THE PEROXY-ACID TREATMENT PROCESS:
AN INVESTIGATION OF PROCESS MECHANICS

By

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ABSTRACT

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Polycyclic aromatic hydrocarbons (PAHs) are a group of hydrophobic organic contaminants (HOCs) that are found throughout the environment. Like other HOCs, they persist in the natural environment and represent a threat to human health due to their propensity to initiate genetic mutations and cause cancer. The peroxy-acid process utilizes a mixture of organic acids and hydrogen peroxide to initiate the formation of oxidative species which have been effective in degrading PAHs in small scale experiments with freshly contaminated soils and sediment.

Experiments were conducted to determine if the peroxy-acid process could effectively treat Superfund Site soil heavily contaminated with PAHs (*e.g.*, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h,)anthracene and benzo(g,h,i)perylene). Initial tests exposed 150 g of Superfund Site soil to 450 ml of a 3:3:9 (v/v/v) hydrogen peroxide/acetic acid/deionized (DI) water reaction ratio for 24 hrs. Results demonstrated that this treatment strategy was unable to bring about a reduction in PAH contamination. Further studies were conducted

on smaller quantities of Superfund Site soil (5 g) where hydrogen peroxide volumes were increased in an attempt to increase treatment effectiveness. Ratios of 6:3:9 and 9:3:9 (v/v/v) hydrogen peroxide/acetic acid/DI water, with total volumes of 18 ml and 21 ml respectively, were also unable to treat this complex soil matrix.

Subsequent studies carried out in simple systems containing glass beads contaminated with benzo(a)pyrene revealed several relationships important to the efficacy of treatment with the peroxy-acid process. The formation of peracetic acid (PAA) was controlled by the ratio used to mix hydrogen peroxide, acetic acid and water. A 5:5:5 (v/v/v) hydrogen peroxide/acetic acid/DI water mixture produced approximately 2.3 % PAA in 24 hours, compared to the roughly 0.5 % PAA formed with 3:3:9 (v/v/v) hydrogen peroxide/acetic acid/DI water over the same amount of time. Adding sulfuric acid to both ratios increased the amount of PAA formed in 24 hours confirming its role as a catalyst in the reaction. Each of these reactive mixtures was applied to benzo(a)pyrene contaminated systems and a good correlation was found between the amount of PAA formed and benzo(a)pyrene degraded. Using a ratio of 5:5:5 (v/v/v) hydrogen peroxide/acetic acid/DI water with the addition of sulfuric acid (1 ml), an 87.6 % degradation of benzo(a)pyrene contaminated glass beads (500 mg/kg) was observed in 24 hrs.

The relationship between organic acid structure and treatment efficiency was tested by comparing the results from experiments with several organic acids. Malonic acid, a dicarboxylic acid, was found to be comparable with acetic acid in its ability to degrade benzo(a)pyrene contaminated glass beads. Hexanoic acid, a carboxylic acid with a six carbon chain, was able to achieve a more complete treatment of benzo(a)pyrene

when compared to acetic acid, which was postulated to result from its ability to solubilize this highly hydrophobic contaminant. The physical properties of the reactive vessels were also manipulated to study their effect on treatment efficiency. The degradation of benzo(a)pyrene increased with an increase in the mass of glass beads added to the reactor, as well as with an increase in the reactor mixing rate. All of these findings demonstrated the importance of mass transfer in treating hydrophobic PAHs.

The results from experiments conducted on simplified systems led to a different treatment approach for the more complicated Superfund Site soil. The strategy utilized system agitation along with the implementation of a pre-mixed hydrogen peroxide/acetic acid solution. The premixed solution was able to degrade all of the PAHs present in the complicated matrix. Likewise, by first extracting PAHs from the soil matrix with hexanoic acid, and then treating with hydrogen peroxide and sulfuric acid, nearly all of the PAHs studied (*e.g.*, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h,)anthracene and benzo(g,h,i)perylene) were degraded in 24 hrs.