Activation Technologies
Grand Forks

Grand Forks Activation Technologies
120 North Washington Street
Grand Forks, ND 58203-3451
Phone/Fax (701) 772-1733

PROJECT TITLE:

LOW-COST METALS ADSORBENTS FROM LIGNITE (NDIC-LRC)

GFAT Proposal No. 95-1004

Submitted to:

Ms. Karlene Fine

North Dakota Industrial Commission
600 East Boulevard Avenue
State Capitol, Ground Floor
Bismarck, ND 58505-0001

Applicant:
Grand Forks Activation Technologies
120 North Washington Street
Grand Forks, ND 58203-3451

Principal Investigator: Curtis L. Knudson, Ph.D

Date of Application: 7-1-95

Amount of Request: $27,000

TABLE OF CONTENTS

Page

LOW-COST METALS ADSORBENTS FROM LIGNITE (NDIC-LRC)

1.0 TECHNICAL ABSTRACT

Objective: The objective of this work is to define the feasibility of the commercialization of a process using lignite fines for the removal of contaminant heavy metal cations from large volumes of ground water and to locate interested end-users and potential sponsors.

Expected Results: The expected results are that end-users can be located to utilize the fines produced during the physical cleaning of lignite and investors to develop the technology. Finding a value-added market for water washed, screened fines from the physical cleaning plant (for which the economics are presently being assessed) would make such a plant much more viable.

Duration: The duration of the project will be from August 30, 1995 to May 31, 1996.

Total Project Cost: The amount requested from the North Dakota Industrial Commission is $27,000 which is matched by industrial funds for a total of $54,000.

Source	Investment
Knife River Coal Mining Company	$ 5,000
Grand Forks Activation Tech.	22,000
North Dakota Industrial Commission	27,000
Total	$54,000

Participants: The industrial participants will be the Knife River Coal Mining Company and Grand Forks Activation Technologies (GFAT). GFAT has submitted a proposal to DOE for its share of the funding (see attached). Knife River Coal Mining Company funding is contingent on the North Dakota Industrial Commission's approval of this proposal and GFAT obtaining its funding.

Additional technical participants are Dr. Robert Baldwin who will participate via a subcontract to the Colorado School of Mines and Dr. Chris Lafferty who will participate via a subcontract to the University of Kentucky, Center for Applied Energy Research.

KNIFE RIVER
COAL MINING COMPANY
A Subsidiary of MDU Resources Group, Inc.

1915 North Kavaney Drive
Bismarck, ND 58501-1698
(701) 223-1771
(701) 255-0560 (FAX)

Mine Locations:
Beulah, N D
Gascoyne, N D
Savage, MT

June 26, 1995

Dr. Curtis L. Knudson
Grand Forks Activation Technologies
120 North Washington Street
Grand Forks, ND 58203-3451

Dear Dr. Knudson:

RE: Use of physically cleaned coal as adsorbent for metals removal from contaminated water

Knife River Coal Mining Company will provide funding support to Grand Forks Activation Technologies for this project with funding not to exceed $5,000. The funding support is subject to the following conditions:

1. GFAT will secure approval of the project from the Department of Energy and the proposed funding of $22,000 from DOE.
2. GFAT will secure approval of the project and obtain matching funding from the North Dakota Lignite Research program in an anticipated amount of $27,000 for the project.

Knife River only has an interest at this time in the conceptual proposal indicated as Concept 1 in your June 21, 1995 letter.

Knife River requires that you furnish copies of all applications and information related to this project that is supplied to the Department of Energy or the Lignite Research Program.

Should the project be undertaken Knife River will require written progressive and final reports as the project progresses.

Please consider this letter your authorization to utilize amounts as necessary of the physically cleaned coal from previous projects in tests related to the above stated proposed project.

Sincerely,

Curtis L. Blohm

Curtis L. Blohm
Vice President
Engineering & Environment

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2.0 PROJECT SUMMARY

Knife River Coal Company and Grand Forks Activation Technologies (GFAT) are presently developing an economic assessment for the construction of a demonstration physical cleaning plant at the Beulah Mine. This includes the selection and sizing of processing equipment and vendor testing of selected equipment. In the preliminary design stage, it was determined that the minus 20 mesh material may not be processed. If the plant was designed to produce a 1/2" by 1/4" physically cleaned product then excess minus 1/4" material may be available. If a value added market could be found for fines, the overall economics of a physical cleaning plant would be enhanced.

