

## **Report for 2001MS1621B: A Single Technology for Remediating PDAs, Nitro/Nitrate Residues, PCBs, CAHs, Herbicides and Pesticides from Soils and Sludges with Na/Nh3.**

- Water Resources Research Institute Reports:
  - Pittman, Jr., C.U., and J. He, 2001, Dechlorination of PCBs, CAHs, Herbicides and Pesticides in Soils, Sludges, DNAPLs and Bulk With Na/NH<sub>3</sub> at Ambient Temperature, Mississippi Water Resources Research Institute, Mississippi State University, Mississippi State, Mississippi, 44 pages.
- Book Chapters:
  - Lipnick, R.L., R.P. Mason, M.L. Phillips, and C.U. Pittman, Jr., 2002, Chemicals in the Environment: An Overview, Editors R.L. Lipnick, R.P. Mason, M.L. Phillips, and C.U. Pittman, Jr., Chapt. 1 in Chemicals in the Environment: Fate, Impacts and Remediation, ACS Symposium Series, Vol. 806, Washington, DC, Oxford Press, pages 1-24.
  - Pittman, Jr., Charles U., Jinbao He, and Guang Ri Sun, 2002, Solvated Electron (Na/NH) Dechlorination of Model Compounds and Remediation of PCB and CAH Contaminated Wet Soils, Editors R.L. Lipnick, R.P. Mason, M.L. Phillips, and C.U. Pittman, Jr., Chapter 25 in Chemicals in the Environment, ACS, Washington, DC, Oxford Press, pages 419-433.
- Conference Proceedings:
  - Pittman, Jr., C.U., and J. He, 2001, Dechlorination of PCBs and CAHs Using Na/NH<sub>3</sub>: Application to Soil Remediation "in" Proceedings of the 31st Mississippi Water Resources Conference, Mississippi Water Resources Research Institute, Mississippi State, Mississippi, 75-84.
- Other Publications:
  - Lipnick, R.L., R.P. Mason, M.L. Phillips, and C.U. Pittman, Jr., 2002, editors of Chemicals in the Environment, ACS Symposium Series 806, ACS, Washington, DC, Oxford Press, pages 1-508.

Report Follows:

## PROBLEM AND RESEARCH OBJECTIVES:

Polynuclear aromatic hydrocarbons (PNAs) from creosote wood treatment plants and nitrated organic residues from munitions/explosives/propellant manufacturing contaminate soils at over 120 sites, many in the Southeastern US. Polychlorinated biphenyls (PCBs) and other chlorinated compounds are distributed in soils, sludges, estuaries, etc. at over 400 sites in the United States. Chlorinated aliphatic hydrocarbons (CAHs), widely used for degreasing/cleaning engines, auto parts, electronic components and dry cleaning, occur as serious contaminants at 358 major hazardous waste sites in the United States. This demonstrates a national need for a variety of rapid remediation methods. CAHs migrate vertically through soils to form dense nonaqueous phase liquids (DNAPLs) on aquifer bottoms. *Ex-situ* methods of CAH decontamination/destruction are needed for soils, sludges, bulk zones (DNAPLs in the vadose zone) and industrial process wastes. We propose a single reduction technology to destroy PNAs, nitrated organics PCBs, CAHs and other chlorinated pesticides and herbicides using solvated electron chemistry ( $\text{Na}/\text{NH}_3$ ) at room temperature applicable to *ex-situ* and some *in-situ* treatments. Since nitro and nitrate compounds are readily reduced, we think  $\text{Na}/\text{NH}_3$  reduction can decontaminate soils around ammunition and ordinance plants.

