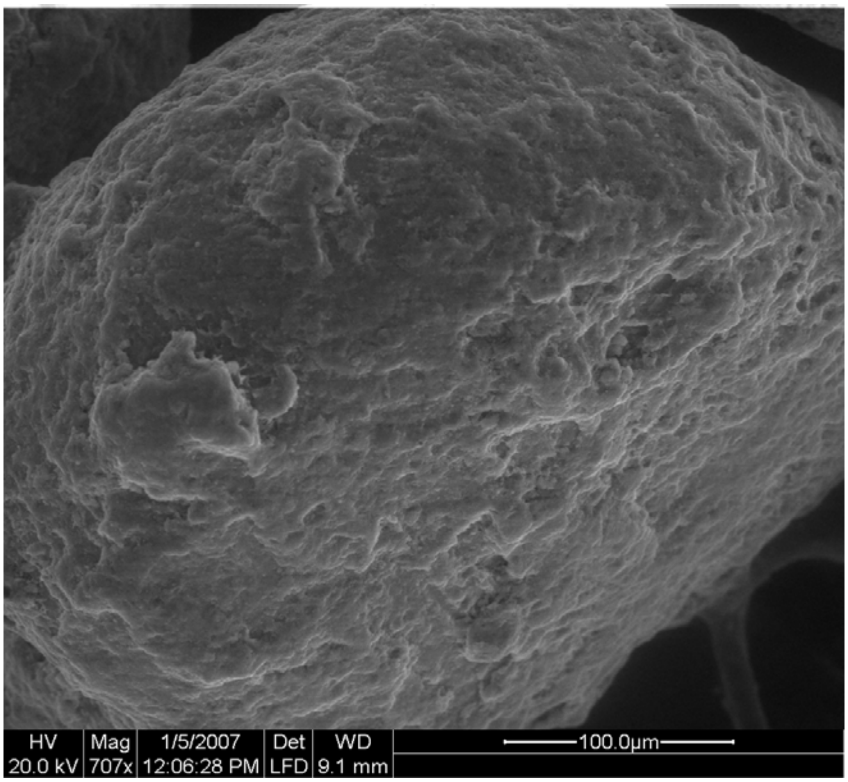

Figure 5.1.11D. SEM image of Waste Green Sand at 707x.

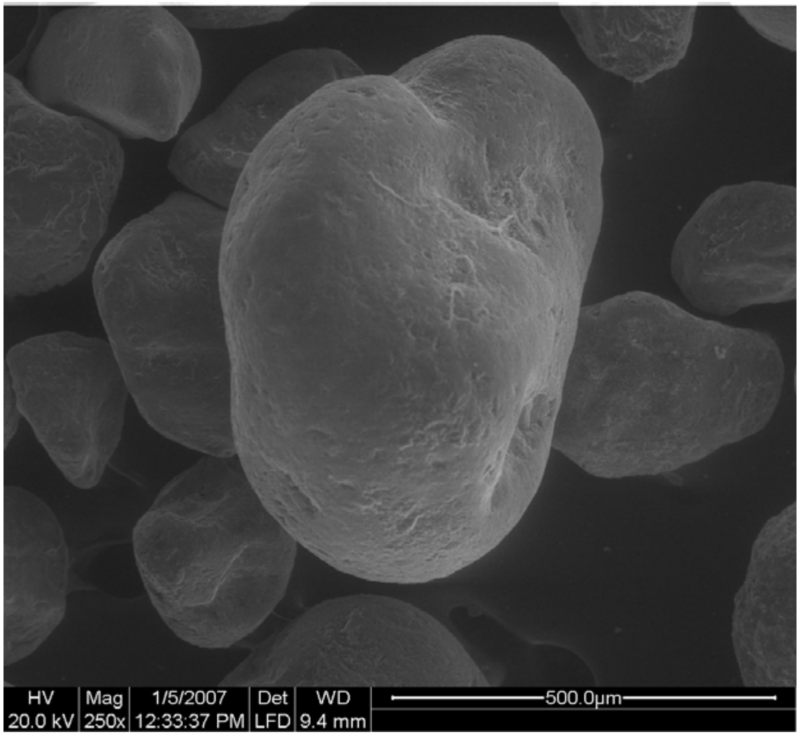

Figure 5.1.11E. SEM image of reclaimed sand (Tube A – R17, sample A2) at 250x.

