

Managing groundwater plumes of dissolved nitroaromatic and cyclic nitramine compounds is a high priority at military facilities where site management costs can be very high. A novel approach to control plume migration utilizes electrolytic permeable reactive barriers to degrade these chemical *in situ*. This research focuses on characterizing the relationship between electrode surface morphology and composition with the rate of electrochemical reduction for mixtures of cyclic nitramines and nitroaromatics. The electrode material studied consists of a mixed metal oxide ($\text{IrO}_2/\text{TiO}_2$) coated titanium mesh (Ti/MMO). The surfaces of previously unused electrodes are relatively rough and fractured, exposing large amounts of IrO_2 . Observed first-order heterogeneous rate constants, at cathode potentials of -1.2 V vs. the standard hydrogen electrode, for 1,3,5-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) on fresh electrodes are approximately 0.1 cm min^{-1} in experiments with a single reactant. These are roughly two to three orders of magnitude larger than reduction kinetics on Fe^0 surfaces for TNT and RDX, respectively.

Two important factors that have the potential to affect the application of these electrolytic permeable reactive barriers have been investigated. The first of these is the presence of contaminant mixtures; cyclic nitramines and nitroaromatics are often co-contaminants in the environment and mixture effects were expected to alter the electrochemical reaction rates of TNT and RDX. To address this issue, electrode surface reaction kinetics were measured in multi-reactant batch degradation experiments using Ti/MMO cathodes. The target compounds were two nitroaromatics, TNT and 2,4-dinitrotoluene (2,4-DNT), and two cyclic nitramines, RDX and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine (HMX). When mixtures of species were present, the expected inhibition of the degradation kinetics according to a pure inter-species competition model was not observed. In the absence of inhibition, a mechanism based on an initial reaction step with adsorbed hydrogen is proposed that agrees with the observed reaction kinetics. Adsorbed hydrogen, an intermediate in the hydrogen evolution reaction (HER), is formed at the surface of iridium oxides, which are a stable HER electrocatalyst. Therefore, reduction of the target compounds is likely associated with the availability of iridium oxide on the electrode surface.

The second factor affecting implementation of this technology is the aging of the electrode material. Surface morphology and composition evolution after artificial aging were assessed using scanning electron microscopy and energy dispersive x-ray spectroscopy. After aging, the roughness and iridium fraction of the cathode surface decreased. Electrochemical reduction kinetics of cyclic nitramines and nitroaromatic mixtures were re-evaluated using an artificially aged electrode that exhibited these surficial transformations. The correlation between surface structure/composition changes and mixture reaction kinetics will be discussed in this presentation. Overall, this research presents a new cathode material for the electrochemical reduction of a prevalent organic contaminant in the context of a system that may be deployed in field-scale implementations.