

Mechanisms of Advanced Oxidation Processing on Bentonite Consumption Reduction in Foundry

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Prior full-scale foundry data have shown that when an advanced oxidation (AO) process is employed in a green sand system, the foundry needs 20–35% less makeup bentonite clay than when AO is not employed. We herein sought to explore the mechanism of this enhancement and found that AO water displaced the carbon coating of pyrolyzed carbonaceous condensates that otherwise accumulated on the bentonite surface. This was discerned by surface elemental analysis. This AO treatment restored the clay's capacity to adsorb methylene blue (as a measure of its surface charge) and water vapor (as a reflection of its hydrophilic character). In full-scale foundries, these parameters have been tied to improved green compressive strength and mold performance. When baghouse dust from a full-scale foundry received ultrasonic treatment in the lab, 25–30% of the dust classified into the clay-size fraction, whereas only 7% classified this way without ultrasonics. Also, the ultrasonication caused a size reduction of the bentonite due to the delamination of bentonite particles. The average bentonite particle diameter decreased from 4.6 to 3 μm , while the light-scattering surface area increased over 50% after 20 min ultrasonication. This would greatly improve the bonding efficiency of the bentonite according to the classical clay bonding mechanism. As a combined result of these mechanisms, the reduced bentonite consumption in full-scale foundries could be accounted for.

Introduction

Foundries employ green sand to create molds that molten metal is poured into. When forming cast iron and gray iron, the green sand molds generally contain silica sand (82–90%), bentonite clay (5–8%), bituminous coal (3–6%), and water (2–4%). When casting complex metal shapes, core sands can also include organic resin binders. During the casting process, fine particulate dust exits with the exhaust air from metal pouring, mold cooling, and shakeout. Historically, the dust is captured by a dust collection system, and then landfilled with waste green sand. Due to its small particle size and high content of polycyclic aromatic hydrocarbons

(PAHs) condensate, its transportation and disposal pose considerable hazards to human health and the environment (1–4). As the dust contains valuable green sand raw materials, for example, coal and active clay (bentonite clay that can provide bonding strength), reclamation and reuse of the dust within the green sand foundry would offer a fruitful opportunity for pollution prevention and material conservation. However, the dust could not be directly recycled to the green sand system because it contains too many sand fines that would cause low permeability of the green sand mold and increase casting defects.

Recently, an innovative advanced oxidation-dust-blackwater (AO-DBW) clarifier system (Sonoperoxone by Furness-Newburge) has been installed in 25–30 foundry lines to process and reclaim the dust (5–7). These foundries together have the capacity to produce 10–15% of all of the nation's cast iron. The baghouse dust is first blended with water to form a slurry, and then the slurry is conditioned with ozone (to near saturation), hydrogen peroxide (100–300 ppm), ultrasonication, and (optionally) underwater plasma. The AO-dosed slurry then flows through a blackwater clarifier that separates the reusable active clay and coal that settles slowly, from the nonreusable silica sand fines and dead clay (thermally destroyed clay) that settle more quickly to the bottom. The AO-treated effluent from the clarifier, which contains much of the active clay, is recycled back to the sand cooler or muller for a next casting cycle, while the solid waste is disposed. Full-scale foundry results have shown that a considerable fraction of the clay can be captured and recycled: when the dust enters the AO-DBW system, it contains about 30–40% active clay by weight. After the AO conditioning, the waste solids that settle in the clarifier contain only about 3% active clay. In comparison, the effluent solids that are recycled to the sand cooler or muller contain 50–60% active clay (6, 8).

Following the AO-DBW system installation and operation, these foundries experienced a reduction in clay and coal consumption by 20–35% (5, 6, 8), and at the same time, diminished their air pollutant emissions by 20–75% (5, 7, 9). The reasons for the emission reduction due to AO processing have been addressed in other publications (5, 10). The objectives of this study herein are to explore the possible mechanisms of how the AO processing could diminish the clay consumption.

We herein hypothesized that several events occurring in the AO-DBW system are responsible for the diminished clay consumption. First, sonication could detach the clay platelets from the sand fine surface (11, 12). This would allow the clay platelets to settle more slowly than the silica fines in the blackwater clarifier, and the clay could thus be drawn off for reuse via a side discharge port. This would improve clay reclamation efficiency of the blackwater clarifier.

In addition, we hypothesized that the ultrasonication could favorably change the agglomerating properties of the clay with respect to its foundry application: the deagglomeration and the delamination of the clay platelets by ultrasonics (13, 14) could greatly improve the bonding efficiency of bentonite according to the classical clay bonding mechanisms; that is, hydrated bentonite forms bonding film that coats the sand grain surfaces and holds them together (15). As a result of the deagglomeration and delamination of the clay, more external clay surface per mass of clay would be available for bonding, and the thickness of the bonding film between the sand grains could be reduced, while it would still be able to provide the same bonding strength. Thus, the amount of clay in the mold could be

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reduced without sacrificing mold strength properties, and this would also result in less burnout of the clay in the casting process.

Also, it was found that when clay was heated in the presence of coal or core binders (organic resins), the pyrolysis products of coal and core binders could condense over the clay particle surface. Others have found that these condensed pyrolysis products are mostly polycyclic aromatic hydrocarbons (PAHs) and other organic compounds (1–3, 16). These PAHs are hydrophobic and have a greater tendency to bind with the clay (17–19). The covering of clay surface by PAHs could profoundly alter the surface chemistry of the clay. It has been shown that organic coatings of clay and sand could render the soils more hydrophobic, especially when the organic compounds contained methyl, methylene, and methane groups (20, 21). Further, Shih (1991) and Hofmann's (1985) results implied that the PAH covering was the main reason for the clay to lose much of its methylene blue (MB) adsorption capacity and bonding capacity (22, 23). As a result, the green compressive strength (GCS) of the green sand mold was dramatically reduced (22). Rationally, the authors herein perceived that additional makeup clay is needed in full-scale foundries to supplement the lost bonding capacity of the clay that was covered by the pyrolysis products, in addition to the amount of makeup clay that is added to replace the thermally destroyed clay during the casting process.