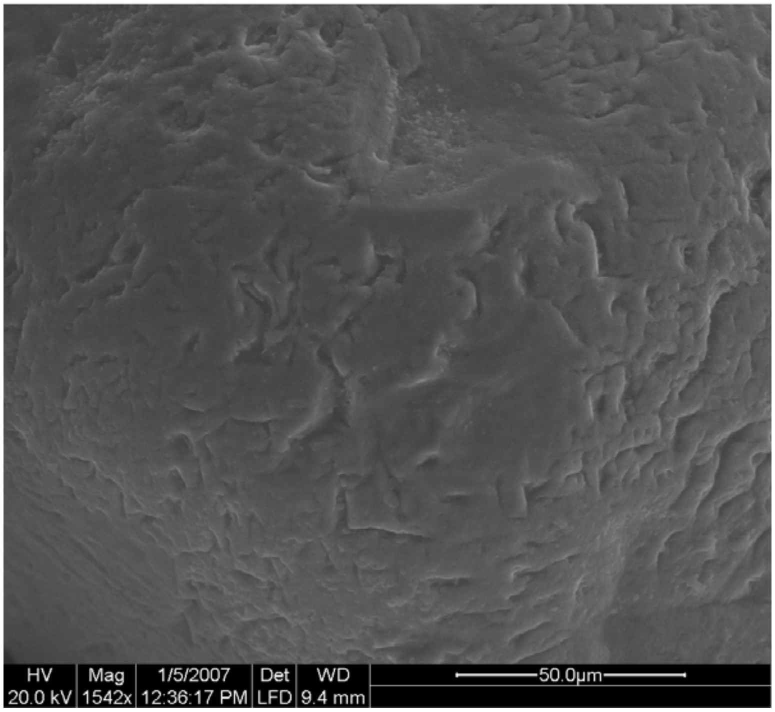

Figure 5.1.11F. SEM image of reclaimed sand (Round 17, Tube A, discharge 2) at 1542x.

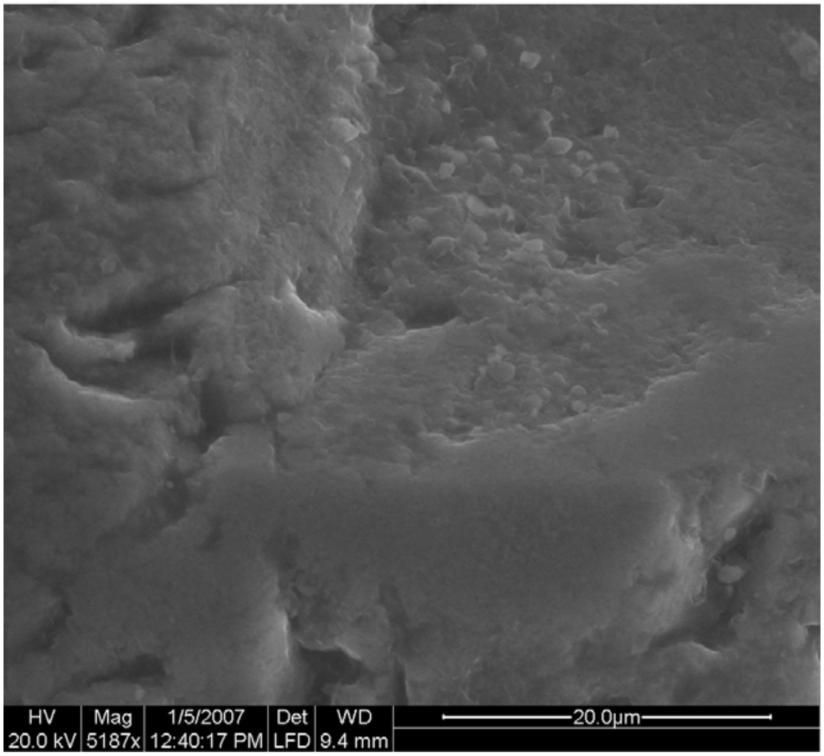

Figure 5.1.11G. SEM image of reclaimed sand (Round 17, Tube A, Sample 2) at 5187x.

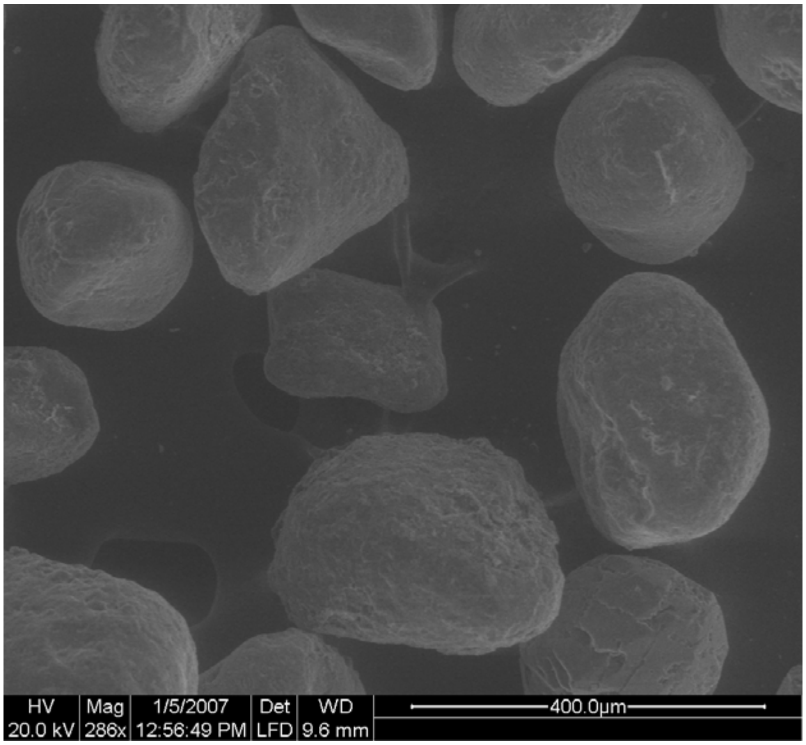

Figure 5.1.11H. SEM image of reclaimed sand (Round 17, Tube B, Sample 3) – 286x.

