

# THE ION EXCHANGE PROPERTIES OF LOW RANK COALS ON ACTINIDES AND OTHER HEAVY METALS

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## ABSTRACT

The removal of heavy metal and low-level radioactive wastes from the environment and their subsequent immobilization in an appropriate repository is one of the major environmental challenges facing our nation. The scope and magnitude of the contamination at many DOE and Superfund sites are such that successful remediation will require the development of new, inexpensive technologies which remove, in an environmentally acceptable manner, the heavy metal and radioactive wastes from contaminated soil and water. In this paper, we will present the preliminary data on the viability of using low rank coals or lignites as a novel, inexpensive material to remove actinides and other metals from the aqueous system, and the effects of high radiation on ion-exchange properties of lignites.

## INTRODUCTION

After more than a half a century of nuclear processing activities by DOE and its predecessors, a wide range of wastes and environmental problems exists at more than 100 contaminated installations in 36 states and territories.<sup>(1)</sup> Uncontained hazardous and radioactive contaminations in soil and ground water exist throughout the DOE complex. The calls for developing cost-effective technologies to remove radioactive and toxic metal contaminants from the waste processing streams and ground water, and to reduce secondary waste volumes are the top priority for environmental restoration at the DOE sites.

In groundwater, the most common binary contaminant found in the DOE sites is a mixture of radionuclides, metals, and chlorinated hydrocarbons. The most important metal contaminants identified are lead, chromium, arsenic and zinc; radionuclide contaminants are tritium, uranium, strontium, plutonium, cesium, cobalt, technetium, and iodine.<sup>(2)</sup> At the Waste Treatment Facility at Los Alamos National Laboratory (LANL) and Rocky Flat Plant (RFP), the principle metal contaminants found in these processing streams are plutonium (Pu) and americium (Am). Waste water streams generated from the research operations, reactors, and radiochemical production facilities such as Savannah River Site, Oak Ridge Y-12 Plant, Fernald Plants, and Hanford Site contain a wide spectrum of radionuclides (e.g., strontium, cesium, technetium, nickel, uranium, thorium, and radium), heavy metals, reactive chemicals, and organic solvents.<sup>(1)</sup>

Clearly the scope and magnitude of the contaminations at various DOE sites require the development of new, inexpensive technologies which would remove, in an environmentally acceptable manner, the heavy metal and radioactive wastes from contaminated soil and water. Conventional treatments of radioactive waste water at the DOE sites are the precipitation methods, which generate large volumes of secondary radioactive sludge waste. The other common technologies for removal of heavy metals from ground water and waste water are ion exchange resin based processes; however, these commercial resins are usually very costly (> \$10/lb) and generate secondary acid waste from the regeneration process.

In the past few years, the University of Kentucky Center for Applied Energy Research (CAER) and Department of Chemistry have developed a system based on the unique ion exchange properties of low rank coals for the treatment of large volumes of water containing low to moderate levels of metal contaminations.<sup>(3),(4),(5)</sup> Because of the cationic selectivity of lignites

on a high charge density metal, a collaborative effort between the University of Kentucky and Inorganic Elemental Analysis group (CST-8) at LANL will attempt to address the needs of DOE environmental cleanup of actinides and other heavy metals from the aqueous system, and reduce the generation of secondary sludge waste from the waste water treatment process. Our goals are (1) to develop a novel, inexpensive material to remove actinides (Pu, Np, Am, and U) and heavy metals from the waste water streams and ground waters, (2) to understand the ion exchange mechanism of actinides with low rank coals, and (3) to study the effect of radiation on ion exchange properties of lignites.

#### ION-EXCHANGE PROPERTIES OF LIGNITES

Low rank coals, brown coals or lignites are characterized by low specific energy, high oxygen and moisture contents and poor internal strength (the latter excludes underground winning of low rank coals). The high moisture content of the coal retards efficient combustion and must be removed by energy consuming processes prior to combustion. An economical use of brown coal for power generation is feasible only when the combustion process is located close to the coal supply, minimizing the amount of transport required between coal source and power station. The high oxygen contents of low rank coal does however impart one unique property to these coals, that of the ability to remove cations from solution via ion exchange with carboxylic acid and phenolic hydroxyl functional groups on the coal surface. These functional groups undergo dissociation in solution to form a negatively charged site upon the coal surface which is subsequently capable of complexing cationic species from solution to form a stabilized coal-metal structure. The dominant functional group responsible for the ion exchange process has been shown to be the carboxylic acid group. These weak acid sites are virtually completely dissociated at solution pH's greater than 4, and would therefore be ideal for the treatment of most natural water samples which routinely display pH values between 4 and 9. The coal however, would not be suitable for treating many industrial waste streams which have pH values often less than 1. Slight adjustment of pH to the waste streams may be required.