Advanced oxidation processes (AOPs) have been defined broadly as those aqueous phase oxidation processes that are based primarily on the intermediacy of the hydroxyl radicals (OH^\bullet) in driving the oxidation processes (24). In the most commonly used AOPs, ozone, hydrogen peroxide, ultrasonics, ultraviolet radiation, etc. are used individually or in different combination forms to generate the hydroxyl radicals (24–26). The hydroxyl radicals react with organic compounds by abstraction of H-atom, addition to double, triple, or aromatic bonds, and reaction with S or N atoms. As oxidizing agents, hydroxyl radicals are far more powerful than the commonly known strong oxidants such as molecular oxygen and ozone. Organic compounds are oxidized much faster by OH^\bullet , and complete destruction and mineralization of even refractory organic compounds can be achieved when at high enough concentration (higher than used herein) of advanced oxidants (e.g., ozone, hydrogen peroxide, and their derivative species such as hydroxyl radicals) (24–26). Earlier Penn State work has shown that when a 3% hydrogen peroxide solution is heated to 70 °C, it will remove asphalt from glass surfaces within 3–10 min. Elevated pH and iron presence accelerated these removal mechanisms (27, 28). Moreover, ozone has been applied to remediate soil or sediments that are contaminated with PAHs (29).

Although it would be unwieldy in foundries to dose a high enough advanced oxidant level to mineralize the organic coating on clay particles, we herein hypothesized that a considerable lower dose of the advanced oxidants could displace the pyrolysis products of the coal from clay surfaces, and then render the clay surfaces more able to bond to sand and to other clay particles. Thus, via this mechanism, it would be possible to reduce the amount of new bentonite addition for each metal casting cycle that is necessary to maintain stable green sand properties, and, as a method of environmental pollution prevention, this would in turn diminish the amount of clay and other green sand components that would need to be landfilled or beneficially reused.

The main objectives of the research reported herein were to understand the underlying mechanism by which this advanced oxidation process facilitated diminished clay consumption and therefore prevented pollution in a green sand foundry, specifically:

(1) Establish the extent to which ultrasonics (as a component of AO) could dislodge clay platelets from silica fines when sonically conditioning baghouse dust.

(2) Evaluate the effects of ultrasonics on clay deagglomeration and delamination that facilitate more external clay surface per mass of clay for bonding.

(3) Test the hypothesis that the advanced oxidation process cleaned the surfaces of the clay platelets when they are in a foundry green sand environment, and rendered the clay surface as more available to adsorb water and positively charged methylene blue.

Methods and Materials

The baghouse dust used in this research was shipped from a full-scale foundry (Neenah Foundry, Neenah, WI). The baghouse dust was sampled while an advanced oxidation blackwater system was in operation at Neenah Foundry. This dust contained 37% active clay (measured by methylene blue adsorption) and 22% loss on ignition (i.e., organic coal, water of hydration, etc. that released mass in an air-burning environment).

The bituminous coal was also shipped from Neenah Foundry, but it had not yet been processed at the foundry. The coal was ground to pass a 150 μm sieve (#100) at Penn State prior to use. The western sodium bentonite (foundry grade) was acquired from American Colloid Co., which we then crushed to pass a 150 μm sieve (#100) prior to use. The silica sand used in the test was washed silica sand from Wesdron Silica Co. (Wesdron, IL).

The TAP water used in these experiments was The Pennsylvania State University groundwater that has a nearly neutral pH. The hardness and alkalinity were low, and the iron concentration was about 0.01–0.03 ppm (30).

The AO water used in tests herein is defined as that which has been generated from a pilot Sonoperoxone AO system (Furness-Newburge, Versailles, KY). The AO system employed hydrogen peroxide (1000 ppm), ozone (to saturation), ultrasonic (50 kHz), and underwater plasma to condition the TAP water for 30 min. During this period, 60 L of water was circulated at 350 L/min through the system. Hydrogen peroxide was manually added to the system, and ozone was constantly injected into the flow. In the circulation, the water flowed through an ultrasonic generator and was subjected to cavitation. After the treatment, the AO water contained various advanced oxidants, for example, approximately 880 ppm hydrogen peroxide, 0.06 ppm ozone, 0.7 ppm hydroxyl radicals, and other radicals as monitored by the Penn State research team (30).

Ultrasonic Reclamation of Clay Contents from Dust. Baggouse dust (5 g) from the full-scale foundry was added into 200 mL of deionized water in a lab ultrasonic bath (47 kHz, 60 W) (Branson 1210 OR-MT, VWR). In one test, the slurry was merely stirred for 30 min, while in the other parallel tests, the ultrasonics were applied for an array of times (1–30 min) during the stirring. The different compositions of the dust were then physically classified by size via the centrifuge method that is used in soil sampling (31). Sand fines ($> 50 \mu\text{m}$) were separated from the suspension by gravity settling, while silt (50–2 μm) and coarse clay (2.0–0.2 μm) were classified by centrifugation at 300 and 2400 rpm, respectively. The suspended solids in the supernatant after these treatments comprised medium and fine clay ($< 0.2 \mu\text{m}$).