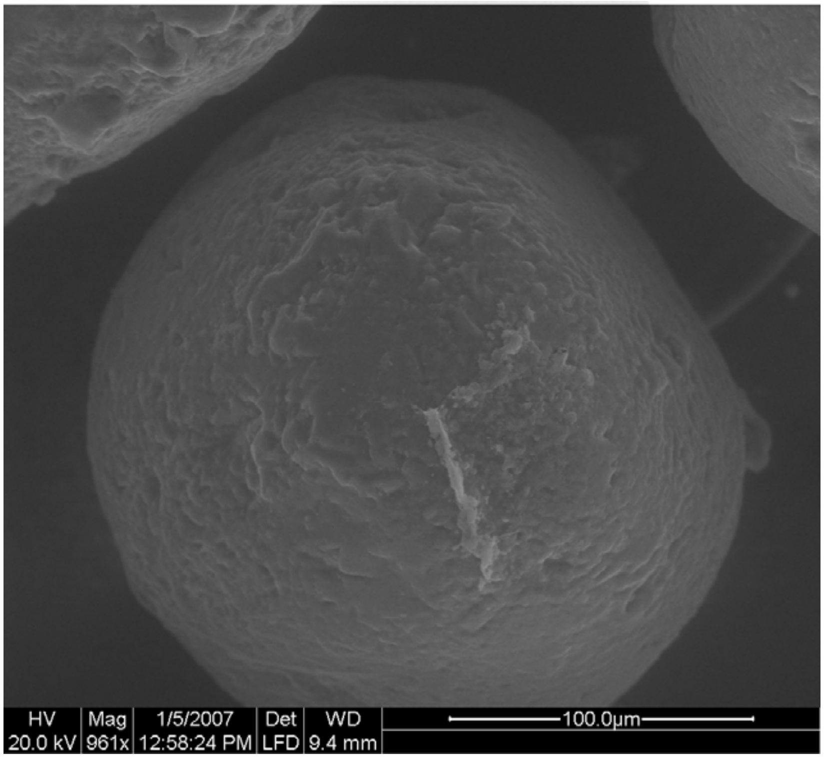

Figure 5.1.11I. SEM image of reclaimed sand (Round 17, Tube B, Sample 3) – 961x.

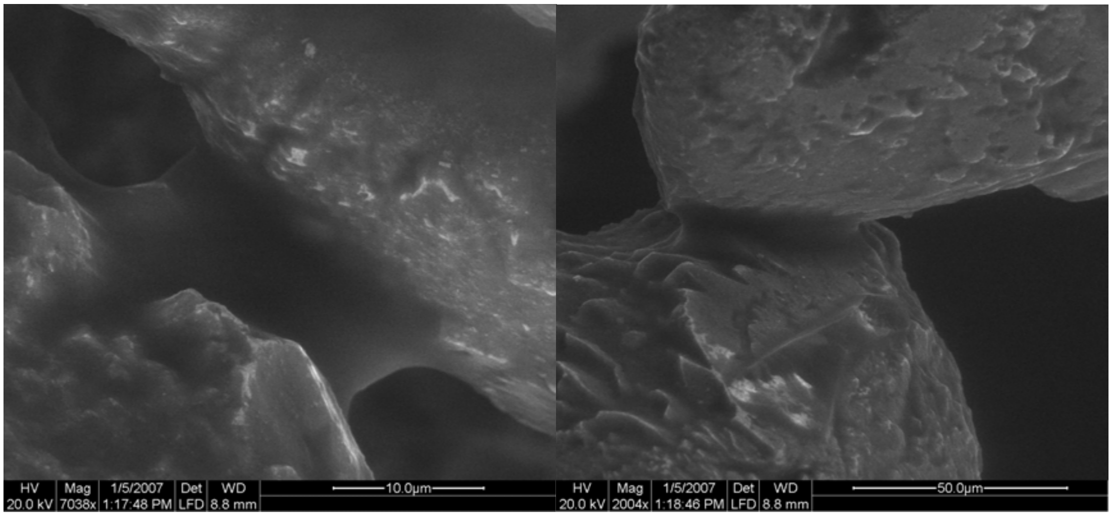

Figure 5.1.11J. SEM image of Phenolic-Urethane bound dog bones at 7038x (left) and 2004x (right).

