

# ADVANCED OXIDATION TO REDUCE EMISSIONS IN FOUNDRIES FROM COAL PYROLYSIS

Yujue Wang, Fred Cannon  
*The Pennsylvania State University*

*Corresponding author e-mail address: yxw147@psu.edu*

## **Introduction**

Foundries employ green sand molds, which contain coal, silica sand, clay, water, and core binders. This represents one of the largest non-combustion users of coal. When the coal experiences high temperature during the metal casting process, it undergoes pyrolysis reactions and can generate significant amounts of volatile organic compounds. Some of the compounds are released as hazardous air pollutants, while others that are released from the coal that is closest to the molten metal, will re-attach to clay surfaces that are further away from metal via chemical deposition. This carbon on the clay surface hampers the clay's ability to exhibit compressive strength, and hence more clay must be added. This carbon coating can be removed by an innovative advanced oxidation (AO) system [1], which has shown promising results in several U. S. foundries. This AO process diminishes air pollutants by 30 to 70% [2][3]; and this process has also diminished the clay and coal consumption by 20-40% [4][5]. This represents an important portion of costs in the foundries. The AO systems treat the water that is used in the green sand molding process by coupling ozone, hydrogen peroxide, ultrasonics, and underwater plasma. This generates advanced oxidants that react with the green sand in a manner that removes carbon from clay surfaces that had deposited following coal pyrolysis. As a consequence, full-scale foundries have found that they can achieve the same green compressive strength with 20-40% less clay additions when AO treatment is used [5]. The main objectives of this paper are:

1. To gain a better fundamental knowledge of how advanced oxidation affects green sand physicochemical properties.
2. To evaluate the effects of AO treatment on emissions via bench-scale analytical techniques;

It is hoped that these evaluations could deliver key information to the present understanding of AO performance in full-scale foundries.

## **Experimental**

Green sands from foundry were used in the study. These contained 7-8% active clay, 5-6% coal and other ignitable organics, 3-4% water, and the balance sand or inactive clay. The green sands were previously treated with either AO water or tap water during the casting process in the foundry. At Penn State, they were remoisturized with various AO

water or tap water to study the effects of array of AO treatment conditions on green sand emissions.

The testing conducted at Penn State included:

1. Green sand properties characterization: the effects of AO treatment on green sand properties were investigated. Specifically, pore volume distribution, m-xylene adsorption capacity, water vapor adsorption capacity, and thermogravimetric properties of green sands that were AO or tap water treated were measured and compared.
2. Green sand emissions monitoring: The effects of AO treatment on green sand emissions were investigated with laboratory facilities. The green sand was pyrolyzed in thermogravimetric analyzer (TGA) or curie-point pyrolyzer to simulate some of the intense thermal features during casting condition that the green sand experienced in foundry. The emissions were analyzed with gas chromatography-flame ionization detector (GC-FID).

## Results and Discussion

It was found that AO treated green sand possessed much higher pore volume in the micropore and mesopore range, as shown in Figure 1. It seems that more coals in the green sand were activated when AO water was used than when tap water was used; and clays retained more pore volume during the casting process under the AO condition.