Bentonite's Particle Size Distribution Analysis. Bentonite clays were dispersed in deionized water with a magnetic bar that stirred for 12 h, and then they were characterized for their particle size distribution and light-scattering external surface area with a particle size analyzer-Mastersizer S (Malvern Instrument, Southborough, MA). To determine the effect of ultrasonics, the bentonites that were mixed for 12 h were then subjected to the ultrasonication (50 kHz)

TABLE 1. Designation of Samples Used for Surface Elemental Analysis and Water Vapor Adsorption Test

sample	explanation
CLAY/COAL	nonheated mixture of clay and coal
CLAY400	pure bentonite clay heated at 400 °C for 30 min
CLAY/COAL400	mixture of bentonite and coal heated at 400 °C for 30 min
CLAY/COAL400-AO	mixture of bentonite and coal heated at 400 °C for 30 min, followed by advanced oxidation (AO) washing and 105 °C curing overnight
CLAY/COAL400-TAP	mixture of bentonite and coal heated at 400 °C for 30 min, followed by tap water (TAP) washing and 105 °C curing overnight

treatment in the pilot Sonoperoxone AO system for 1, 10, or 20 min. The H₂O₂, O₃, and underwater plasma components of the Sonoperoxone system were not turned on during this time. Samples were collected after three ultrasonic treatments, and then they were monitored for particle size distribution and surface area.

Bentonite's Thermal Durability Evaluation. The thermal durability of bentonite that was moisturized with either the AO water or the TAP water was measured by the methylene blue (MB) adsorption test (32). The same method has been used in foundries for many years to determine the active clay contents within the green sand matrix. When the clay is heated to progressively higher temperatures, its capacity to sorb positively charged methylene blue correlates well with the green compressive strength and other properties that are important for mold performance (23, 33). Also, the MB uptake capacity of bentonite at elevated temperatures had been used as an indicator of the thermal durability of bentonite in the auto industry and by many researchers (32, 33).

To test the possible effects of AO processing on the bentonite's thermal durability and surface activity, 1 mL of AO water or TAP water was added to 1 g of western bentonite, and then the samples were heated in a muffle furnace at an array of temperatures (200–700 °C) for 1 h in air. After that, 0.3 g of this heated bentonite sample was mixed with 4.7 g of silica sand to make the total weight of 5 g, and then the MB uptake capacity of the mixture was measured by the American Foundry's Society (AFS) standard ultrasonic mixing and MB titration method (34).

Chemical Reactivation of Bentonite by Advanced Oxidation. To test the chemical reactivation of heated bentonite–coal mixture via AO, dry western bentonite was mixed with dry bituminous coal in a ratio of 5:4 by weight. The mixtures were then heated in a thermogravimetric analyzer (TGA) (Cahn TG-131, Cerritos, CA) chamber to an array of final temperatures (200–700 °C) with a half of an hour holding time. The heating procedure was conducted under a nitrogen atmosphere to allow coal to undergo pyrolysis reactions rather than burning. This nitrogen atmosphere simulated the starved air conditions within a green sand mold during abrupt and intense heating. For comparison, pure bentonite samples (without coal addition) were heated in the TGA in the same manner as for the mixtures.

After the heating, the mixtures (bentonite and coal) were divided into two subsample groups. For one group, 10 mL of AO water was used to wash the 3 g of clay/coal mixture, while for the other group 10 mL of TAP water was used to wash the 3 g mixture. The mixtures were then dried at 105 °C in the muffle furnace in air overnight, and then stored in the desiccator before testing. As the mixtures did not experience the ultrasonic conditioning during the washing, the AO and TAP washing could only chemically affect the mixtures.

We measured methylene blue (MB) uptake capacities of (a) the pure bentonite samples, (b) mixtures of bentonite and coal, (c) AO-washed mixtures of bentonite and coal, and (d) TAP-washed mixtures of bentonite and coal. For each

test, a sample containing exactly 0.3 g of bentonite (after TGA heating, AO or TAP washing, and 105 °C curing) was mixed with an appropriate amount of silica sand to make the total weight of 5 g. MB uptake capacity of the mixture was then measured by the AFS standard ultrasonic mixing and MB titration method (34).

Energy-Dispersive X-ray Spectroscopy. To examine both the extent to which the clay surface was contaminated by coal pyrolysis products, and also the effects of AO- or TAP-washing on clay surface cleaning, surface elemental distribution of the samples (Table 1) that were heated to 400 °C were analyzed by energy-dispersive X-ray spectroscopy (EDS) with an environmental scanning electron microscopy (ESEM) instrument (FEI Quanta 200, Hillsboro, OR). Next, 4–5 tiny areas (about 10–25 μm^2) on the clay particle surfaces were randomly chosen and bombarded with an electron beam (no separate phase of carbon, e.g., coal particles, was detected to reside on the analysis surfaces under the ESEM). When the electrons struck the sample surface, X-rays were emitted from the atoms comprising the surface. The number and energy of X-rays that were emitted during the bombardment were measured by an EDS X-ray detector. As the energy of the X-ray is characteristic of the element from which the X-ray was emitted, and the number of the X-ray is proportional to the amount of the element present in the sampled area, a spectrum of the energy versus relative counts of the detected X-rays was obtained to semiquantitatively evaluate the elemental distribution on the clay surface.

Water Vapor Adsorption. These same samples (Table 1) were also used in water vapor adsorption tests. These tests were conducted to evaluate the effects of surface coating of carbon and AO- or TAP-washing on the clay's surface chemistry with respect to foundry application, as clay relies on hydration to develop the bonding strength (35, 36). The water vapor adsorption capacities of these samples were measured gravimetrically in a desiccator at room temperature (22 ± 0.5 °C). Sample weights were measured every 2 h, and, during this period, the humidity in the desiccator was maintained at a stable equilibrium value by injecting water vapor. After this 2 h, the humidity was then increased to a higher level for the next equilibrium measurement.