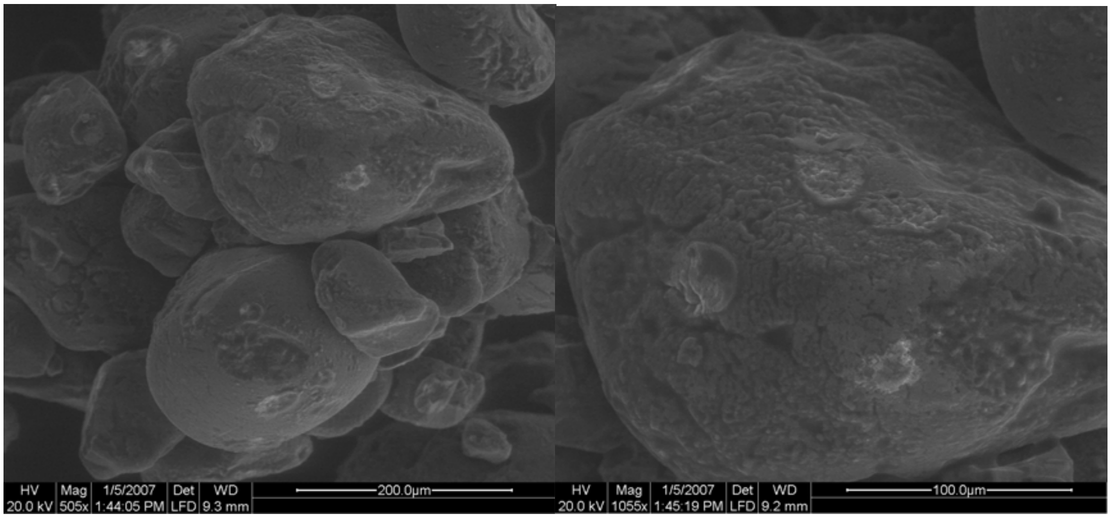

Figure 5.1.11K. SEM image of Phenolic-Urethane bonded core facture sufaces at 505x (left) and 1055x (right).

5.2 Baghouse Dust Processing

5.2.1 System operation

The authors transitioned the ultrasonic-cavitation-settling (UCS) system into full operation over the course of a year, while gradually ramping up the concentration of the baghouse dust in the AO water slurry. Before August, 2006, this plant 3 operation employed exclusively an AO-clearwater system with no bag house dust added. Then the slurry transitioned to 0.25 lb of bag house dust per gallon of AO-laden water for about 3 months. Then, the slurry solid content was increased to 0.5 lb/gal for 4 months, and then finally to 0.75 lb dust/gal AO water subsequently. At the highest slurry concentration, the UCS system used all the foundry sand system baghouse dust that was generated. Higher slurry solids concentrations may be employed but that would have required rerouting of other on-site baghouse sources that are not in reasonable proximity to the AO-BW-UCS system

5.2.2 Clay consumption per ton of iron poured

Increases in baghouse dust slurry solids content concentration reduced the sand system bond consumption, from an average 163.5 lbs of bond required per ton of molten iron poured for the original AO-CW system, down to 143.1 lbs/ton when the AO-BW-UCS system was used (Figure 5.2.2 and Table 5.2.2). It is noted that the July '06 and July '07 data have been omitted from these appraisals since July experiences schedule shutdowns, which incur significantly different material consumption than an average month. During the initial AO-BW-USC operating period, when 0.25 lbs BHD/gal water was processed, there was a slight change in clay consumption per ton of iron poured (Figure 5.2.2). In November 2006, the AO-BW-USC solids ratio again increased to 0.50 lbs BHD/ gal water, which enabled sand system bond consumption to drop to 153 lbs clay/ton Iron. When the solids loading was increased yet further to 0.75 lbs BHD/gallon processed, bond consumption dropped to an average of 144.8 lbs/ton (Figure 5.2.2 and Table 5.2.2). As previously mentioned at this highest solids loading the foundry consumes all nearby baghouse dust. The foundry is seeking alternative ways to transport sand system baghouse dust to the processing system, which is expected to further decrease sand system bond consumption.

