

# MODELING THE MASS TRANSFER OF AIR-PHASE VOLATILE ORGANIC COMPOUNDS THROUGH GAC DURING LOADING AND ADVANCED OXIDANT REGENERATION

Paul David Paulsen and Fred S. Cannon  
Department of Civil and Environmental Engineering  
The Pennsylvania State University, University Park, PA 16802

## Introduction

The Pennsylvania State University Applied Research Laboratory has been researching the TerrAqua TAES advanced oxidation system for controlling volatile organic compound (VOC) emissions from the U.S. Marine's vehicle painting facility in Barstow, California. The TAES system primarily consists of three processes: an ozone-UV chamber, a water absorption unit, and a granular activated carbon (GAC) adsorption unit that is regenerated with ozone and advanced oxidants. The objectives of this research have been to: (1) characterize diffusion rates of VOCs into and out of GAC, both with and without UV-ozone and (2) determine the extent to which UV-ozone enhances regeneration of GAC.

Desorption of VOCs from individual activated carbon grains was analyzed from the perspective of an internal mass transfer limiting condition. Analysis employed the thermogravimetric analyzer (TGA) to determine equilibrium relationship between adsorbed and gas phases of the VOC and to determine effective diffusion coefficients for this internal mass transfer. We hypothesized that under ozonation, advanced oxidants striking the carbon grains would alter the potential field of the carbon surface -- making the carbon less attractive to VOCs. This change in the carbon surface potential would result in a different equilibrium between the VOC's adsorbed and gas phases, increasing both amount of VOCs desorbed and the VOC desorption rate

## Experimental

In order to simplify the system as much as possible, the only VOC adsorbed to the GAC was methylisobutylketone (MIBK). Tests were conducted in the reaction chamber of an ATI-Cahn TG-131. The TGA maintained constant control of temperature with a computer controlled furnace-thermocouple system, and it maintained control of chemical species concentration through continual gas replacement occurring in a plug flow reaction chamber. All experiments consisted of loading virgin GAC sample with MIBK-laden air stream

until equilibrium was reached, and then unloading GAC with a lower MIBK concentration under various test conditions. The TGA instrument monitored GAC loading by measuring weight change, yielding very precise and accurate adsorption values throughout an experiment for situations where the only VOC in the system was MIBK. However, during ozone tests, reactions of ozone and MIBK produced a multiple species system, making it necessary to use gas chromatography (GC) to determine the amount of adsorbed MIBK. GC samples were produced by carbon disulfide extraction of the GAC sample for 24 hours after the end of each TGA test.

## Results and Discussion

Figure 1 shows equilibrium isotherms for the compound MIBK at 25 degrees Celsius before, during, and after ozonation.

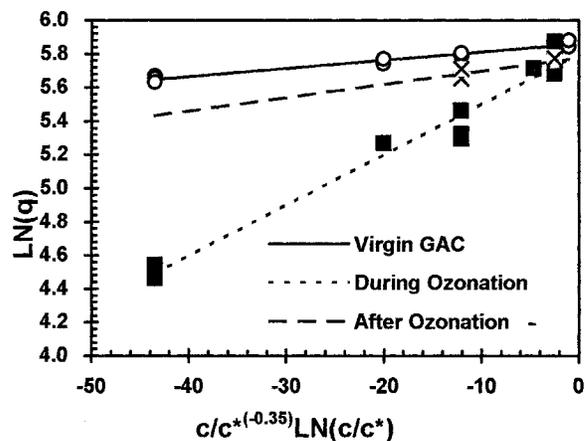


Figure 1. MIBK Adsorption Isotherms for Virgin GAC, GAC under ozonation, and GAC after ozonation fitted to the equation:  $\ln(q) = \ln(K) + B(c/c^*)^{-0.35} \ln(c/c^*)$

and after ozone regeneration. Equilibrium data was fitted to a modified Freundlich equation that relates adsorbed phase concentration (q) to the vapor phase concentration (c) normalized by the saturation vapor concentration (c\*). Modification of the Freundlich

equation (a) enhanced the correlation of data and (b) yielded a common isotherm slope independent of temperature. These equilibrium equations were used in the model to obtain effective diffusivities from TGA test data. The term  $K$  in the isotherm is the adsorbed MIBK concentration when the vapor phase is saturated and the term  $B$  is the isotherm slope. Adsorbed phase concentrations are in the units of mg MIBK per g GAC. Presence of ozone radically reduced the ability of GAC to retain adsorbed volatiles particularly when vapor phase MIBK concentrations drop (Figure 1). After ozonation, GAC returns almost to its original adsorption capacity. Adsorption capacity being slightly reduced from GAC chemical composition change caused by ozone reactions with surface.

