Chlorinated solvents, such as perchlorethylene (PCE) and trichloroethylene (TCE), as well as other chlorinated ethenes and ethanes, have long been used as dry cleaning solvents and degreasers, along with other applications. Due to this use, contamination of groundwater sources with chlorinated solvents is widespread in the United States. Contaminated sites include dry cleaning facilities and airfields. Ninety percent of the Superfund sites in the state of Arizona have measureable amounts of PCE and TCE. These solvents are highly stable and possibly carcinogenic, with the greatest risk coming from long term, low level exposure to contaminated water. Current remediation efforts often involve soil-vapor extraction (SVE) followed by exposure to a granular activated carbon (GAC) bed. This technology is non-destructive, simply removing the contaminant from the gas stream, and requiring further treatment to destroy the contaminant and regenerate the GAC. This research group has proposed a gas phase catalytic system, using a three-way catalyst, as a viable technology to replace GAC in remediation efforts.

The proposed catalyst is Al_2O_3 supported Pt/Rh, better known as a three-way catalyst found in automobile catalytic converters. This catalyst is used to reduce NO_x and oxidize CO and hydrocarbons, making it ideally suited to the reducing-oxidizing (redox) conditions proposed. Catalysis of chlorinated hydrocarbons creates issues as well. Catalytic oxidation of PCE requires high temperatures, with experiments showing only 30% conversion at catalyst surface temperature (CST) of 500 °C in air. Furans and dioxins, which are potentially more harmful compounds, can also be produced at lower temperatures (200-400 °C) during catalytic oxidation. Poisoning of the catalyst due to chlorine exposure is also a long term issue. Catalytic reductive dechlorination is capable of 100% conversion of PCE at a CST of 300 °C with a gas stream of 6% H_2, but conversion drops to <10% within 3 hours due to coking. The use of both oxygen and a reductant source, creating redox conditions, allows for complete PCE removal at temperatures greater than 300 °C, without the associated problems of coking and chlorine poisoning. As the initial goal of this project was to evaluate an alternative remediation technology, the experimental system has been designed to simulate SVE gas. Nitrogen, oxygen and the reductant are combined with a nitrogen stream saturated with PCE, and passed through a 1 in diameter by 1 in length catalyst supported in a quartz tube located in a tube furnace. Residence times (RT) within this system range from .005 s to 0.5 s depending on flow rate and temperature. The catalyst used in the experiments is purchased with a Pt/Rh ratio of 3/1 and a total metal loading of 5 g/ft^3. The catalyst is a cordierite monolith with channels having a 1 mm x 1mm cross section. The wash coat is γ-Al_2O_3, cerium zirconium oxide and trace constituents.

In order for the proposed catalytic system to have value, the catalyst must remain active indefinitely, demonstrating that redox conditions are effective over simple catalytic oxidation and reductive dechlorination. The catalyst deactivates in less than 3 hours at 300 °C with a RT of 0.3 s when the flow stream is 6% H_2. This deactivation is due to coking, which is readily removed by cleaning the catalyst at 500 °C in air. Deactivation is less immediate during catalytic oxidation, but has longer term consequences as poisoning of the Pt and Rh with chlorine is not easily remedied. A complete carbon balance under reducing only conditions (6% H_2, 0.3 s RT) indicate that the reduced products of PCE are methane, ethane and ethylene. No chlorinated byproducts were detected. Initially, methane is the primary product, but as catalytic activity decreases due to coking, ethane becomes more prominent, followed by an increase in ethylene. This lends to the idea that there are different sites on the catalyst, leading to different adsorption geometries and different reaction mechanisms. Initial experiments under redox conditions indicate that an H_2/O_2 ratio of 2/1 is ideal, which is also the stoichiometric ratio for the combustion of H_2. Conversion of PCE is nearly 100% in the CST range of 100 to 500 °C at 2%

H_2 and 1% O_2, while dropping to ~70% at 500 °C with 2% H_2 and 8% O_2. A carbon balance performed under redox conditions (4% H_2, 2% O_2, 0.1-0.5 s RT) indicates that the reduced products (methane, ethane and ethylene) are present at temperature less than 500 °C, but that the primary product is CO_2. No chlorinated byproducts were detected.

Hydrogen proved to be prohibitively expensive for use in remediation efforts, alternative hydrogen sources, namely C1-C4 alkanes, were studied. Increased conversion of PCE was seen as the carbon chain length increased, which also correlated with decreasing C-H bond dissociation energy (~440 kJ/mol for methane, ~400 kJ/mol n-butane). Methane proved to have negligible improvement on oxygen only conditions, although deactivation was not present. Although conversion of PCE with each of these compounds is less than that when H_2 is present, they are better suited for use in remediation due to the high concentration of oxygen (17-21%) in SVE gases. While the stoichiometric ratio for H_2/O_2 is 2/1, it is 1/5 for propane/O_2, meaning less reductant is needed to run at ideal conditions at high O_2 concentrations. Propane was chosen as the reductant for further studies due to low cost and availability. PCE removal reaches 100% at 525 °C in air when the propane concentration is 1% and the RT is 0.3 s. Results also indicate that PCE is removed at a greater percentage than propane during the entire temperature range (400-650 °C) despite the large difference in concentrations (500 ppmv PCE, 1% propane). As indicated previously, the O_2/propane ratio is important in maximizing PCE conversion. Experiments indicate that the ideal ratio is the stoichiometric ratio for the combustion reaction, with conversion dropping quickly at ratios <5 due to coking, while approaching catalytic oxidation conversion levels more gradually as the ratio increases above 5. The concentration of PCE affects the overall conversion as well, with a conversion of ~80% with 100 ppmv PCE dropping to ~20% with 800 ppmv at 425 °C in air with 1% propane.

Initial steps have been taken to model this reaction. A first order (with respect to PCE) Langmuir-Hinshelwood model with a number of assumptions has been explored. The reaction occurs in a PFR with adsorption and desorption fast enough to be considered an equilibrium process. There is no interspecies competition for sites. The change in propane concentration is not accounted for and oxygen is assumed to play no role in the kinetics, although inhibition due to high levels of oxygen has been proven. The apparent 1st order rate constant is adjusted for temperature using an Arrhenius expression and apparent activation energy, while the equilibrium constant is adjusted using an Arrhenius expression with the molar enthalpy of desorption. The model fits current data well, while having difficulties predicting changes in removal due to O_2 concentration and propane concentration changes.