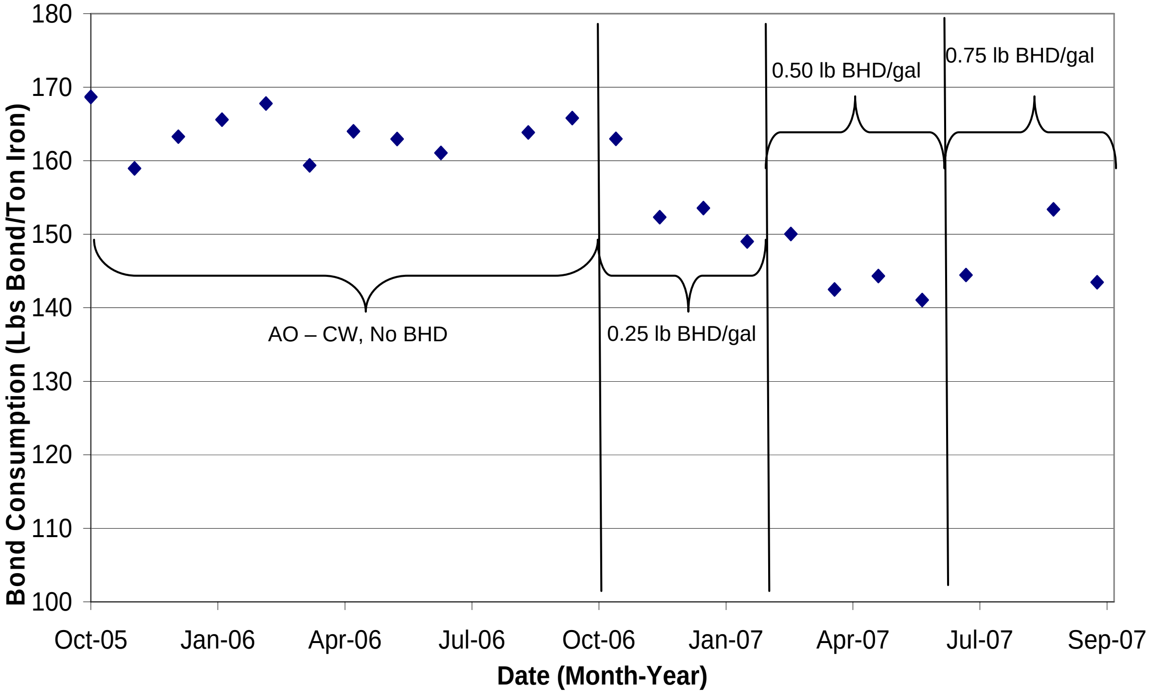

Figure 5.2.2. Bond consumption (Lbs Bond/Ton Iron) compared to baghouse dust (BHD) reclamation progression.

Table 5.2.2. Comparison between clay consumption per ton metal poured prior to ultrasonic-cavitation device and current operation.

Time Period	**Operations Protocol**	**Lbs Clay used/Ton Metal Poured**
Oct. '05 - June '05	AO - Clearwater	163.5 lbs/ton
Mar. '07 - June '07	AO slurried with baghouse dust; processed via ultrasonics-cavitation-settling; 0.75 lbs BHD/gal AO water	144.8 lbs/ton
Reduction	-	18.7 lbs/ton
Reduction (percent)	-	11.4 %

5.2.3 Baghouse Dust Profiled with Respect to Time

The variations of input baghouse dust were monitored through the first year that the ultrasonic-cavitation device was in operation. During this time, the LOI, MB Clay and grain fineness numbers of the baghouse itself all increased. Specifically, while progressing from a slurry concentration of 0.25 to 0.75 lbs/gal, the LOI content of the bag house dust increased from 13.2% to 17.7%, while its MB Clay content increased from 20.5% to 35.5% (Table 5.2.3). Concurrently, the AFS washed silica grains within the baghouse dust progressed to where it had less 70, 100, and 140 screen sand, and more 200, 270 screen and Pan fines (Figure 5.2.3). This transition was reflected in an increased GFN for the baghouse dust from 95 to 190.

Intriguingly, AO-USC system operations progressed from initial operation where the settling pipes discared some silica fines during initial startup, to conditions where the settling pipes discharged virtually no silica fines after about 9-10 months after startup.

In overview synopsis, this means that less of these larger silica grains became loosened from the green sand matrix during air exhausting to these baghouse collectors; and only the finest grains of silica, clay and coal ever traveled to the exhaust collection system. Thus, when this AO-UCS system operated under these conditions at steady state, the larger silica grains were less likely to get transported to the bag houses.

Table 5.2.3. Baghouse Dust parameters; Percent LOI, Percent MB Clay and GFN described with respect to the date sampled

	Bag house dust slurry (lb/gal)	**Loss on Ignition**		**MB Clay**		**Grain Fineness Number**	**Baghouse Dust Feed Rate (lb/gal)**
Date		**50 g sample**	**15 g sample**	**10 min - ultrasonics**	**Additional ultrasonication (Time)**		
8-22-06	0.25	9.9	13.5*	20.5	-	95	0.25
6-26-07	0.75	11.5	15.7	29.0	34.5 (20 min)	173	0.75
8-8-07	0.75	13.0*	17.7	35.5	38 (30 min)	190	0.75
% Change in year		+31	+31	+73	-	+100	-

Computed Value, as per 50g to 15g ratio determined with June 26 results.