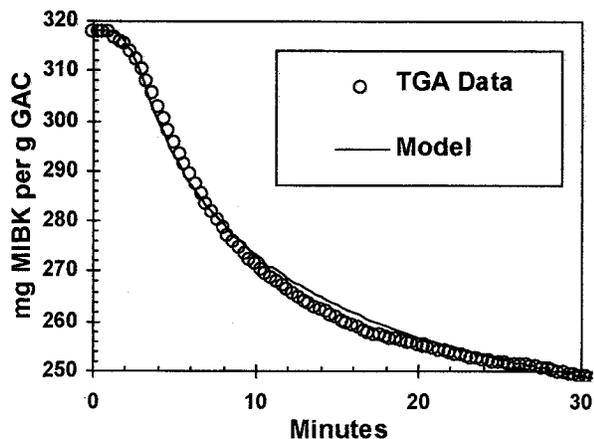


Figure 2. Comparison of Model and TGA Data for MIBK Desorption from GAC at 75 Celsius.  $D_e/r^2 = 1.55$ .

Effective diffusion coefficients ( $D_e/r^2$  where  $r$  represents a diffusion controlling radius) at 25, 50, 75, and 105 degrees Celsius were calculated by comparing model calculations of MIBK desorption with TGA test data (Figure 2). The model differed from the TGA data

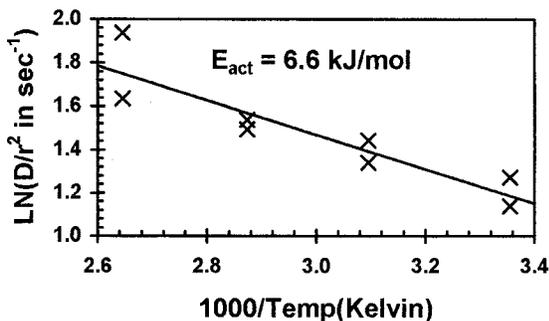


Figure 3. Arrhenius Plot of Effective Diffusivities.

by an average of 1.44 mg MIBK per g GAC for the 181 points shown in Figure 2.

Figure 3 shows these normalized diffusion coefficients graphed in an Arrhenius plot. The effective activation energy for this internal diffusion process was found to be 6.6 kJ/mol, suggesting that activated diffusion was rate controlling.

Figure 4 shows the amount of MIBK left adsorbed to carbon after 14 hours regeneration with and without ozone. Virtually no adsorbed MIBK can be measured using the GC method after 14 hours ozone regeneration at 75 and 105 degrees Celsius. At 25 Celsius, the presence of 400 ppm ozone yielded almost 50% more removal after 14 hours when compared to an MIBK-free air stream without ozone.

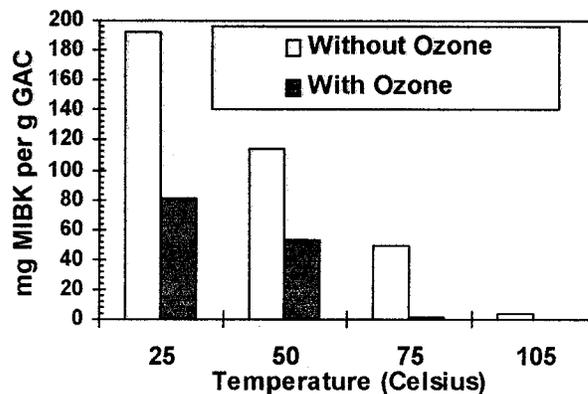


Figure 4. MIBK mass remaining on GAC following 14 hour regeneration with and without ozone, using Gas Chromatography.

## Conclusions

The temperature dependence and the magnitude of the diffusion coefficients obtained established that activated diffusion controls the kinetics of MIBK desorption from GAC. The presence of ozone enhanced regeneration both by ozone reaction with the adsorbed MIBK creating VOCs less able to adsorb to GAC than MIBK and possibly by ozone altering the potential field of the GAC, temporarily making the GAC less able to adsorb MIBK or other VOCs.

## Acknowledgements

We would like to thank the following for funding this research: the U.S. Marine Corps via the Strategic Environmental Research and Development Program (SERDP) and the U.S. Department of Education via the Graduate Assistance in Areas of National Need (GAANN) Fellowship Program.