This proposed work would determine the feasibility of the concept to utilize lignite fines in the removal of metal cations from acidic mine water and other metals contaminated water (see Attachment for further details). Grand Forks Activation Technologies would assemble the information as described in Table 1. This information will be utilized by Pacific Northwest Laboratory (PNL), a DOE National Laboratory managed by Battelle Memorial Institute, to develop a Tech Brief for distribution to potential sponsors. GFAT will develop a presentation and make at least one presentation to prospective sponsors of further work at a meeting sponsored by DOE.

3.0 PROJECT DESCRIPTION (see Attachment)

4.0 SUCCESS MEASUREMENT STANDARDS

The measurements of the success of this work are as follows:

1. Wet screened North Dakota Lignite is found to be a suitable from removing cations from actual waste water.

2. End-users are Identified.

3. Sponsors are located to proceed to demonstration/commercialization.

5.0 BACKGROUND (see Attachment)

6.0 QUALIFICATIONS (see Attachment)

7.0 VALUE TO NORTH DAKOTA

North Dakota's economy stands to gain from this undertaking. If successful, a market would be found for washed, classified lignite fines. This would create, what could be, a very large market for fines which are not desirable as combustion fuel.

8.0 MANAGEMENT

The management of this work will be the responsibility of the Project Manager/Principal Investigator, Curtis L. Knudson of Grand Forks Activation Technologies. He will be responsible to maintain close contact with the co-industrial partner, Curtis Blohm of the Knife River Coal Mining Company, and Clifford Porter of the Lignite Research Council to inform them of research results and any changes in work that may be necessary.

Dr. Knudson will be responsible for collecting, and assembling data and information from GFAT, Dr. Baldwin, and Dr. Lafferty into the required reports. This is readily accomplished by fax or documents attached to E-Mail. These methods were used to obtain their contributions to the proposal.

9.0 TIMETABLE

The timetable to complete the tasks and reports is listed as follows:

Project Area	Completion Date
Project Initiation	Aug 30, 1995
Task 1,2,3: Experimentation	Dec 31, 1995
Procurement of water Samples	
Lignite Preparation/Acid Neutralization	
Lignite Ion Exchange Tests	
Task 4: Process Economics and Reporting	
Project Report (Table 1)	Jan 8, 1996
Presentations	to be Determined
Project Report to NDIC-LRC	May 31, 1996

10.0 BUDGET

A. PERSONNEL	$/hour	Hours	Wage	Fringe 16.78%	TOTALS
C.Knudson	$32.00	140	$4,480	$752	$5,232
M.Pedersen	$14.00	320	4,480	752	5,232
Lab Asst.	$6.50	100	650	109	759
TOTALS		560	$9,610	$1,613	$11,223

B. CONSULTANTS		0
C. LEASED EQUIPMENT		0
D. PURCHASED EQUIPMENT		0
E. TRAVEL		
two trips by air to Denver, CO	2,030	
TOTAL TRAVEL		2,030
F. OTHER DIRECT COSTS		
1. Materials, Supplies, and Shipping	1,000	
2. CSM Subcontract	9,000	
3. CAER Subcontract	22,000	
4. Other, phone, etc	386	
TOTAL OTHER DIRECT COSTS....................		32,386
G. TOTAL DIRECT COSTS		45,639
H. INDIRECT COSTS 18.32%		8,361
I. TOTAL COSTS		54,000
J. FEE OR PROFIT (waived due to DOE requirements)..........		0
TOTAL AMOUNT OF THIS PROJECT		$54,000

The proposed work will be done on a fixed-price basis. The distribution of costs between budget categories (labor, travel, supplies, equipment, subcontracts) is for planning purposes only. The principal investigator may, as dictated by the needs of the work, reallocate the budget among approved items or use the funds for other items directly related to the project, subject only to staying within the total dollars authorized for the overall program. Financial reporting will be at the total project level.