Table I gives the typical cation exchange capacities of various North American lignites. The cation exchange capacities of these coals are considerable lower than those measured for commercially available synthetic ion exchange resins (~ 0.4-1.0 meq/g c.f. 7-10 meq/g for commercial resins) however the lower cost of the coal (~ \$10/ton) compared to the commercial resins (~\$10/lb) makes the cost per unit volume of solution treated significantly lower for the coal based process. Table II shows the calculated cost per liter for both a brown coal and synthetic resin based process treating several different 100 ppm solutions. The processing costs listed in Table II show that the lignite based process is cheaper than a resin based system by a factor of 170, although the total mass of adsorbent used in the coal based process is 18 times that of the resin. However, for the proposed solutions to be treated, e.g. groundwater containing low to moderate levels of contamination, processing costs are envisaged to be the main criteria in determining which process would be used, and would therefore favor the implementation of a coal based system.

TABLE I. Cation Exchange Capacities (meq/g) measured for North American Lignites (1000 ppm solution, 5 g coal/100 mL solution)

Metal	West Kentucky	North Dakota	East Texas
Cd	.35	.38	.37
Pb	.20	.22	.21
U	.16	.17	.17
Hg	-	.22	

TABLE II. Cost per Liter (cents) to treat 100 ppm Solution of Divalent Metal. Using Brown Coal and Resin Based Systems

Metal	Brown Coal @ \$10/ton 0.4 meq.g <sup>-1</sup> .	Ion Exchange Resin @ \$30/kg 7.0 meq.g <sup>-1</sup> .
Cu <sup>2+</sup>	7.88 x 10 <sup>-3</sup>	1.351
Cd <sup>2+</sup>	4.44 x 10 <sup>-3</sup>	0.763
Hg <sup>2+</sup>	2.49 x 10 <sup>-3</sup>	0.427
U <sup>2+</sup>	2.10 x 10 <sup>-3</sup>	0.360

## APPROACH

A series of standard adsorption experiments, principally in batch mode, will be conducted on the Western Kentucky lignites with solutions containing actinides (e.g.,  $^{239}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{237}\text{Np}$ , and  $^{234}\text{U}$ ). Some of the key variables that are known to effect lignite exchange capacity, which will be investigated as initial part of the study include:

- Cation exchange capacity as a function of solution pH.
- Cation competition effects.
- Effect of multiple low loading contacts compared to single high loading contacts.

Quantitation of radionuclide adsorption will be performed using a combination of liquid scintillation and alpha spectroscopy. The experiment will be conducted in a wide range of radioactivity (from several hundred pCi/L to mCi/L level) in order to simulate the radioactive contaminants present in the ground water to the waste processing streams.

In addition to adsorption study, a sample of Western Kentucky lignites is currently exposed to a ~ 2.5 rem per hour gamma-radiation source (radiation dose = ~2.5 rads per hour). We plan to expose this sample to the radiation source with several thousand rads (> 2 months) and examine the structure of functional groups in the lignites after irradiation. This will give us some opportunities to compare the ion exchange capacities of lignites before and after exposing to relatively high radiation field.

## EXPECTED RESULTS

The analytical results from the proposed experiment are not available at the time of publication. From the previous work,<sup>(3),(4),(5)</sup> a single 5% loading w/v (2.5 grams of coal dry weight per 50 mL of solution) of Western Kentucky and East Texas lignite removed greater than 99% of the uranium from a 1000 ppm uranium (uranyl nitrate) solution. We anticipate that the other highly charged actinide species (Pu, Am, Np) will interact with lignites similar to uranium in the aqueous system.

## CONCLUSION

The success of developing a system, which utilizes low-rank coals as an ion-exchange media for removals of radionuclides and heavy metals in environmental cleanup and waste water treatment, would dramatically reduce the cost of expensive environmental remediation and industrial waste stream treatments.

## REFERENCES

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