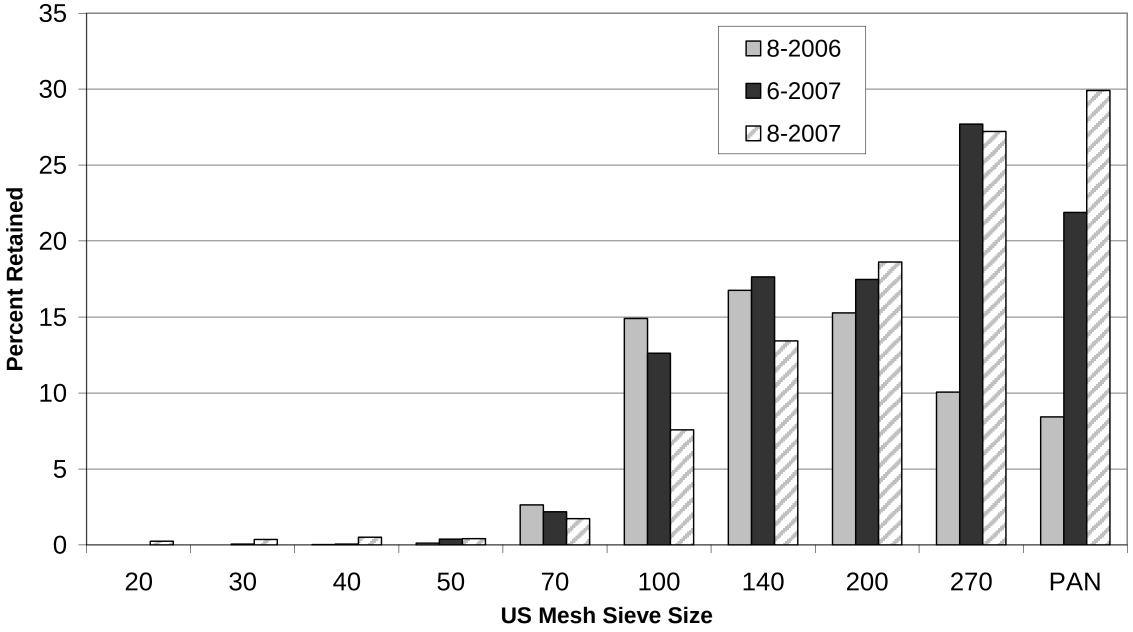

Figure 5.2.3. Baghouse Dust Sieve Analysis sampled from input to ultrasonic-cavitation device with respect to sample dates of August 22, 2006; June 26 2007; and August 8 2007.

5.2.4 Mold Cooling and Shake-out Emissions Comparison

VOC emissions for the AO-CW process were compared to AO coupled with UCS, operating with 0.75 lb BHD/ gallon of AO water. During each of these trials, the foundry employed a phenolic urethane core binder (1.1%), although the supplier was different during operations of AO-CW than for AO-UCS. When operating in AO-CW mode, VOC emissions averaged 0.67 lb/ton iron, whereas with UCS, emissions averaged 0.20 lb/ton iron, as presented in Figure 5.2.4. A portion of this change could have been attributed to the change in binders to a “low emission” binder.

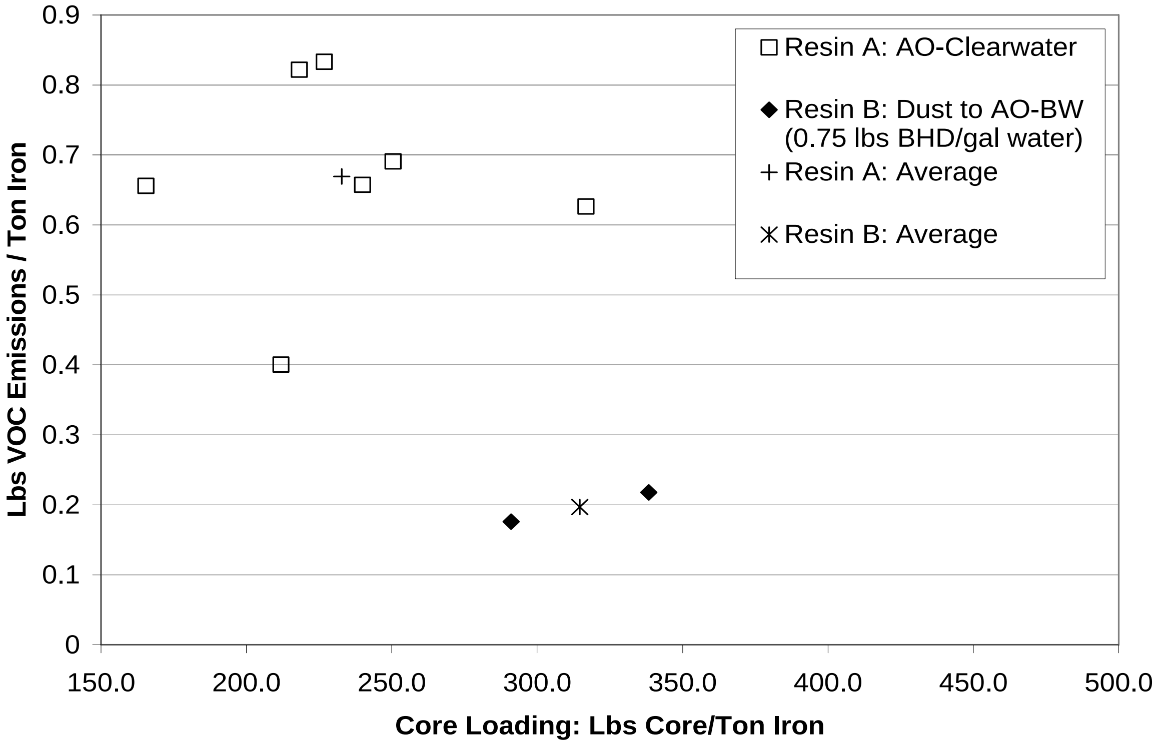

Figure 5.2.4 Pounds of VOC's emitted per ton of Iron pour with respect to pounds of core per ton of Iron – for Mold Cooling and Shake-out. The x-axis represents pounds of phenolic urethane core binder per ton of iron poured

6 Discussion

6.1 Waste Green Sand Reclamation

Processing waste green sand via an ultrasonic-cavitation system effectively cleaned waste green sand so as to reclaim the sand. This process can effectively reclaim clay, coal and silica sand. The ultrasonic-cavitation system reduced MB Clay from 7.92% to 0.4-0.6% and it reduced LOI from 3.8 to 0.4-0.6%. This reclaimed sand could be used in the core room as a replacement for new sand, yielding dog bones with 120 psi tensile strength when the core sand included 60% reclaimed sand and 40% new sand. Even when the LOI was 1%, tensile strengths of 123 psi could be achieved with 33% reclaimed sand 67% new sand, and 1.1% binder. Sieve distribution and fineness control is essential to all foundries, and this novel reclamation process offers a method to reduce fines while retaining well over 10% US Mesh size #140 sand grains. Also, the LOI tended to increase as the percent #140 increased, but hydrogen peroxide and ozone diminish the amount of LOI for a given #140 mesh fraction. Future laboratory work and continued study during full-scale implementation will enhance the knowledge associated with this system –to make technologies available to foundries for optimum sand operation.