11.0 MATCHING FUNDS

GFAT from DOE (1)	$22,000
GFAT from KRCMC (2)	5,000
NDIC-LRC to GFAT (3)	27,000
TOTAL PROJECT COST	$54,000

(1) Proposal submitted June 29, 1995. Starting date August 30, 1995, if approved for funding.
(2) Approved by Knife River Coal Mining Company contingent on funding approval by DOE and NDIC-LRC.
(3) Requested funds from the North Dakota Industrial Commission.

12.0 TAX LIABILITY

Grand Forks Activation Technologies (GFAT), Dr. Curtis L. Knudson, and none of his activities/involvements have any outstanding tax liabilities owed to the city of Grand Forks, the states of North Dakota, Oregon, or other state governments, or the United States of America or any other entities.

TABLE 1

REPORT REQUIREMENTS/DELIVERABLES
(excerpted from DOE proposal request)

The standard format for technical reports (presented below) allows PNL to assist in preparing "tech briefs" which are a promotional and information tool for each of the concepts. These will receive wide distribution and can be used throughout the life of the concept. The innovator will be required to provide a report (approximately 10 pages) containing the following content with regards to his/her concept:

Introduction. The introduction will describe the problem/need being addressed and a brief "state of the art" review of competing technology.

Description of the Concept. This section describes the concept, its potential for technical success, and its current development status. An illustration of the concept should be included.

Economics and Market Potential. This section shall include a discussion of the economics of a target entry market and a list of other market sectors where the concept may be applied.

Key Experimental Results. A large amount of data are not expected and experimental results are frequently not impressive at this stage of development, but honest reporting increases an investors' confidence in the experimenter. A few key data points are more important than large quantities of data at this stage.

Future Development Needs. This section shall address both the immediate steps and additional linger term steps that need to be taken to implement widespread use. The target market identified earlier will provide focus to this section.

Contacts. This will allow an interested company or investor to contact the investigator for more detailed information.

PNL will edit the reports to fit its format and style. For ease of editing, the material shall be provided on a PC or PC-compatible disk (Word Perfect or ASCII). The text shall be single-spaced, block style (this page is an example). Send original illustration/s so that clear camera ready copies can be prepared; photocopies cannot be used. The originals can be returned if requested. Photographs or photocopies of photographs will not be accepted as they cannot be prepared in the time frame PNL has for publication of these reports.

The report is due January 8, 1996. This date is extremely important to allow PNL time to prepare and print the tech briefs.

<u>Final Report:</u> The tech brief and a copy of the presentation will serve as the final report for this project.

ATTACHMENT

Solicitation:

INNOVATIVE CONCEPTS FOR TRANSPORTATION AND ENVIRONMENT

Solicitation No. DE-PS48-95R810531

Part A - DECLARATION OF FOCUS AREA:

Low-cost Adsorbents for Recovering Metals from Waste Streams containing Low-to-medium levels of Metals.

Concept Title: LOW-COST METALS ADSORBENTS FROM LIGNITE

Submitted to:

Dennis D. Maez, Contracting Officer
DOE - Denver Support Office
Golden, CO 80401-2266
(303) 231-5750 ext.110

Submitted by:

Grand Forks Activation Technologies
120 North Washington Street
Grand Forks, North Dakota 58203-3451
(701) 772-1733 (voice or fax)

Project Manager:	Dr. Curtis L. Knudson
co-Principal Investigators:	Dr. Curtis L. Knudson Grand Forks Activation Technologies Dr. Robert Baldwin Colorado School of Mines Dr. Chris Lafferty University of Kentucky

Joint Funding Investors

North Dakota Lignite Research Council*
Knife River Coal Mining Company**

*Contingent on approval of the LRC and NDIC.
**Approved, contingent on funding by all agencies.

