Annual Report

Engineered Natural Geosorbents for *In Situ* Immobilization of DNAPLs and Heavy Metals

U.S. Department of Energy – Project Number 86797

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9/15/02–6/15/03

A. Research Objective

The overarching goal of the proposed research is to develop a comprehensive data and mechanistic knowledge base with respect to the binding and sequestration reactions of organic DNAPL components and heavy metals with different types of soil matrices. A principal ultimate use of this knowledge and information base will be its application as a platform for designing specifically engineered natural geosorbents (ENGs) capable of *in-situ* long-term immobilization of non-aqueous phase organic liquids and heavy metals at contaminated DOE sites and facilities. The sorption and sequestration performance of ENGs for DNAPLs and heavy metals will be monitored and evaluated by measuring their environmental mobility (desorption and leaching) and bioavailability (toxicity and bioaccumulation) to indicator organisms. Appropriate field tests will be designed to demonstrate the efficacy of *in-situ* immobilization and inactivation of DNAPLs and heavy metals using the engineered natural geosorbents.

B. Research Progress and implications

The report summarizes work after 1 year of a 3-year project. Progresses in three specific areas of investigation are summarized below, and the implications of the results are discussed.

1. Production of engineered natural geosorbents (ENGs)

An innovative technology has been developed for effecting rapid diagenesis-like transformations in geologically young NOM to produce more condensed materials that are capable of effectively sorbing organic contaminants from environmental systems. A number of natural organic materials, i.e., a sorghum moss peat (MI peat), oak leaves, green ash leaves, red maple leaves, pine bark, corn stalk and soybean stalk, were treated using liquid-phase water at superheated temperatures and pressures in a batch reactor under an inert atmosphere (N_2). Conditions for the treatment were optimized in terms of temperature, time, moisture content, catalyst addition, etc. After treatment under various conditions, the materials were removed from the reactor, dried in a hood, then ground and sieved for characterization of their physicochemical properties and their sorption capacities for DNAPL as functions of treatment conditions

2. Characterization of the physicochemical properties of ENGs

Sharp changes in the physicochemical properties of treated peat were observed in terms of surface area, surface morphology, elemental composition and molecular structure. Surface area measurements revealed that peat samples treated at 50°C and 100°C have essentially the same surface area as the original peat ($\sim 0.55 \text{ m}^2/\text{g}$), but an order of magnitude increase then occurred at 150°C, followed by a gradual decline to a level about four-fold greater than that of the untreated peat (i.e., $\sim 2.2 \text{ m}^2/\text{g}$) at 300°C. Surface morphology characterizations using scanning electronic microscopy (SEM) revealed significant changes in surface structure as the peat became more condensed at increased temperature. Elemental composition analyses showed that carbon and nitrogen contents were found to increase linearly, while oxygen and nitrogen contents decreased linearly when temperatures increased from 50°C to 200 or 300°C. The correlation coefficients (R^2) ranged from 0.768 to 0.982. The carbon and oxygen contents were changed much more sharply than those of hydrogen and nitrogen. The atomic ratios of hydrogen to carbon (H/C) and oxygen to carbon (O/C) decreased linearly as temperature increased, with correlation coefficients (R^2) ranging from 0.840 to 0.999. The results are consistent with increasing degrees of geochemical maturation as increasing treatment temperatures.

Fig 1. Effect of treatment temperature on the elemental composition and contents of organic materials (C: carbon, O: oxygen, H: hydrogen and N: nitrogen)

The functional group characters of the treated and untreated materials were examined by fourier transform infrared spectroscopy (FTIR) and solid-state carbon-13 nuclear magnetic resonance (^{13}C -NMR). For example, the FTIR spectra of corn stalk and soybean stalk treated at different temperatures were shown in Fig 2. Bonded -OH groups ($3440\text{-}3400\text{ cm}^{-1}$) significantly increased for soybean stalks and did not change for corn stalk. When treatment temperatures increased from 150 and 200°C , aliphatic C ($2930\text{-}2910\text{ cm}^{-1}$), aromatic C (1704 cm^{-1} , $1630\text{-}1610\text{ cm}^{-1}$), epoxide or phenolic C ($1370\text{-}1270\text{ cm}^{-1}$), and carbohydrate ($1070\text{-}1050\text{ cm}^{-1}$) were remarkably increased for both corn stalks and soybean stalks.

Fig 2. FTIR analyses of corn stalk and soybean stalk samples treated by superheated water at different temperatures

The NMR spectra of MI peat samples showed that alkyl C and aromatic C significantly increased when temperature increased from $50\text{-}250^{\circ}\text{C}$, while carbohydrate C, carboxyl C and carbonyl C decreased (Fig 3). The results of these analyses clearly show diagenetic-like transformation of the treated materials with increasing temperatures of the liquid-water phase used for treatment. Peat samples treated at 250°C had similar ^{13}C -NMR spectra. The hydrophobicity index (HI) and aromaticity index (ArI) were calculated for MI peat samples. HI and ArI increased from 0.831 to 4.19 and from 0.71 to 1.178, respectively, with increasing treatment temperatures

Fig 3. NMR analysis of MI peat at different temperatures

3. Characterization of the sorption and desorption properties of ENG's for TCE, PCE and metals

The sorption/desorption properties of the modified natural organic materials were examined with respect to tetrachloroethylene (PCE) and trichloroethylene (TCE), two major components of DNAPLs that have been extensively found in DOE contaminated sites and facilities. Initial tests to examine the sorption and desorption behaviors were conducted by adding fixed amount of treated and untreated organic materials, i.e., corn stalk, soybean stalks, oak leaves, red maple leaves, green ash leaves and pine bark, to aqueous solutions containing PCE (5000 ppb) at room temperatures for few days. After completion of the sorption steps, the organic material samples were placed in fresh water solution to examine the extent to which the sorbed PCE was then desorbed. As illustrated in Fig 4, significantly greater amount of the PCE was sorbed by treated samples than by untreated materials. Sorption capacities of pine bark, corn stalk and soybean stalk were increased up to 13.5 times after they were treated with superheated water at 200°C. Desorption was greatly decreased for treated materials.