Results

Ultrasonics Effect on Baghouse Dust Reclamation. The enhanced reclamation of clay contents (mostly active bentonite and coal particles) due to bath ultrasonication has been shown in Figure 1. When the slurry was merely stirred without ultrasonication, the sand fines plus silt constituted 93% of all of the particles by weight, while the clays constituted 7%. However, with 5 min of ultrasonics, the sand fines plus silt had declined to 77% of the mass, while the clays had increased to 23%. This means that the clays that appeared in these size classifications became discrete particles as the ultrasonics caused them to be dislodged from the sand fines and silt surface. Following 30 min of ultrasonics, the clays constituted 28% of the weight.

Ultrasonics Effect on Clay Particle Size and Light-Scattering External Surface Area. The size reduction of

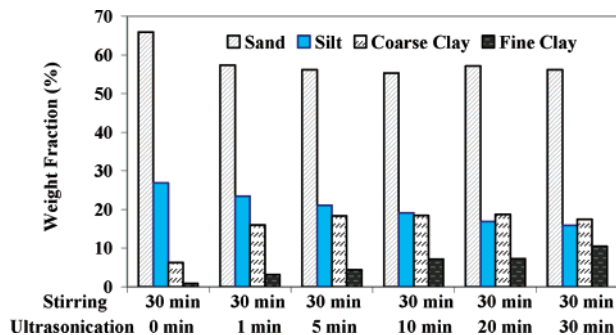


FIGURE 1. Effects of ultrasonics on clay reclamation.

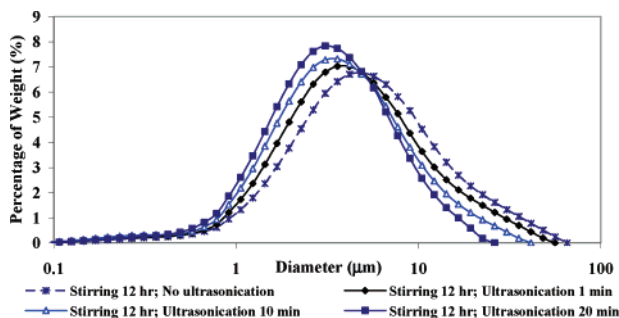


FIGURE 2. Effects of ultrasonics on particle size distribution of clay.

TABLE 2. Effects of Ultrasonication on Bentonite's Physical Properties

stirring time (h)	ultrasonication time (min)	average particle size		light-scattering external surface area	
		d_{50} (μm)	% change	(m^2/g)	% change
0.5	0	4.57		0.83	
12	0	4.66	+2.0% ^a	0.92	+10.8% ^a
12	1	3.88	-15.1% ^a	1.06	+27.7% ^a
12	10	3.34	-26.9% ^a	1.25	+50.6% ^a
12	20	3.00	-34.4% ^a	1.27	+53.0% ^a

^a Percent change relative to sample stirred for 0.5 h without ultrasonics.

bentonite alone due to pilot-induced ultrasonication was clearly manifested in Figure 2. It is discerned that mechanical stirring had little effect on particle size or light-scattering external surface area (calculated on the basis of the particle size distribution), with the average particle size remaining at $4.6 \mu\text{m}$ and the average surface area remaining at 0.83 – $0.92 \text{ m}^2/\text{g}$ after 12 h of mixing; see Table 2. In contrast, the ultrasonic treatment dramatically altered these parameters: after 20 min ultrasonic treatment, the average particle size declined to $3.0 \mu\text{m}$, while surface area increased to $1.27 \text{ m}^2/\text{g}$. Time is another vital factor: longer ultrasonication time could achieve better results of particle size reduction. We herein proposed that the particle size reduction and surface area increase reflected the deagglomeration and delamination mechanisms as the bentonite particles experienced the high energies from collapsing microbubbles (13, 14).

Effect of AO on Clay Reactivation. We also sought to discern whether advanced oxidants could influence the clay that is within the green sand matrix when the green sand experiences elevated temperatures that simulate metal pouring. Under these circumstances, the sonication bubbles are not being generated within the green sand. Rather, the combination of the ozone, H_2O_2 , and sonic interacting with one another and with the baghouse dust components could plant radical scavengers within the blackwater (i.e., mix of baghouse dust and water) that could be aggressively reactive

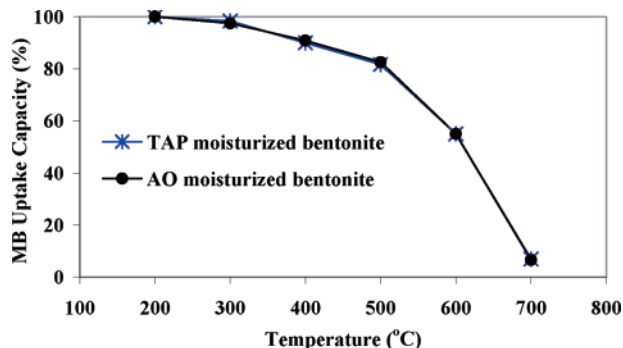


FIGURE 3. Effect of advanced oxidation (AO) treated water versus tap water (TAP) moisturization on thermal durability of clay that is heated in air to the temperatures shown (100% = $0.374 \text{ g MB/g clay}$, the value for clay that was first heated at 200°C).

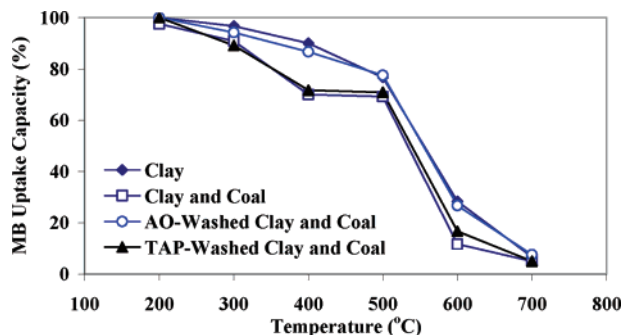


FIGURE 4. Effects of pyrolysis products of coal and AO- versus TAP-washing on MB uptake capacities of clay that is heated in N_2 to the temperatures shown (100% = $0.374 \text{ g MB/g clay}$, the value for clay that was first heated at 200°C).

at the elevated temperatures (but only slowly reactive at ambient temperature). It was hypothesized that the advanced oxidants could either (a) alter bentonite clay itself (i.e., independent of coal influences) or (b) alter the manner in which a carbon coating thermally accumulated on clay when the clay was heated in the presence of the coal. We conducted controlled experiments to discern between these two possibilities.