PART B - TABLE OF CONTENTS:

PART D - TECHNICAL NARRATIVE:

Subpart 1: Abstract

The concept covered in this proposal is directed towards determining the feasibility of commercializing a process using low-cost lignite and/or waste calcium carbonate for the removal and subsequent immobilization/recovery of contaminant heavy metal species from large volumes of groundwater and other aqueous systems containing low to moderate levels of contamination ($<$1,000 ppm). While conventional treatment technologies would be technically suitable for such applications, the processing cost involved would preclude all but the most environmentally hazardous scenarios where cost is of secondary importance. It is therefore apparent that any successful technology developed to treat such a situation would have to be extremely cost effective and have very low overall operating costs.

Moderately acidic ($>$pH 4) metals contaminated water can be treated with only coal to immobilize metal ions. However, "acid mine drainage" is at low pH due to the presence of sulfuric acids formed by the oxidation of metallic sulfur compounds and also contains metal cations in environmentally significant concentrations. Calcium carbonate is known to neutralize sulfuric acid while precipitating calcium sulfate reducing the total ionic strength of the solution. Low-rank coals, especially high-sodium lignites, are known to act as weak cation exchange material and to immobilize metals out of solution at a pH greater than 4. The concept of this proposal is to utilize waste, calcium carbonate rich, landfill sludge from water treatment as well as fines and reject fines from a lignite physical cleaning plant to clean-up acidic mine water. The evaluation of the feasibility of the this concept can be accomplished by the collaborative efforts of Grand Forks Activation Technologies, University of Kentucky, and Colorado School of Mines personnel with funding support provided by this proposal, the North Dakota Lignite Research Council, and Knife River Coal Mining company. A limited number of tests will be performed using real, available contaminated water and feedstocks to enable the development of an economic assessment of the concept. The information will be assembled and presented to prospective groups interested in further development or application of the concept.

Subpart 2: Qualifications

Dr. Curtis L. Knudson
Sole Proprietor, Grand Forks Activation Technologies

Dr. Curtis L. Knudson will be the Project Manager and the primary co-Principal Investigator of this effort. He received a Ph.D. in analytical Chemistry from the University of North Dakota in 1975 and was employed at the Energy Center in Grand Forks, North Dakota, to develop the CO-Steam Liquefaction Project. This facility was defederalized and is presently a non-profit, contract research laboratory (Energy & Environmental Research Center) affiliated with the University of North Dakota (UND-EERC). Through the years, Dr. Knudson has been a Project Manager responsible for the administration of over $1 million per year in research funding and 3 to 20 research professionals. On August 15, 1994, he started Grand Forks Activation Technologies (GFAT) with the aid of U.S. DOE SBIR Grant# DE-FG02-94ER81773.A000. Since initiation, GFAT has been awarded two additional contracts by the North Dakota Industrial Commission (NDIC) through the Lignite Research Council (LRC) with financial support of the Knife River Coal Mining Company (KRCMC) totaling $202,649 for the research and development of an enhanced, physically cleaned lignite fuel. Dr. Knudson remains employed at UND-EERC (49%) as a consultant on projects he has been involved in and is the Principal Investigator of an on-going grant with U.S. Department of Agriculture funded at over $200,000/year since 1988. As an EERC employee, he has been the Principal Investigator or participated in a number of recent projects related to the proposed concept **(1,2,3)**.

Dr. Knudson is listed as the inventor or one of the inventors on 6 patents in the areas of coal liquefaction (#4,337,142 and #4,846,963), oil agglomeration of lignite (#5,032,146 and #5,162,050), and the production of leonardite char adsorbents (#5,254,521 and #5,405,593 and was the scientist (in 5 of the patents) that worked with the patent attorneys. Dr. Knudson has published or presented numerous papers in his years of coal research, most recent are contract final reports **(1,2,4)**. Recent contracts have dealt with reducing sulfur emissions and altering ash fusion properties of lignite using ion exchange treatment and physical cleaning. Clifford Porter (701-258-7117) has followed this work for the North Dakota Lignite Research Council and Curtis Blohm (701-223-1771) has followed the work for the Knife River Coal Mining Company.

Dr. Knudson's Ph.D. work was performed using cation exchange resins to concentrate and analyze chromium and mercury ions from water and resulted in three peer reviewed publications **(5,6,7)**.