Fig 4. Sorption of PCE by treated and untreated organic materials

Complete isotherms for sorption and desorption of TCE by MI peat samples treated at temperatures ranging from 50°C to 300°C for five hrs with 50% water content and an N₂ atmosphere were determined. The Freundlich model given below was used for analysis of the equilibrium sorption and desorption data.

$$q_e = K_F C_e^n \quad (1)$$

The terms q_e and C_e in Equation 1 are solid phase and residual solution phase equilibrium concentrations, respectively, K_F is the Freundlich unit-capacity coefficient, and n is a parameter relating to both the relative magnitude and diversity of energies associated with a particular sorption process. The results of the model fits to the sorption and desorption data are shown in Figure 5, and the related model parameters and hysteresis indices (HI) sorption and desorption are summarized in Table 1. Values of K_F can be observed to increase with increasing treatment temperature for both sorption and desorption. The decreasing n values with increasing temperatures for both the sorption and desorption indicate increased isotherm nonlinearity with increased temperatures of treatment. There are strong correlations between values of K_F and n and treatment temperatures and atomic ratios of oxygen and carbon (O/C) with correlation coefficients (R^2) ranging from 0.841 to 0.983. The K_F values of desorption were much greater than that of sorption, which indicated that there was hysteresis phenomena for its sorption and desorption by the peat samples. Its HI decreased with increasing treatment temperatures.

The sorption and desorption isotherms of PCE by treated MI peat were also determined. Their sorption capacities for PCE were also increased with increasing treatment temperatures.

Table 1. Freundlich parameters of Michigan peat treated at different temperatures for TCE

Peat	Sorption			Desorption			Hysteresis Index
	K_F	n	R^2	K_F	n	R^2	C_e (100ppb)
Raw	0.229	0.887	0.993	0.591	0.959	0.994	2.600
100°C	0.663	0.871	0.995	1.578	0.877	0.976	1.603
150°C	1.095	0.829	0.992	3.255	0.823	0.977	1.893
200°C	1.202	0.782	0.996	4.173	0.768	0.967	1.709
250°C	2.086	0.768	0.981	6.190	0.732	0.976	1.514
300°C	1.857	0.792	0.996	5.991	0.725	0.990	1.370

Fig 5. Isotherms for sorption (A) and desorption (B) of TCE by MI peat treated at different temperatures

The sorption and desorption of ENG for heavy metals were also measured. MI peat was found to have very strong sorption capacity for cadmium (Cd^{2+}) and lead (Pb^{2+}). For example, 99.4% of lead was sorbed from aqueous solution at 100 ($\mu\text{g}/\text{ml}$) with solid:water ratio of 1:400 by raw peat and only 0.26% of sorbed lead desorbed from peat. Its sorption and desorption for lead did not significantly change for peat samples treated at 100°C to 200°C, then its sorption significantly decreased and its desorption remarkably increased for peat treated at 250°C and 300°C. Similar results were found for their sorption and desorption for cadmium.

4. Implications of results

Chlorinated aliphatic hydrocarbon DNAPLs and heavy metals remain among the most difficult contaminants to remediate. The *in-situ* irreversible immobilization and inactivation of DNAPLs and heavy metals proposed by using ENGs to sequester them indefinitely is expected to provide a cost-effective and non-intrusive solution to these difficult remediation problems. These ENG originate as natural organic materials, and will become incorporated into components of soil or sediment at contaminated sites through natural humification processes. They are therefore expected to be environmentally benign and effectively eliminate production of secondary wastes and the necessity of treatment/disposal off-site. In addition to having tailored sequestration properties, the engineered geosorbents can be designed to improve environmental conditions for the growth of indigenous microorganisms by providing nutrients/substrates and by reducing the toxicities of contaminants at high concentrations. This should lead to enhanced ongoing natural attenuation and eventual complete detoxification of contaminated sites. The rigorous scientific approach we will take to development of fundamental sequestration relationships in the proposed research should further lead to discovery of related methods for other important contaminants (e.g., polycyclic aromatic hydrocarbons, energetic compounds such as TNT, RDX, etc., pesticides, etc.) commonly present at DOE and other federally owned energy and defense related facilities.

C. Future Research Plans

The three specific studies and experiments described below are planned for the next budget period.

- 1). Complete characterization of the physicochemical and sorption and desorption properties of modified natural organic mater and other soil organic matter with respect to DNAPL compounds and heavy metals.
- 2). Initiate aging experiments for DNAPLs and heavy metals in clean soils with and without the selected ENGs. elucidate the effects of biological treatments of natural organic matter on the physicochemical properties and structures, and their potential applications of these materials for reducing the environmental mobility and bioavailability of organic contaminants in soil and water systems.
- 3). Monitor and evaluate sorption and sequestration performance of ENG in contaminated soils by measuring their environmental mobility (aqueous desorption with superheated water extraction technology and leaching with columns) and bioavailability (toxicities or bioaccumulation by selected plants and earthworms).

D. Publication

One manuscript is in preparation.

- 1) Effect of superheated water treatment on physicochemical properties of modified natural organic matter and its sorption capacity for trichloroethylene and tetrachloroethylene.

E. Project-Generated Resources

A patent disclosure on the methods for generating engineered natural organic matter is being filed.