The goal of the proposal research is to develop a generalized technology to decontaminate soils (*in-situ* and *ex-situ*) and sludges contaminated with PNAs, Nitrated organics, PCBs, CAHs, chlorinated pesticides and herbicides. We have recently demonstrated that neat PCBs and PCB-contaminated soils and CAH-contaminated soils (as received clay, loam, sandy soils containing up to 30% water) can be decontaminated in liquid ammonia slurries when treated with either  $\text{Na}/\text{NH}_3$  or  $\text{Ca}/\text{NH}_3$ . PCB-destruction efficiencies >99.9% were achieved in 30 sec. at room temperature. The products were biphenyl and NaCl. We determined water can be present yet acceptable PCB and CAH destruction occurred at reasonable Na consumption. Can wet sludges be economically treated? This chemistry destroys carbon tetrachloride, tetrachloroethylene, trichloroethylene, trichloroethane (major CAH-pollutants) rapidly in soils in the presence of water. Will this scale up economically? Demilitarization has emphasized nitro and nitrate compound contamination of nitration factory soils. Can these residues be reduced rapidly by  $\text{Na}/\text{NH}_3$  or  $\text{Ca}/\text{NH}_3$  in soils? Several nitroaromatics have been quantitatively reduced using  $\text{Na}/\text{NH}_3$   $\text{Na}/\text{ethylenediamine}$  in our labs. Polynuclear aromatic hydrocarbons, PNAs, are rapidly reduced in  $\text{Na}/\text{NH}_3$ . Can this be extended to soils and sludges? The major goal is to develop solvated electron chemistry (e.g.  $\text{Na}/\text{NH}_3$ ,  $\text{Ca}/\text{NH}_3$ ) as a single, multifunctional, portable technology applicable to both on site *in-situ* and on site *ex-situ* destruction of PCBs, PNAs, CAHs, and ammunition/explosive residues. The major focus is to demonstrate a new remediation technology.

## METHODOLOGY:

This research will be largely devoted to studies of principles involved in the solvated electron ( $\text{Na}/\text{NH}_3$ ,  $\text{Ca}/\text{NH}_3$  and related systems) reductions of neat PCBs, CAHs, CFCs, organic nitro/nitrate compounds and the like. These reductions are aimed at dechlorinations and defluorinations of PCBs, CAHs and CFCs and nitro/nitrate group reductions. Most of the work will be carried out in glass laboratory reactors or small metal reactors with analysis by gas chromatography, high pressure liquid chromatography and mass spectrometry. Pure substrates, substrate mixtures will be reacted in liquid  $\text{NH}_3$  with Na or Ca (e.g. solvated electrons). The level of accuracy must be on the order of 4% although typical reactions on well defined compounds will be on the order of 2%. No higher accuracy will be required because we will be testing ideas and theories. Since most reactions will be run on high concentrations this level of accuracy will be easy to obtain. However, two classes of experiments will be performed where higher levels of analytical proficiency will be required. These are mentioned below.

Soils which are purposely contaminated with PCBs or CAHs will be prepared at levels of about 2000-700 ppm. These soils will then be treated with Na/NH<sub>3</sub>, Ca/NH<sub>3</sub> solutions followed by soil isolation. Analytical determinations will then require detection of only a few parts per million of the PCB or CAH contaminants that remain. These lower levels of contaminants require specific careful analytical methods and acceptance criteria. Such analyses will be conducted in the Mississippi State Chemical Laboratory (MSCL) which operates under strict QA procedures including GLP. The MSCL is a national laboratory for doing soil pesticide screens for the U. S. Department of the Interior, Division of Wildlife and Fisheries. However, even in these cases we will be searching for trends within a series and not highly accurate absolute measurements. For example, starting at 2000 ppm of contaminant treatments A, B and C might give 50, 20 and 5 ppm of residual contaminant. For theory development and process understanding,  $\pm 40\%$  accuracy could easily be tolerated. Reproducibility, precision, standardization methodology however will be carried out in accord with MSCL's QA/QC plan for this sort of work.