6.2 Baghouse Dust Processing

Previous work has determined that AO significantly helps reduce a green sand system's VOC emissions during mold cooling and shake-out, particularly when coupled with a blackwater clarifier. The full-scale trials herein appraised whether the same favorable results could be achieved with a novel ultrasonics-cavitation-settling system that requires 1/5th as much floor space and costs 20-30% as much as a BW clarifier. The results indicate that indeed, the UCS system achieved favorable bond reductions that were similar to the reductions that have been achieved when employing AO with a blackwater clarifier. It is anticipated that when more than 0.75 lbs BHD/gallon AO water are processed, bond consumption will decrease yet further. This process enables more foundries to utilize AO technology, due to the smaller footprint and cost requirements, while achieving reduced emissions and material reduction capabilities as previously-available with the AO blackwater clarifier systems.

7 Conclusion

The UCS system offers an extremely effective means to recover waste green sand and baghouse dust. Waste green sand can be recovered, while simultaneously recovering valuable clay and coal in the blackwater effluent. This exceeds the capabilities of any previous sand reclamation unit. This positive outcome can be directly attributed to the unique surface cleaning capabilities of ultrasonics, the favorable synergistic chemistry when advanced oxidation is coupled with ultra-sonication, intelligent particle collision and the ability to discretely separate silica from blackwater. The UCS system also offers an improved alternative to the conventional blackwater settling system. This improved system maintains the ability to reduce VOC emissions as well as recover valuable clay from baghouse dust. Overall, the ultrasonic-cavitation system provides a sustainable solution to foundries for cost-saved material recovery, while simultaneously reducing VOC emissions.

8 References

1. Neill, D.A.; Cannon, F.S.; Voigt, R.C.; Furness, J.C.; Bigge, R. “Effects of advanced oxidants on green sand system performance in a black water system,” *American Foundry Society Transactions*. 2001, 937-955.

2. Land, J.D.; Voigt, R.C.; Cannon, F.S.; Furness, J.C.; Goudzwaard, J. Luebben, H. “Performance and control of a green sand system during the installation and operation of an advanced oxidation system,” *American Foundry Society Transactions*, 2002, 110, 705-715.

3. Wright, J.R.; Take a New Look at Sand Reclamation. *Foundry Management and Technology*. v 129, March 2001, p22-23.

4. Granlund, M.J.; Swenson, L.; “Sand Reclamation=Sand Savings with Proper Planning,” *Modern Casting*, v 92, n 8, August, 2002, p 29-31.

5. Hoyt, Daryl; “Should Your Foundry Be Reclaiming Its Sand?” *Modern Casting*, v91, n8, August 2001. p40-41.

6. “Controlling Hot-Sand Improves Quality, Efficiency,” *Foundry Management and Technology*, v 133, n 1, Jan. 2005. p30-31.

7. Cannon, F.S.; Furness, J.C.; Voigt, R.C. “Economical use of advanced oxidation systems for green sand emission reduction,” 12th American Foundry Society International Environmental, Health and Safety Conference; Lake Buena Vista, FL, Oct. 9-11, 2000; pp317-332.

8. Goudzwaard, J. E.; Kurtti, C. M.; Andrews, J. H.; Cannon, F. S.; Voigt, R. C.; Firebaugh, J. E.; Furness, J. C.; Sipple, D. L. “Foundry emissions effects with an advanced oxidation blackwater system,” *Am. Foundry Soc. Trans.* **2003**, *111*, 1191-1211.

9. Wang, Y.; Cannon, F.S.; Komarneni, S.; Voigt, R.C.; Furness, J.C.; “Mechanisms of advanced oxidation processing on bentonite consumption reduction in foundry,” *Environmental Science and Technology*, v 39, n 19, Oct 1, 2005, p 7712-7718

10. Wang, Y.; Cannon, F.S.; Voigt, R.C.; Komarneni, S.; Furness, J.C.; “Effects of advanced oxidation on green sand properties via iron casting into green sand molds,” *Environmental Science and Technology*, v40, n9, May 1, 2006, pp3095-3101.

11. Farmer, A.D.; Collings, A.F., Jameson, G.J.; “Effect of ultrasound on surface cleaning of silica particles,” *International Journal of Mineral Processing*, v 60, n 2, Sep, 2000, p 101-113.

12. Riesze, P.; Kondo, T.; “Free Radical formation induced by ultrasound and its biological implications,” *Free Radical Biology and Medicine*, v 13, 1992, p247-270.