Dr. Robert Baldwin
Colorado School of Mines

Dr. Robert Baldwin will be a co-Principal Investigator and Task Leader of Task 1. He received his Ph.D. in Chemical and Petroleum Refining Engineering from the Colorado School of Mines in 1975. He is presently the Head of Department and a Professor at the

Colorado School of Mines and has been the Principal Investigator on research contracts totaling over $3.5 million in sponsored research since 1975. He is presently the Principal Investigator of contracts with U.S. DOE, Procter and Gamble Foundation, and ARCO, Inc. The ARCO project (funded at $80,000 for 2 years) entitled "Research on Remediation of Acid Mine Drainage" is entirely pertinent to the development of this proposed concept. Via a subcontract to the Colorado School of Mines, Dr. Baldwin will participate in this project providing mine water occurrence information as well as samples for evaluating the proposed concept.

Dr. Chris Lafferty
Univ. of Kentucky, Center for Applied Energy Research (CAER)

Dr. Chris Lafferty will be a co-Principal Investigator and Task Leader of Task 3. He obtained a Ph.D. in chemistry from the University of Strathclyde in Glasgow, Scotland in 1992. He is presently employed as a Research Chemist at the Center of Applied Energy Research (CAER), University of Kentucky, Lexington. He has published a number of papers in refereed journals in the area of removing metals from water using low rank coals. Six papers he has co-authored are listed in the references of this proposal **(8,9,10,11,12,13)**. Via subcontract to GFAT, the excellent, demonstrated capabilities of CAER will be utilized to perform metals ion exchange tests on lignite samples to determine their properties.

Subpart 3. Specific Concept Description

Technical Discussion

Although each element of this concept is not unique the overall concept integrating the elements is original. Elements of the concept are as follows:

- Assembling a technical team and obtaining financial support
- Determining locations and obtaining metals contaminated water
- Source of feedstocks
  - lignite as an ion exchange medium and preparation methods
  - finely divided calcium carbonate for acid neutralization
- Testing of feedstocks with mine water
- Treatment method for ponds or run-off
  - batch or batch settling
  - mix tanks followed by settle tanks
  - bed or column
- Disposal and/or recycling of spent feedstocks
- Economic considerations
  - Cost of feedstocks
  - transportation of feedstocks and costs
  - water treatment methods, equipment, and operating costs.
- Demonstration testing
- Commercialization

The testing in this proposal will provide information for use in designing various treatment methods for acidic mine water whether in a pond or in a run-off situation. For instance in a pond application Ca-sludge could be sprayed on the surface and allowed to settle neutralizing acid (batch-settle) followed by spraying on lignite which would then settle collecting metal contaminants. The settled material would be vacuumed from the bottom and collected using a centrifuge or by filtration. For run-off streams, passing the water through a bed, column, or slit trench containing granulated, high sodium lignite would both neutralize the water and remove metal ions. Considerations of other elements are presented in the following sections.

Background/State of Art

Mining activities during the last century have left a legacy of environmental problems which are now the focus of a great deal of research (**14,15**). Among the more serious of these problems is that of acid mine drainage. Mining operations in hard rock formations have the net effect of creating porosity and permeability for groundwater flow. Exposure of sulfide minerals to air by mining operations facilitates formation of water-soluble inorganic sulfates, which in turn are transported from the mines as dissolved and/or suspended solids. The pH of these water streams tends to be relatively low due to the presence of sulfates (*in situ* formation of sulfuric acid). Hence, many abandoned mines have become significant sources for pollution due to the phenomenon of "acid mine drainage". Levels of metals in these streams varies from zero to several thousand parts per million. Particularly troublesome metals that can be mobilized by these processes include chromium, cadmium, mercury, lead, zinc, and arsenic.

Examples of sites where these problems exist are abundant throughout the United States. Some of the more imposing problem areas are associated with large open-cast mines where enormous volumes of highly contaminated water are present. As one example, the Berkeley Pit mine outside of Butte Montana currently contains over $1X10^9$ gallons of water with pH of 2, and with high concentrations of environmentally hazardous metals. The mine is currently filling with water at a rate of approximately $1X10^6$ gallons per day due to groundwater flow. The need clearly exists for cost effective remediation methods.