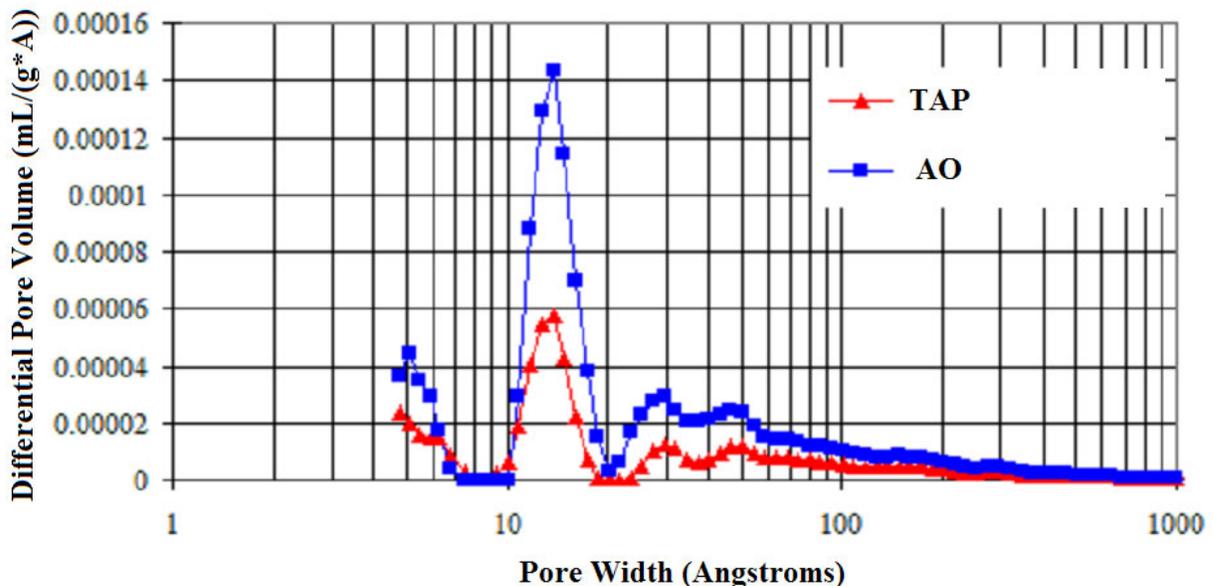


Figure 1. Differential pore volume distribution for TAP and AO green sand samples

Corresponding to the higher pore volume, the AO green sand also exhibited higher m-xylene adsorption capacity than did TAP green sand, as shown in figure 2. So more volatiles organic compounds (VOC) will be retained in the coal/clay/sand matrix and

subjected to the subsequent AO degradation, or chemical vapor deposition, instead of emitting as air pollutants in the full-scale foundry.

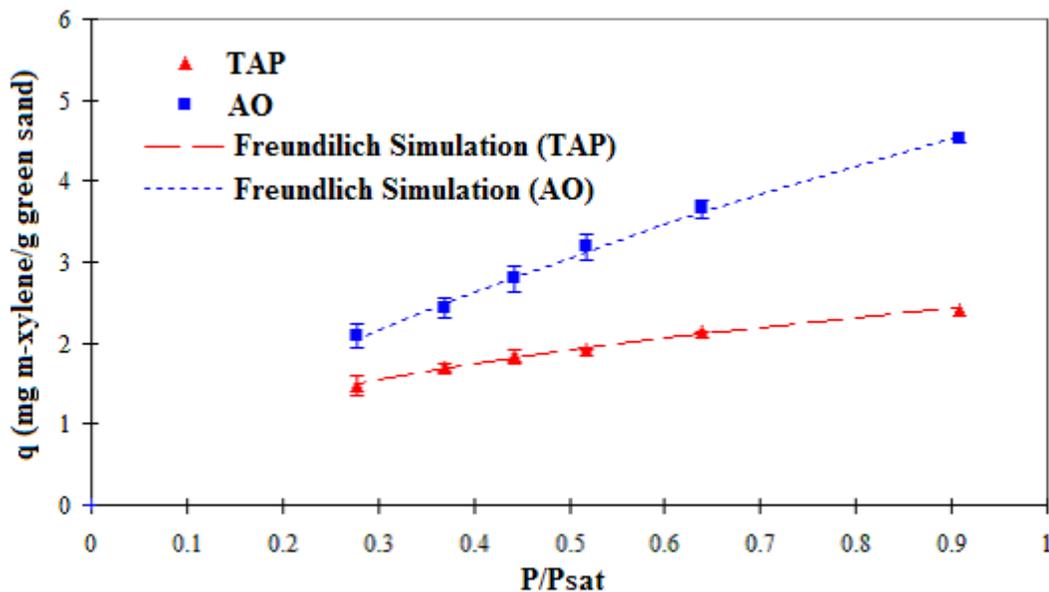


Figure 2. m-xylene adsorption isotherm of TAP and AO green sand samples.