To test (a), the AO effects on bentonite clay by itself, we monitored the methylene blue uptake capacities of bentonite samples that were moisturized with either the AO water or the TAP water, followed by heating to an array of temperatures (200 – 700°C) (Figure 3). The results of all of the samples were normalized to the MB uptake of clay alone that had experienced 200°C (i.e., $0.374 \text{ g MB/g clay}$). The MB uptake capacities showed no difference when AO water was used, as compared to when mere TAP water was used (Figure 3). It could be seen that the thermal decomposition of western bentonite began at 400°C , and by 700°C , the bentonite was totally degraded and could not adsorb hardly any methylene blue dye. As shown, the AO moisturization had no effect on the thermal durability of bentonite, and this highlights the perspective that the bentonite clay is not directly affected by the advanced oxidants that were contained in the AO water. Thus, hypothesis (a) above was deleted as the AO mechanism.

The next set of experiments tested hypothesis (b), which pertained to the interaction of clay and coal, relative to methylene blue uptake. First, we compared MB uptake by bentonite alone versus a mixture of clay and coal (see Figure 4). These two samples had not been moisturized, as had the samples for the Figure 3 data. In Figure 4, all of the values have been normalized to a percentage of the MB uptake value of the pure bentonite sample heated at 200°C (i.e., $0.374 \text{ g MB/g clay}$). As shown in the figure, at 200°C the

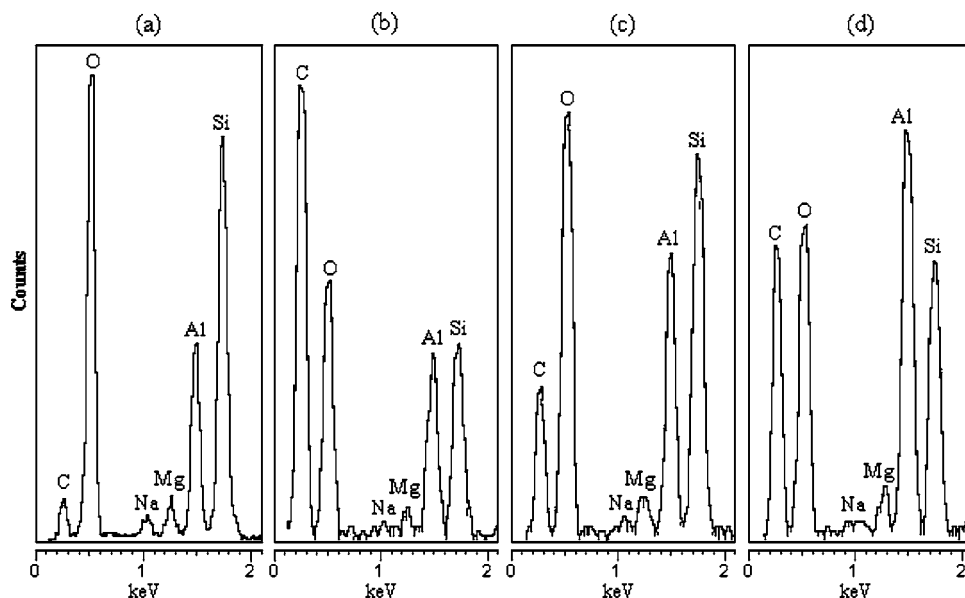


FIGURE 5. Energy-dispersive X-ray spectroscopy of (a) CLAY400, (b) CLAY/COAL400, (c) CLAY/COAL400-AO, and (d) CLAY/COAL400-TAP.

bentonite that was mixed with coal behaved quite similarly to the pure bentonite, and this means there is not much interaction between coal itself and bentonite at 200 °C. However, as the heating temperature increased above the temperature at which the coal began to pyrolyze (i.e., above about 230 °C) (10), the MB uptake capacities of the bentonite–coal mixture declined more readily than for the bentonite alone. This effect was most significant at the temperature of 400–600 °C, where MB values for the clay–coal mixture were only 4/10 to 9/10 of the value for the clay alone. In concurrence, our previous study showed that the coal lost the most mass and generated the most pyrolysis products at temperatures between 400 and 600 °C under the same heating condition (10).

After this experiment, the clay/coal mixtures (from each temperature exposure) were washed in either the AO water or the TAP water, and then dried at 105 °C in air. It was found that the AO-washing and 105 °C curing almost completely restored the MB uptake capacities of the clay/coal mixtures for a given TGA heating temperature, and this effect was manifested throughout the full range of prior temperature thermal exposure. In contrast, the TAP water washing offered almost no improvement in MB uptake.

