



## **WATER RESOURCES RESEARCH GRANT PROPOSAL**

**Title:** Decontamination of Acid Mine Drainage by Treatment with Solid Humic Acid

**Focus Categories:** TRT, NPPWW

**Keywords:** Humic Acid, Metals, Decontamination, Adsorption, Mine Water, Acidity, Column Elution

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**FY 2000 Federal Funds:** \$15,000

**FY 2000 Non-Federal Funds:** \$30,263

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**Congressional District:** First

### **Statement of Critical Regional or State Water Problems**

Large scale mining operations in the Intermountain West have had a widespread impact on the regional watershed since last century. Acid mine drainage (AMD), especially, has adversely affected the water the region not only implicates active mines, but also the tailings of those that have ceased production. In Northern Idaho, the Kellogg-Wallace area is a case in point, involving metal leaching into the St. Joe and supply through the mobilization of toxic heavy metals. The ecological damage that continues to be done in Ceour d'Alene Rivers, and metal sludge deposition in Lake Ceour d'Alene. In Western Montana, the Berkeley Pit near Butte is the embodiment of a mine water pollution scenario, with zinc and copper contamination ca. 5000 times greater than the state standard, and iron levels about 1000 times higher. Remediation strategies in all cases are bedeviled by both the scale of the problem and the acidity (pH ~2) of the medium. This latter circumstance often leads to degradation of extraction agents, adding to the cost of treatment.

### **Statement of Results or Benefits**

Decontamination of acidic waters with humic materials, especially humic acid (HA), has several attractive features. HA is a natural substance with remarkable complexing abilities for heavy metals. It does not dissolve in acids and, despite its name, buffers aqueous solutions at near-neutral conditions. Its use in the past has been hampered by limited availability, although HA is one of the most abundant organic materials on earth. Being distributed throughout soil and water, it generally required extensive extraction for large scale isolation. However, a crude leonardite humic acid (LHA, a mined material),

with an HA content of 70-80%, has become available in bulk and has shown an excellent affinity for metals. Development of this crude LHA as a decontaminant for AMD offers the benefit of effectiveness at low cost. Moreover, it is a material that need not be reconstituted after use, and has virtually no pollution potential of its own.

### **Nature, Scope, and Objective of the Research**

Humic acids (HAs) are a major depository of carbon in soil and natural waters. They interact extensively with both metals and organics, and are among the prime transport agents in surface and ground water<sup>1,2</sup>. These properties leading to this also make HAs amenable for use as extractants in water decontamination. Some processes based on this concept have been published, but they utilized either alkali-extracted HAs<sup>3</sup>, or a manufactured product<sup>4</sup>. This adds expense and complexity to the procedures, making them less attractive for routine use.

In our laboratory we have recently shown that a crude HA material, found in several locations extending from British Columbia through Wyoming and North Dakota into New Mexico, has excellent metal extraction properties<sup>5</sup>. The material in question, crude leonardite HA (LHA), is associated with lignite deposits and is available in vast quantities. Its present use is limited to soil structure improvement, for which it is spread on the land and worked into the top soil. A quantity of LHA was made available to us by an agricultural supply firm in Kennewick, WA, from whom we learned that the material as delivered (0.1 - 0.6 mm particle diameter) had been subjected to minimal milling only<sup>6</sup>. We have shown<sup>5</sup> that the material can be used as a solid extractant for simulated acidic waste solutions containing  $Pb^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Sr^{2+}$ ,  $Cd^{2+}$ ,  $As^{3+}$ ,  $Ag^+$ , and  $Mg^{2+}$ . Typical conditional stability constants for metal-LHA complexes were 4.6 -5.5 (log  $K_o$  values). Column capacities for single solutes were in the range 0.15 (Ag) - 2.22 (Pb) mg metal/g LHA. For mixed solutes, capacities were in the  $1.2 \times 10^{-3}$  to  $1.1 \times 10^{-2}$  mmolmetal/g LHA range. Extraction efficiencies were highest for Pb, Cu, and Sr, and lowest for Mg, which is fortunate because magnesium removal is not likely to be a priority.

It has become clear that LHA can be developed as a practical and inexpensive metal extractant for water purification. Solution acidity, which is a problem for most other materials, is actually an enabling factor for LHA. Its solubility decreases with pH, and is very low at pH 2. This is *a priori* desirable, both from a standpoint of extractant preservation and eventual water purity. The data presently in hand were obtained with very small quantities of the relevant materials and e.g. 1.66 g LHA was used for dry packing the extraction columns and with simulated waste solutions. It is necessary at this stage to move on to somewhat larger scale operations (although still bench top) and real acid mine drainage. The two salient points that will be addressed in the proposed research are metal/acidity removal (decontamination) and disposal/reclamation of contaminants.