It was found that AO treated green sand also changed the pyrolysis behavior of the coal component of green sand. Green sand treated with various AO water lost less mass during a TGA test than green sand that was treated with tap water in the temperature range of 400 to 500°C, over which green sand released most of VOC emissions (Figure 3). The less mass loss in this temperature range resulted in less VOC emissions in the TGA test as shown in Figure 4.

Surface elemental composition analysis of clay revealed that when coal underwent pyrolysis reaction, the pyrolysis products of coal could form a coat on the clay platelet (Figure 5). The surface carbon contents on the clay that was heated together with coal was much higher than pure clay, as manifested by the carbon peaks in Figure 5 a and b. And it was found that AO water could remove most of the carbon contents from the clay, while tap water could not (Figure 5 c and d).

Because of the hydrophobic characteristics of carbon, the water vapor adsorption capacity of clay that was coated with coal pyrolysis products was significantly diminished (Figure 6). This greatly hampered the clay's foundry functionality since clay depended on the hydration to develop bonding strength for the green sand mold. Figure 6 also shows that AO treatment fully restored the water vapor adsorption capacity of clay, while tap water could not achieve the same effect. It was apparent that AO treatment could restore the damaged foundry properties of clay and improve the efficiency of clay in the green sand.

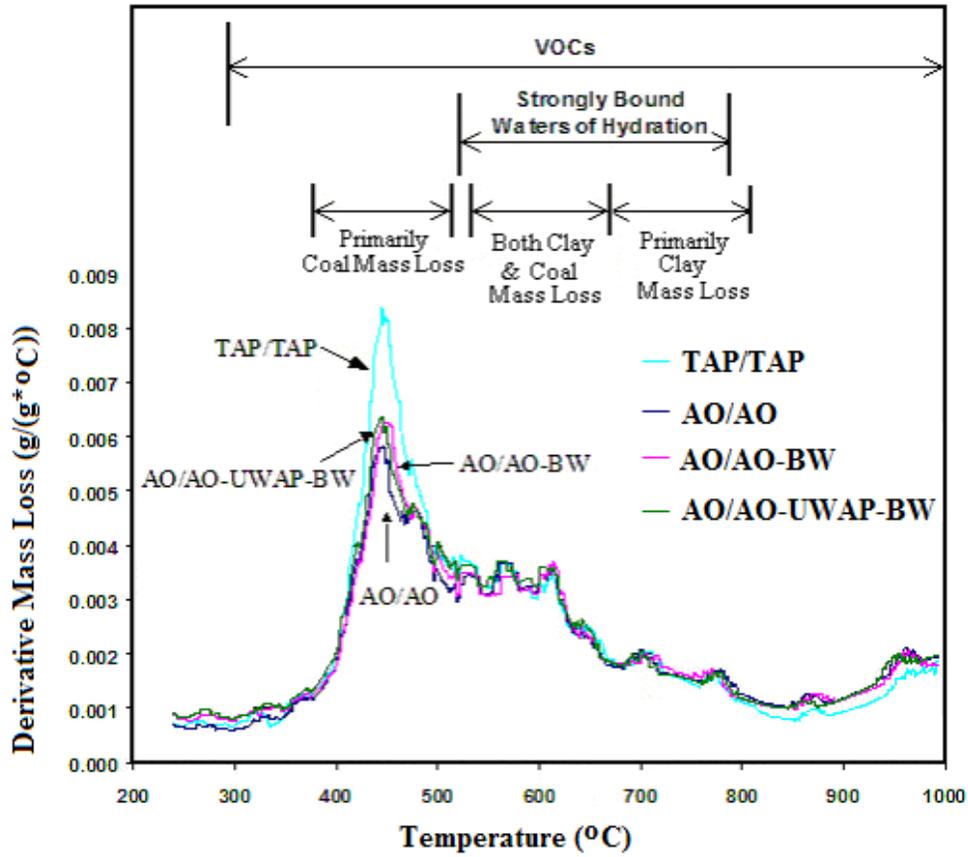


Figure 3. Derivative of the mass loss per °C for the TGA mass loss tests of TAP and AO green sands that were re-moisturized with tap water or a variety of AO-water.