Surface Elemental Analysis. With energy-dispersive X-ray spectroscopy (EDS), we conducted surface elemental analysis of the four samples from Figure 4 that had experienced 400 °C (refer to Table 1 definitions). The CLAY400 sample exhibited very little carbon on its surface (Figure 5a). In contrast, the CLAY/COAL400 that had been heated to 400 °C without subsequent washing exhibited a surface carbon peak that was nearly twice as high as for oxygen and silicon peaks (Figure 5b), although no separate phase of carbon, that is, coal particles, was visually detected to reside on the analysis areas under the ESEM. The oxygen and silicon peaks originated from the oxygen and silicon atoms in the basal structure of the clay and were assumed to be stable. The comparison of these two surfaces shows that the pyrolysis products of coal evenly coated the clay surface as an envelope, as the EDS spectrum was quite reproducible at the different locations on the clay surface. The AO-washing and 105 °C curing removed most of this surface carbon to the extent that the carbon peak was 30–40% as high as for oxygen and silicon (Figure 5c). In contrast, TAP-washing and 105 °C curing removed a considerably smaller fraction of the carbon, to

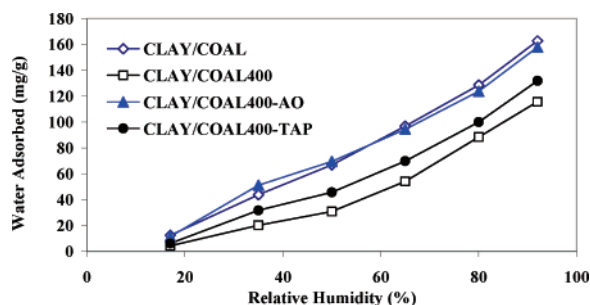


FIGURE 6. Effects of pyrolysis products of coal and AO/TAP-washing on water vapor adsorption capacities of clay.

the extent that this carbon peak was about equal to oxygen and silicon (Figure 5d). These results showed that the AO-washing removed most of the pyrolysis products of coal from the bentonite. We submit that it was this carbon removal that restored the MB uptake capacities of the bentonite.

Water Adsorption. The AO treatment also improved water adsorption of the same samples, as depicted in Figure 6. A nonheated mixture of clay and coal adsorbed 162 mg water/g solids at 92% relative humidity, whereas at this same humidity, only 118 mg/g of water was adsorbed onto the CLAY/COAL mixture that had been heated to 400 °C. When this heated mixture was then washed in TAP water and cured at 105 °C, the product improved water adsorption only slightly to 132 mg/g. However, when the heated mixture was washed in AO water and then cured at 105 °C, nearly all of the water adsorption capacity of the unheated materials was restored: 158 mg/g of water moisture could be adsorbed at a 92% relative humidity.

Discussion

As shown in Figure 1, the mechanical stirring could not generate sufficient shear strength to detach the bentonite particles from the sand surface. This means that at full-scale foundries that employ conventional clarifier systems to process baghouse dust without ultrasonics, most of the clays in the dust would settle with the sand fines and be disposed as solid waste. However, even short times of ultrasonication greatly increased the clay contents in the dust by detaching bentonite particles from the sand fines. The detachment of clay from sand fine surface is mainly achieved by the large

TABLE 3. Full-Scale Operation Performance at Neenah Foundry (Neenah, WI) and Wheland Foundry (Chattanooga, TN), As Influenced by Advanced Oxidation (AO)

green sand properties	Neenah Foundry			Wheland Foundry		
	non-AO	AO	% change	non-AO	AO	% change
green compressive strength (GCS) (psi)	33.3	34.6	+4%	26.0	31.0	+19%
methylene blue (MB) clay (%)	10.1	8.3	−20%	8.8	9.0	+5%
GCS/MB clay (psi/%)	3.3	4.2	+26%	2.95	3.44	+17%
clay consumption (lb/ton iron poured)	136.5	93.8	−31%	120.5	86.9	−28%

but very localized cavitation force generated by the instantaneous formation and collapsing of microbubbles in water (11). Particularly, because of the weaker solid–liquid interactions at the interface of hydrophobic particles, the cavitation occurs much more readily at the dust particles' surfaces that were coated with the pyrolysis products of coal and became hydrophobic (37). These baghouse-derived clays represent valuable recyclable material that could be returned to a green sand system in full-scale foundries that employ ultrasonics and AO systems that include ultrasonics. Every day at Neenah Foundry, approximately 4 tons of such baghouse-derived clays are reclaimed and recycled by the AO-DBW system, and this accounts for a significant portion of the total clay requirements in this foundry. Effectively, this has facilitated a 25–35% drop in clay consumption.

Besides the detachment of clay particles from sand fines, the results herein showed that ultrasonication decreased clay's particle size and increased its light-scattering external surface area. This is mainly through the deagglomeration of the clay agglomerate and the delamination of clay platelets by ultrasonics (13, 14). This considerable decrease in particle size and increase in surface area would greatly improve the bonding efficiency of the bentonite according to the classical clay bonding mechanisms (15). The underlying principle was that if the clay particle sizes were smaller (and specifically thinner), then the external surface areas per mass of clay would be higher. Thus, a higher proportion of this clay surface would be physically available to bond with sand grains and with other clay platelets. Previous study has shown that there was a clear and direct relationship between the clay surface area and the green strength of the green sand mold (36). This implies that by employing ultrasonics, unit clay additive mass could be diminished while maintaining the same net surface area and thus bonding strength for baghouse-derived clay that is recirculated into a green sand system. This facilitated the increased green compressive strength per methylene blue clay (GCS/MB clay) that has been observed in full-scale foundries (Table 3) (6, 8).

We observed that there was a carbon covering that originated from coal pyrolysis and this covering masked the foundry properties of bentonite; this rendered the clays less able to adsorb MB and surface bond with water molecules. As mentioned before, the pyrolysis products of coal were mostly PAHs (1–3, 16). These compounds could volatilize into the gaseous phase at the high temperatures that were generated near the molten metal surface when metal was poured into the green sand mold, but then they could recondense on the surface and in the interlayers of the bentonite clay as the volatiles dispersed away from the hot metal interface toward the cooler mold regions, or as the green sand cooled near the metal surface. This blocked the cation exchange sites of the bentonite, thus causing the reduced MB uptake capacity of bentonite (Figure 4).

