

Project Summary  
U.S. Department of Energy

Ionizing Radiation Induced Catalysis  
on Metal Oxide Particles

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High-level radioactive waste storage tanks at DOE sites contain significant amounts of organic components (solid and liquid phases) in the form of solvents, extractants, complexing agents, process chemicals, cleaning agents, and a variety of miscellaneous compounds. These organics pose several safety and pretreatment concerns, particularly for the Hanford tank waste. Many currently proposed tank waste cleanup alternatives encounter potential safety and/or pretreatment problems associated with organics. Remediation technologies are needed that significantly reduce the amounts of problem organics without resulting in toxic or flammable gas emissions and without requiring thermal treatments. These restrictions pose serious technological barriers for current organic destruction methods, which use oxidation achieved by thermal or chemical activation.

This project focuses on a novel approach for destroying organics found in high-level mixed waste prevalent at DOE sites. In this project, we have studied the destruction of organics, such as those found in Hanford tank waste, using reduction/oxidation (redox) chemistry resulting from exposure of typical photocatalytic materials to ionizing radiation (e.g., gamma radiation). Conceptually, this process is an extension of photocatalytic processes known to occur with visible and ultraviolet (UV) light at the interfaces of metal oxide photocatalysts (such as titanium dioxide,  $\text{TiO}_2$ ). In these processes, energy is absorbed by the photocatalyst from light resulting in electron being excited within the photocatalyst. The excited electrons become available for reaction with solution species such as water, while the 'holes' (electronic states in the photocatalyst previously occupied by the excited electron) then strip electrons from adsorbed organic species resulting in oxidative destruction of the organic. The energy separation between the hole and the excited electron reflects the redox capability of the excited electron/hole ( $e^-/h^+$ ) pair, and is dictated by the energy of the incident light and the electronic properties of the photocatalyst. Unfortunately, application of visible or UV light to large scale photocatalytic processes is severely limited by their marginal transparency into most metal oxide catalysts. Additionally, the relatively weak photon energies of visible and UV light limit the types of metal oxide catalysts that can show results. The use of ionizing radiation overcomes optical transparency limitations associated with visible and UV light (e.g., gamma-rays penetrate much farther into materials than either visible or UV light) and permits the use of wider variety of metal oxide catalysts that opens the door to a potentially greater degree of redox capabilities than those photocatalysts that can only be used with visible or UV light. The use of ionizing radiation offers several attractions. For example, the process operates at ambient temperature and pressure eliminating many safety concerns associated with hydrothermal or calcination approaches. The metal oxide catalysts are robust and stable in both radiation chemically corrosive environments. Another advantage of this approach is that conceptually no additional safety concerns other than those required for handling mixed waste should be required, and existing radiation sources available at the Hanford Site, specifically,  $^{137}\text{Cs}$  capsules, could be employed

In the three years of this program, we examined in detail the radiocatalytic destruction of EDTA, a typical chelating agent found in DOE tank waste, over various  $\text{TiO}_2$  catalysts. Our results show that exposure of solutions containing EDTA and  $\text{TiO}_2$  to gamma radiation resulted in significant catalytic destruction of EDTA over that observed in absence of  $\text{TiO}_2$ . This is as the case under conditions that might be encountered with tank waste (high pH, high electrolyte concentration and with the presence of chelating cations such as strontium). The mechanism for this destruction however does not appear to be the same as that of UV-based photocatalysis. We have conducted similar studies on smaller probe organic molecules (such as ethanol, formic acid, and acetic acid). UV-based experiments do show significant destruction of these small organics, in agreement with the literature, whereas our results show that solution-phase radiolytic processes dominate those associated with the  $\text{TiO}_2$  surface to the extent that any catalytic effects are not detected. Therefore, we conclude that organics can be destroyed over typical metal oxide photocatalysts using ionizing radiation as the light source. However, the mechanism and viability of this approach have not been determined.

On fundamental side, this project has significantly added to the fields understanding of how ionizing radiation interacts with metal oxides and initiates chemical processes at their interfaces. This project has been highly productive in term scientific output and collaborations. To date, this project has resulted in approximately 10 publications in peer reviewed journals, with at least 5

additional manuscripts under review or soon to be submitted. Results from these works have been presented at over 15 national and international scientific meetings and at invited talks at 5 academic institutions (Univ. of Washington, Univ. of Illinois, Univ. of Puerto Rico, Notre Dame Univ. and Texas A&M Univ.). As a result of this project, collaborative interactions have been developed between PNNL and the following institutions: Univ. of Puerto Rico, Univ. of New Mexico, Univ. of Zurich and New Mexico Tech.