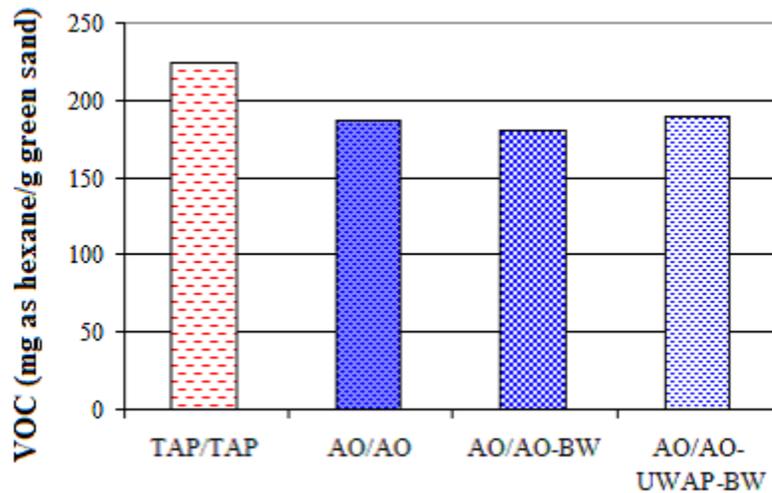


Figure 4. Total VOC<sub>(C6-C16)</sub> as Hexane emissions per gram of green sand, TAP and AO green sand samples in remoisturized conditions.

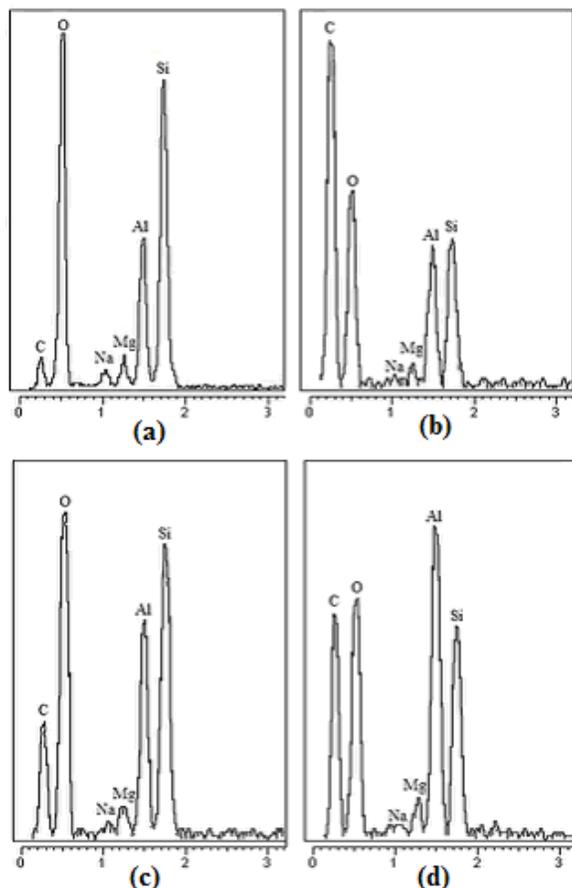


Figure 5. Surface elemental analysis of: (a) clay heated alone at 400°C, (b) clay heated with coal at 400°C, (c) AO-washed clay that had previously been heated with coal at 400°C, (d) TAP-washed clay that had previously been heated with coal at 400°C