However, these pyrolysis products were displaced quite readily with the various AO species that are contained in the AO water, as indicated by the surface elemental analysis results (Figure 5). The displacement of hydrophobic PAHs

from the clay surface restored the MB uptake capacity of the bentonite (Figure 4). From the results herein, we discerned that pyrolysis products of coal did not actually increase the thermal degradation rate of the bentonite, as had been inaccurately inferred by Bauck (38). Indeed, the bentonites covered by pyrolysis products of coal do not actually constitute thermally decomposed clay. Rather, their presences are partially masked by the covering during the MB adsorption test.

It has been known that clay particles are very thin, mostly <350 Å (39). Also, they are very flexible and frequently fold and bend like sheets of tissues paper. The thin clay particles bond to other clay particles and to the sand grains mainly through the electrostatic forces between continuous clay particles or clay and sand particles, as well as their linkage interconnection through an oriented water network (36). When comparing the Figures 5 and 6 data, it is discerned that lost water sorption capacity for the heated CLAY/COAL400 mixture mainly occurred because hydrophobic carbon compounds blocked the hydration sites of the bentonite. The carbon covering rendered part of the clay platelet surface hydrophobic and unable to develop rigid adsorbed water layers that could form strong hydrogen bonding with other clay platelets (refer to Odom (35) and Smirown (36)). It also obstructed the development of surface tension between sand grains and clay platelets (36, 40). This would cause a clay platelet to lose much of its bonding capacity, and thus a higher amount of such contaminated clay would be needed to achieve the same green compressive strength when compared with clean clay. We herein concluded that the bonding capacity of a unit clay could be greatly improved when AO processing cleaned the clay surface.

As expressed by the restored MB uptake capacity and water vapor adsorption capacity, when the hydrophobic pyrolyzed coal products that coated the bentonite surface were removed, the damaged foundry properties of bentonite were restored. This, plus the size reduction of clay due to ultrasonics, improved the bonding efficiency of the bentonite clay. As a result, full-scale foundries could maintain the necessary green compressive strength (GCS) with lower concentration of bentonite in green sand, which was observed in full-scale foundries after AO installation and optimized operation (see Table 3) (6, 8). Also, with more baghouse-derived active clay recycled to the sand system with the AO-DBW system, the clay consumption in full-scale foundries is diminished.

Advanced oxidation processes have been used in water and wastewater treatment for several decades (24–26, 41). We herein offer that on the basis of the results presented in this paper, it would be possible to extend the AO processes to the remediation of soils, sediments, or pharmaceutical reactor vessels that are contaminated by PAHs, coal tar, or pharmaceutical intermediates (29, 42, 43).

