

Destruction and Transformation of Pyrene by Mineral Surfaces during Thermal Desorption

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Background/Objectives. Thermal desorption is a soil remediation process where contaminated soils are heated to remove contaminants which are volatilized and collected in the off gas. Current systems are run over a range of temperatures, 100-1000 °C, for periods over 30 days. In situ treatment can be achieved by inserting thermal heater wells into the contaminated soil around a vacuum well. While the primary goal of thermal desorption is volatilization and capture of contaminants, a number of transformation reactions have been observed during treatment. Though some studies have identified by-products from these reactions after treatment, no studies have fully investigated the different reaction pathways and mechanisms (e.g., catalysis versus electron transfer) and how these are affected by soil parameters, such as organic content, mineralogy, and water content. One potentially significant pathway for transformation is the reaction, whether by catalysis or electron exchange, between mineral surfaces and contaminants within the soil. The primary goal of this study is to determine whether the presence of redox active minerals increases the extent of reaction during thermal desorption and whether the associated reaction products are more or less toxic than the parent (i.e., pyrene).

Approach/Activities. Controlled laboratory experiments were performed to determine the effect of different minerals on transformation during thermal desorption. Five common minerals were chosen for this study based on their varying potential for promoting redox reactions: Ottawa sand (SiO_2), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), hematite (Fe_2O_3), magnetite (Fe_3O_4), and birnessite (MnO_2). Individual minerals were spiked with pyrene and heated in a closed reactor vessel with temperature (200-600 °C), water content, and oxygen content varied between experiments. Pyrene was chosen as a model contaminant in this study because it is a common and recalcitrant pollutant, and has distinct by-products because it is composed of only aromatic carbon rings. The extract from the thermally treated minerals and the headspace were analyzed to determine the extent of degradation of pyrene as well as byproduct formation.

Results/Lessons Learned. Initial experiments were run with crystalline pyrene added to a given mineral sample without solvent and purged with nitrogen to remove oxygen gas. These experiments were run at 200 °C and 400 °C, and more degradation of pyrene into smaller byproducts such as 2- and 3-ring PAHs, biphenyl, and light gases occurred at the higher temperature. When solvent (methanol) and oxygen were introduced into the system the same general trends were observed and additional oxygenated products formed, such as dibenzofuran and benzophenone. Minerals that are more redox active have shown a greater potential for degradation of pyrene. The overall trend for pyrene degradation, starting with the highest percent degradation, is birnessite > magnetite > hematite > kaolinite > sand. Additional experiments were performed at 600 °C with birnessite and trace amounts of 5 and 6 ring PAH's formed in addition to the smaller by-products observed at lower temperatures. Future experiments will focus on determining under what conditions degradation of pyrene or formation of larger products is favored. These tests will help in understanding how to run thermal desorption systems that achieve treatment without causing further harm to the environment and hopefully aid in the destruction of toxic contaminants during treatment.