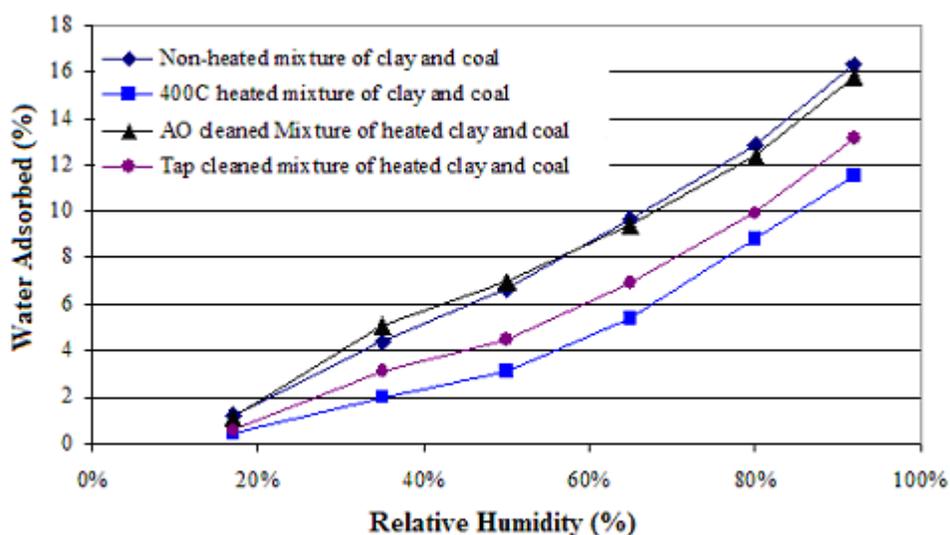


Figure 6. Effects of pyrolysis products of coal and AO/TAP-washing on water vapor adsorption capacities of clay; as indicator of hydrophobic/hydrophilic nature of surface

## Conclusions

A common constraint of using coal in green sands is that it can release volatiles and coat clay when it is heated to intense temperatures near the molten metal surface. However, the coal is important because it expands when the clay contracts during thermal treatment; and the coal helps create a smooth metal finish. With AO treatment, the favorable effects of coal use can be preserved, while also overcoming the unfavorable effects.

Specifically, the following conclusion can be made:

1. AO treatment exerted some permanent effects on the green sand structure, as indicated by the higher pore volume for AO-treated green sand than for tap-treated green sand. This markedly increased the m-xylene adsorption capacity of the coal and clay in green sand, which was 50-100% higher for AO green sand than for non-AO green sand.
2. The coal in AO remoisturized green sands released less mass and emissions than did tap remoisturized green sand, as determined from TGA tests. During the TGA-GC-FID tests, the coal in green sands that were remoisturized with various AO waters released 17-22% fewer VOC emissions than did green sand that was remoisturized with tap water.
3. AO treatment removed pyrolyzed coal residues from clay surface and therefore restored the compressive strength of the clay; this resulted in diminished clay consumption as experienced in full-scale foundry.

## References

- [1] Wang, Y., F. S. Cannon, "Mechanisms of advanced oxidation processing on bentonite consumption reduction in foundry", in process.
- [2] Glowacki, C. R., G. R. Crandell, F. S. Cannon, R. C. Voigt, J. K. Clobes, J. C. Furness, B. A. McComb, S. M. Knight, "Emissions studies at a test foundry using an advanced oxidation-clear water system", *AFS Transaction*, Vol. 111, pp. 579-598, 2003.
- [3] Goudzwaard, J. E., C. M. Kurtti, J. H. Andrews, F. S. Cannon, R. C. Voigt, J. E. Firebaugh, J. C. Furness, and D. L. Sipple, "Foundry emissions effects with an advanced oxidation blackwater system", *AFS Transaction*, Vol. 111, pp. 1191-1211, 2003.
- [4] Cannon, F. S., J. C. Furness, and R. C. Voigt, "Economical use of advanced oxidation systems for green sand emissions reduction." Proceedings of the 12<sup>th</sup> International AFS Environmental Health and Safety Conference. Orlando, FL, pp. 315-332, October 9-11, 2000.
- [5] Neill, D. A., F. S. Cannon, R. C. Voigt, J. Furness, and R. Bigge, "Effects of Advanced Oxidants on Green Sand System Performance in a Blackwater System," *AFS Transaction*, Vol. 109, pp. 937-955, 2001.