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Literature Cited

- (1) Moorman, W. J.; Palmer, W. G.; Garner, F. M.; Mulligan, L. T. Carcinogenic potential of foundry pyrolysis effluents. *Am. Foundry Soc. Trans.* **1985**, 93, 23–28.
- (2) Omland, O.; Sherson, D.; Hansen, A. M.; Sigsgaard, T.; Autrup, H.; Overgaard, E. Exposure of iron foundry workers to polycyclic aromatic hydrocarbons: benzo[a]pyrene-albumin adducts and 1-hydroxypyrene as biomarkers for exposure. *Occup. Environ. Med.* **1994**, 51, 513–518.
- (3) Yang, H. H.; Lai, S. O.; Hsieh, L. T.; Hsueh, H. J.; Chi, T. W. Profiles of PAH emissions from steel and iron industries. *Chemosphere* **2002**, 48, 1061–1074.
- (4) Gomes, J.; Lloyd, O. L.; Norman, N. J.; Pahwa, P. Dust exposure and impairment of lung function at a small iron foundry in a rapid developing country. *Occup. Environ. Med.* **2001**, 58, 656–662.
- (5) Cannon, F. S.; Furness, J. C.; Voigt, R. C. Economical use of advanced oxidation systems for green sand emission reduction. *12th Am. Foundry Soc. International Environmental, Health & Safety Conference*; Lake Buena Vista, FL, Oct. 9–11, 2000; pp 317–332.
- (6) Neill, D. A.; Cannon, F. S.; Voigt, R. C.; Furness, J.; Bigge, R. Effects of advanced oxidants on green sand system performance in a blackwater system. *Am. Foundry Soc. Trans.* **2001**, 109, 937–955.
- (7) 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.
- (8) 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. *Am. Foundry Soc. Trans.* **2002**, 110, 705–715.
- (9) Glowacki, C. R.; Crandell, G. R.; Cannon, F. S.; Voigt, R. C.; Clobes, J. K.; Furness, J. C.; McComb, B. A.; Knight, S. M. Emissions studies at a test foundry using an advanced oxidation-clear water system. *Am. Foundry Soc. Trans.* **2003**, 111, 579–598.
- (10) Wang, Y. J.; Cannon, F. S.; Neill, D.; Crawford, K.; Voigt, R. C.; Furness, J. C.; Glowacki, C. R. Effects of advanced oxidation treatment on green sand properties and emissions. *Am. Foundry Soc. Trans.* **2004**, 112, 635–648.
- (11) Farmer, A. D.; Collins, A. F.; Jameson, G. J. Effect of ultrasound on surface cleaning of silica particles. *Int. J. Miner. Process.* **2000**, 60, 101–113.
- (12) Celik, M. S.; Elma, I.; Hancer, M.; Miller, J. D. Effect of in-situ ultrasonic treatment on the floatability of slime coated colemanite. In *Innovations in Mineral and Coal Processing*; Atak, S., Onal, G., Celik, M. S., Eds.; Balkema: Rotterdam, 1998; pp 153–157.
- (13) Mani, G.; Fan, Q.; Ugbole, S. C.; Eiff, I. M. Size reduction of clay particles in nanometer dimensions. *Mater. Res. Soc. Symp. Proc.* **2002**, 740, 113–118.
- (14) Sivakumar, S.; Damodaran, A. D.; Warriar, K. G. K. Delamination through sonication for hydroxy metal oxide sol intercalation of montmorillonite. *Ceram. Int.* **1995**, 21, 85–88.
- (15) Kawatra, S. K.; Ripke, S. J. Developing and understanding the bentonite fiber bonding mechanism. *Miner. Eng.* **2001**, 14, 647–659.
- (16) Ji, S.; Wan, L.; Fan, Z. The toxic compounds and leaching characteristics of spent foundry sands. *Water, Air, Soil Pollut.* **2001**, 132, 347–364.
- (17) Labbe, P.; Reverdy, G. Adsorption characteristics of polycyclic aromatic compounds on clay: pyrene as a photophysical probe on Laponite. *Langmuir* **1988**, 4, 419–425.
- (18) Cosultchi, A.; Bosch, P.; Lara, V. H. Adsorption of petroleum organic compounds on natural Wyoming montmorillonite. *Colloids Surf., A* **2004**, 243, 53–61.
- (19) Lagaly, G. Pesticide-clay interactions and formulations. *Appl. Clay Sci.* **2001**, 18, 205–209.
- (20) Horne, D. J.; McIntosh, J. C. Hydrophobic compounds in sands in New Zealand—extraction, characterization and proposed mechanisms for repellency expression. *J. Hydrol.* **2000**, 231–232, 35–46.
- (21) Capriel, P.; Beck, T.; Borchert, H.; Gronholz, J.; Zachmann, G. Hydrophobicity of the organic matter in arable soils. *Soil Biol. Biochem.* **1995**, 27, 1453–1458.
- (22) Shih, T. S.; Chang, C. C. Effects of preheat and holding time on the properties of green sand. *Am. Foundry Soc. Trans.* **1991**, 99, 631–641.
- (23) Hofmann, F. Investigation on the effect of heat on the bonding properties of various bentonites. *Am. Foundry Soc. Trans.* **1985**, 93, 377–384.
- (24) Esplugas, S.; Gimenez, J.; Contreras, S.; Pascual, E.; Rodriguez, M. Comparison of different advanced oxidation processes for phenol degradation. *Water Res.* **2002**, 36, 1034–1042.
- (25) Weavers, L. K.; Ling, F. H.; Hoffmann, M. R. Aromatic compound degradation in water using a combination of sonolysis ozonolysis. *Environ. Sci. Technol.* **1998**, 32, 2727–2733.
- (26) Mokrini, A.; Ousse, D.; Esplugas, S. Oxidation of aromatic compounds with UV radiation/ozone/hydrogen peroxide. *Water Sci. Technol.* **1997**, 35, 95–102.
- (27) Brant, F. R.; Cannon, F. S. Aqueous-Based Cleaning with Hydrogen Peroxide. *Environ. Health Sci.* **1996**, A31, 2409–2434.
- (28) Zhang, X. Y.; Cannon, F. S. Hydrogen Peroxide Cleaning of Asphalt from Surfaces: Effect of Temperature. *J. Adv. Oxid. Technol.* **1999**, 4, 434–446.
- (29) Zeng, Y.; Hong, P. K. A. Slurry-phase ozonation for remediation of sediments contaminated by polycyclic aromatic hydrocarbons. *J. Air Waste Manage.* **2002**, 52, 58–68.
- (30) Milan-Segovia, N.; Cannon, F. S.; Voigt, R. C.; Furness, J. C. Comparison of OH* Generation for Various Advanced Oxidation Combinations Applied to Foundries. *Ozone: Sci. Eng.*, submitted.
- (31) Tan, K. H. *Soil sampling, preparation, and analysis*; Marcel Dekker: New York, 1995.
- (32) Bastien, P.; Chiesa, F.; Gomez, J. I.; Pacheco, J.; Zegarra, T. Evaluation of bentonite consumption in a recirculating system sand. *Am. Foundry Soc. Trans.* **1993**, 101, 241–246.
- (33) Alther, G. R. Thermal stability of some industrial bentonites. *Appl. Clay Sci.* **1991**, 5, 469–488.
- (34) American Foundrymen's Society Mold and Core Test Handbook, 1983.
- (35) Odom, I. E. Functional properties of Na and Ca bentonites in green sand system. *Am. Foundry Soc. Trans.* **1988**, 96, 229–236.
- (36) Smiernow, G. A.; Doheny, E. L.; Kay, J. G. Bonding mechanisms in sand aggregates. *Am. Foundry Soc. Trans.* **1980**, 88, 659–682.
- (37) St. Slaczka, A. Effects of an ultrasonic field on the flotation selectivity of Barite from a barite-fluorite-quartz ore. *Int. J. Miner. Process.* **1987**, 20, 193–210.
- (38) Bauck, H. J.; Oestlin, D. The influence of core sand, coal dust and other additives on the bentonite consumption in green sand molds. *49th International Foundry Congress*; Chicago, 1982.
- (39) Beermann, T.; Brockamp, O. Structure analysis of montmorillonite crystallites by convergent-beam electron diffraction. *Clay Miner.* **2005**, 40, 1–13.
- (40) Christidis, G. E. Physical and chemical properties of some bentonite deposits of Kimolos Island, Greece. *Appl. Clay Sci.* **1998**, 13, 79–98.
- (41) Singer, P. C.; Rechhow, D. A. *Water quality and treatment: a handbook of community water supplies*, 5th ed.; McGraw-Hill: New York, 1999.
- (42) Chung, H. I.; Kamon, M. Ultrasonically enhanced electrokinetic remediation for removal of Pb and phenanthrene in contaminated soils. *Eng. Geol.* **2005**, 77, 233–242.
- (43) Flotron, V.; Delteil, C.; Padellet, Y.; Camel, V. Removal of sorbed polycyclic aromatic hydrocarbons from soil, sludge and sediment samples using the Fenton's reagent process. *Chemosphere* **2005**, 59, 1427–1437.

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