13. Yasui, K.; Tuziuti, T.; Sivakumar, M.; Lida, Y.; “Theoretical study of single-bubble sonochemistry,” *The Journal of Chemical Physics*, June 2005.

14. Pickrell, K.C.; Sergeant, G.F.; Wolfe, Mary; Wrobel, M.D.; “Tips for Auditing Your Green Sand System,” *Modern Casting*, v 89, n 3, March, 1999, p 30-33.

15. Baker, S.G.; “Building the Foundation for Green Sand,” *Modern Casting*, v 95, n 8, August, 2005, p 26-29.

16. Granlund, M.J., “Understanding the Basics of Green Sand Testing,” *Modern Casting,* v89, n3, March, 1999, p38-40.

17. Milan-Segovia, N., F.S. Cannon, R.C. Voigt, J.C. Furness. Determination of Advanced Oxidants in Aqueous Solutions: Use of Terephthalic Acid Dosimeter for Measurement of OH* Radical Production. Submitted to *Ozone Science and Engineering.* 2006. (12 pp.).

18. Suslick, K. S.; “The Chemical Effects of Ultrasound.” Scientific American, February 1989, 80-86.

19. Odom, I. E. Functional properties of Na and Ca bentonites in green sand system. American Foundry Society Transactions. Volume 96, 1988, 229-236.

20. Smiernow, G.A.; Doheny, E. L.; Kay, J. G. Bonding mechanisms in sand aggregates. Transactions of the American Foundry Society. Volume 88, 1980, 659-682.

21. Fox, J.T., Cannon, F.S., Voigt, R.C., Furness, J.C., Smith, P., Lewallen, S, Goudzwaard, J., Simultaneous Bond and Sand Reclamation using Advanced Oxidation, Induced Particle Collision and Discretionary Settling. American Foundry Society Transactions, Volume 115, 2007.

22. Fox, J.T., Canon, F.S., Voigt, R.C., Furness, J.C., F. Headington, D. Coan, S. Lewallen, Waste Green Sand to Core Sand Reclamation, Demonstration via Casting Study, with Simultaneous Clay Recovery and AO Benefits. (Submitted) American Foundry Society Transactions, 2008.

23. Niemczewski, B.; “Observations of water cavitation intensity under practical ultrasonic cleaning conditions”, *Ultrasonics Sonochemistry*, 2007, 13-18.

24. Hoffman, M.R., Hua, I., Hochemer, R.; "Application of ultrasonic irradiation for the degradation of chemical contaminants in water." Ultrasonics Sonochemistry, Vol. 3, 1996, p 163-172.

25. Lamminen, M.O., Walker, H.W., Weavers, L.K.; "Mechanisms and factors influencing the ultrasonic cleaning of particle-fouled ceramic membranes" *Journal of Membrane Science*, 2004, 213-223.

26. Hart, E.J., Henglein, A. "Sonolysis of Ozone in Aqueous Solution," Journal of Phys. Chem., v. 90, 1996, 3061-3062.

27. Farmer, A.D., Collings, A.F., Jameson, G.J.; "The application of power ultrasound to the surface cleaning of silica and heavy mineral sands." *Ultrasonics Sonochemistry*, 2000, 243-247.

28. Rege, S.U.; Yang, R.T.; Cain, C.A.; "Desorption by Ultrasound: Phenol on Activated Carbon and Polymeric Resin" *American Institute of Chemical Engineers Journal*, July 1998, vol. 44, n. 7, 1519-1528.

29. Chen, D., Weavers, L.K., Walker, H.W., Lenhart, J.J.; "Ultrasonic control of ceramic membrane fouling caused by natural organic matter and silica particles." *Journal of Membrane Science*, 2006, 135-144.

30. Koparal, S., Nii, S., Kawaizumi, F., Takahashi, K.; "Use of Ultrasound for Tar Removal from Tar-Contaminated Sand." Journal of Chemical Engineering of Japan, 2005, Vol. 38, n 10, 835-840.

31. Newman, A.P., Lorimer, J.P., Mason, T.J., Hutt, K.R.; "An investigation into the ultrasonic treatment of polluted solids." Ultrasonics Sonochemistry, Vol. 4, 1997, p 153-156.

32. Lu, Y., Riyanto, N., Weavers, L.K., "Sonolysis of synthetic sediment particles: particle characteristics affecting particle dissolution and size reduction." Ultrasonics Sonochemistry v. 9, 2002, 181-188.

33. Fox, J.T., Cannon, F.S., Voigt, R.C., Furness, J.C., Goudzwaard, J.E., Wosoba, M., Smith, P.B.; Decreased Bond Consumption by Processing Baghouse Dust through Ultrasonic-Cavitation-Settling coupled to Advanced Oxidation. *The 112th Metalcasting Congress,* Atlanta, GA, May 17-20, 2008.

34. Foundrymen's Society Mold and Core Test Handbook (1988)

35. Linsley, R.K., Franzini, J.B., Freyberg, D.L., Tchobanoglous, G., Water-Resources Engineering, Irwin/McGraw-Hill (1992).

36. Bache, D.H., Gregory, R., Flocs in Water Treatment, IWA Publishing, 2007.