## Methods, Procedures, and Facilities

(a) *Decontamination.* The density of LHA is  $0.78 \text{ g/cm}^3$ , so the material floats on water. This is of course impractical for extraction purposes, and we have in the past mixed the material with sea sand at a 1:2 ratio to prevent packings from becoming unstable when open columns and gravity flow were used. The sand also appeared to improve the wetting characteristics of the mixture. As noted above, however, only small quantities of extractant were used, with packing heights of ca. 4 cm in 2-cm diameter columns. This expedited the elution process, but clearly did not establish a functional procedure for larger systems. While no pilot scale operation is planned for the proposed work, the practical aspects of handling larger columns and elution volumes will be investigated. The work will be carried out with glass columns of 50-cm length and 5-cm diameter, which provide the possibility of modest pressurization (i.e. MPLC columns). The optimum formulation of the packing and its introduction into the column for good, even eluent flow will be determined. This may involve alternating zones of sand and LHA, since both eluent channeling and column blockage are problems that will probably have to be contended with. Ideally, gravity flow will be sufficient, but low-level pressurization will also be evaluated. For this, an MPLC system with a peristaltic pump with a 40-psi backpressure capability will be used.

Once good flow characteristics have been achieved, the system capacity for metal extraction will be assessed. This will initially involve simulated acidic waste solutions containing the metals listed above. The column effluent will be analyzed by atomic absorption spectrometry to determine removal efficiencies, both in single- and multiple-pass procedures. Continuous pumping and monitoring will be used to establish efficiency changes as the extractant becomes saturated. After efficiency and saturation characteristics have been determined, a similar series of tests will be run with actual AMD samples obtained from the Bunker Hill waste impoundment at Kellogg, Idaho.

The monitoring described above will also be carried out for eluent pH and effluent clarity. The column feed will initially be at a pH of 2, and while no data exist at this time on buffering associated with elution through this type of column, it is strongly anticipated that the effluent will be much nearer neutrality. This will be determined with a single charge, as well as with continuous elution, in order to evaluate the evolution of the buffer capacity of the column, and the relation (if any) to its metal uptake. At the same time, an eye will be kept on the clarity and color of the effluent. This is relevant in view of possible leaching by LHA, and pertains especially to a brown color that may result from dissolution of traces of fulvic acid (metal leaching will show up in the AA determinations). This color, as well as the possible appearance of particulate matter (turbidity), will be monitored by absorption spectrometry, using a liquid chromatography detector set at 550 nm.

*Disposal/Reclamation.* In most remediation scenarios, decontamination of the polluted medium produces a concentrated form of the contaminant, which must be disposed of as part of the overall process. In the present case, this product consists of solid LHA with an adsorbed metal content that is probably around 0.3% (dry w/w). The spent extractant is of

course wet initially, but it can be air dried after removal from the column. Land filling may be the obvious method of disposal, having the added attraction of the humic material (and the added sand) being of natural origin. On the other hand, reintroduction of the adsorbed contaminants into the environment is likely to be problematic, as is the space requirement of the material in the landfill. Also, in some instances it may be desirable to recover the contaminants.

In the proposed work, this last possibility will be addressed, as far as it involves separation of contaminants from the organic extractant. To this end, the spent LHA will be removed by incineration, leaving only the inorganic materials (mostly as oxides and silicates). To make this a practical proposition, at least part of the sand may have to be removed from the packing. If this appears to be necessary, we will determine whether it can be done satisfactorily by mechanical sieving, or may require batch sedimentation. Incineration will be carried out in a furnace, and the ash will be analyzed. It must of course be understood that the original LHA has an ash content of ca. 13% (subject to some variability), and that most of the material recovered will therefore be of mineral origin. However, previous work has shown<sup>5</sup> that the majority of this is Ca (270 ppm) and Mg (140 ppm) based, with smaller amounts of Cu (40 ppm) present. Pb, Sr, Cd, and Zn were not detected in the LHA analyzed. Acid dissolution of ash obtained from both unused and spent LHA will be carried out, and the metal contents will be compared. This will not only provide a double check on the extraction performance of the material, but it will also indicate whether quantitative reclamation of some of the components is feasible. It is unlikely that this would be of interest with regard to economical recovery, but could be of major importance for the removal of radioactive isotopes such as <sup>90</sup>Sr. In all cases, ash production will be measured to determine the volume reduction from the whole extractant. The calorific content of the spent material will be determined by bomb calorimetry, in order to evaluate its potential as a heating fuel.

### **Related Research**

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Some relevant work is listed under item 12 above. As noted there, practical clean-up procedures using HAs are rare because isolation of the material from soil or water is laborious and would tend to make processes un economical. More emphasis has been given in the past to the use of HAs for the removal of hydrophobic contaminants<sup>7-10</sup>, than for metals. The availability of crude LHA has changed that, being available in bulk, but its unrefined nature has raised its own questions. Most pertinent to the research proposed here is our own work, especially the investigation of the use of LHA for decontamination, recently published in *Environmental Science & Technology*<sup>5</sup>. That study dealt with the fundamental issues involved, and essentially served to establish the feasibility of the methodology. The present proposal may be considered a logical, more practical extension of this work, in which the processes will be scaled up somewhat and important details will be addressed. Both the preliminary and proposed work, however, are based on a vast body of literature that deals with the interactions between metals and humic materials<sup>11</sup>.