The data obtained in this study will be only for our use to establish principles, theories and to compare promising remediation processes employing solvated electrons. Absolutely no regulatory use of this work intended. Furthermore, we do not intend to establish any program to analyze environmentally contaminated sites. Moreover, it is not the intent in this work to establish just how low a residual level the contaminant can be reduced to. Instead we want to study the stoichiometry of Na and Ca use. Thus, as solution or soil concentration of the contaminant is reduced, will the ratio of the moles of toxic substrate destroyed/moles of Na or Ca consumed increase? This can be established in ranges from high starting concentrations to starting concentrations of 50 to 100 ppm. Similar studies will look at the effect of the presence of water on utilization of both Ca and Na. We anticipate these principles can be established without going to highly expensive analytical methodology.

## **SIGNIFICANCE:**

The proposed research will test the hypothesis that PNAs, nitrated organics and virtually all chlorinated organic molecules (PCBs, CAHs and chlorine-containing herbicides and pesticides) can be rapidly and simultaneously remediated at ambient temperature in the presence of water. Furthermore, the proposed work will demonstrate if all of these classes of chlorinated and nitrated organics and PNAs can be economically destroyed while present in soil matrices or as sludge contaminants. At high pollutant dilution (e .g. for example 500 to 10 ppm in soils or sludges) can solvated electron reductions (employing Na/NH<sub>3</sub> or Ca/NH<sub>3</sub>) destroy 99.9% of the toxic/hazardous organochlorine, PNA or nitrated pollutants in the presence of large amounts of water, humic acids, clays, etc.? This requires the relative rates of the toxic/pollutant compound reduction to be far faster ( $\times 10^4$  or  $\times 10^5$ ) than that of water. The reduction rates of organonitro and nitrate compounds will be established in lab solutions and soil decontamination studies to see if either Na or Ca/NH<sub>3</sub> chemistry could be used in demilitarization/environmental restoration. If model PNAs (pyrene, benzo[a]anthracene, chrysene), nitrated organics (TNT, dinitrobenzene, RDX) and CAHs (carbon tetrachloride, tetrachloroethylene and trichloroethane) exhibit rapid reduction kinetics and if soils contaminated with such model pollutants soils are suitably decontaminated, the way will be opened for large scale soil remediation. Furthermore, direct Na or Ca/NH<sub>3</sub> on-site, treatment of excavated soils will be possible. Direct Na or Ca/NH<sub>3</sub> injection into DNAPLs may be a way to *in-situ* treat such dense CAH underground liquid plumes. This would permit CAH remediation prior to more widespread migration and entry of CAHs into groundwaters. Since ammonia is already injected into soils in agricultural practice, injection of Na/NH<sub>3</sub> or Ca/NH<sub>3</sub> solutions directly into certain DNAPLs, appears reasonable. Slurrying soils in liquid NH<sub>3</sub>, followed by treatment with Na and removal of NH<sub>3</sub> has been demonstrated for PCBs and CAHs in our lab.<sup>7-10</sup> Trace ammonia retained by the soils as NH<sub>4</sub><sup>+</sup> ions is a fertilizer.

Benefits Expected from Na/NH<sub>3</sub> Decontamination Processes. Several advantages seem obvious based on work that has been performed so far in our laboratory<sup>7-10</sup> and at Commodore Solutions Technology<sup>11,12</sup> (small startup company) on PCB remediation, both neat and in contaminated soils. Extension to PNAs, CAHs and nitrated organics offers these advantages: (1) Solvated electron soil dehalogenations operate at room temperature or lower. (2) Their rate is very rapid. (3) Ammonia solvent breaks down soil into very small easy-to-slurry particles aiding *ex-situ* treatment possibilities. Even difficult-to-manage clay soils are rapidly broken into a fine dispersion in ammonia. (4) Ammonia is easily removed from slurried soil due to its low boiling point and ammonia can be recovered with well know technology. (5) Liquid ammonia can readily penetrate, diffuse and flow through many soil types and strata making it more likely that *in-situ* treatments of contaminated subsurface zones will work as a lower cost remediation technique. This technology may compete then wherever (1) direct ammonia injection is permissible or (2) soil excavation, followed by on-site treatment and return of remediated soil to the excavation, can be practiced.