Low-rank coals (especially lignites and leonardites) are characterized by low specific energy, as well as high oxygen and moisture contents. The high moisture content of the lignites retards efficient combustion and must be removed by energy consuming processes prior to combustion. However, a large amount of lignites are economically used for mine-mouth power generation. The high oxygen content of low-rank coal does impart, however, a unique property - the ability to remove cations from solution via ion exchange with carboxylic acid and phenolic hydroxyl functional groups on the coal surface.

The ion exchange properties of several low-rank coals have been characterized using a range of commercially significant metals including Cu, Ni, Mn, Co, Fe, Zn, Al, Pb, Cd, Hg, Na, Ag, Cr, and U (**8,9,10,11,16**). Recent results from our laboratory (CAER) using North American lignites for the absorption of U, Pb, Cd, and Hg are presented in Table 1. Note that a single 5% loading w/v (2.5 grams of coal dry weight per 50 ml of solution) of both a

Western Kentucky and East Texas lignite removed greater than 99% of the uranium from a 1000 ppm uranium (uranyl nitrate) solution. Moreover, in a recent study of the removal of lead from a process derived wastewater, it was shown that multiple lignite contacts at low mass loadings (4 @ 1% w/v) were capable of reducing lead concentrations from 8 ppm to below 20 ppb. As can be seen from Table 1, typical cation exchange capacities for the lignites investigated were found to be on the order of 0.2 meq/g (dry weight). Although this value is lower than the capacities of commercially available synthetic ion exchange resins, the low cost of the lignites (ca. $10-$20/ton) greatly favor their use as an industrial ion exchange material in large scale remediation projects.

CAER studies on the cationic selectivity of lignites showed that metals with a high charge density are preferentially adsorbed. Moreover, the adsorption selectivity of lignites for a mixed solution of first order transition metals has a selectivity profile increasing with atomic number, peaking at copper and then decreasing (**9**). This selectivity is consistent with the Irving-Williams order and indicates that the functional group involved in the exchange process contains either a nitrogen or oxygen atom (**17**). Analyses of the raw and exchanged coals revealed that a significant amount of the metals removal was a consequence of forming ion exchanged metal carboxylates on the coal surface (**8**).

The importance of coal oxygen content on the resulting cation exchange capacity of coal has been further demonstrated by investigating the ability of three different coals to remove uranium from a 1000 ppm uranium (uranyl nitrate) solution. As can be seen from the results presented in Table 2, a 1% loading of North Dakota Leonardite (dry, ash free oxygen content of 25.4 wt.%) was able to remove 98% of the uranium from solution whereas a similar loading of Illinois Bituminous (dry, ash free oxygen content of 8.3 wt.%) only removed 2.9% of uranium from solution. Again, these results emphasize that a significant portion of the metal removal is an exchange reaction and not simply adsorption on the surface of the coal particles.

In additional studies regarding the ion exchange properties of North American lignite, it was found that pollutants such as phosphates, cyanides, ammonia and phenol, as well as the traditional heavy metals, could be effectively removed from solution (**18**). A large decrease in B.O.D. (**16**) was also measured after coal was used to treat a refinery waste effluent. This remediation activity was associated with ion exchange on carboxylic acid and phenolic functional groups, whilst dissolved organics were removed from solution via a combination of physisorption and biological oxidation.

One of the main factors controlling the extent of metal exchange from solution is the pH of the solution. The pKa values for model coal compounds containing carboxylic acid functionalities are generally in the range of 4.5 to 5.5. Hence, as the equilibrium pH of a lignite/metal solution approaches or exceeds a pH of 4, a large proportion of the carboxylic acid functionalities on the coal surface dissociate, producing a site which is capable of forming a stable complex with the metal cations in solution. Studies on the kinetics of the adsorption of copper from solution by lignites showed that the exchange process is extremely rapid. All exchange is virtually complete after 5 minutes contact in a stirred solution (**8**).

Table 1. Ion Exchange Properties of Selected North American Lignites

Coal	Dry Mass (g)	Metal	Residual Metal (ppm)	Sol. pH	Exchange Capacity (meq/g)
Blank		Hg (Chloride)	1175	4.97	
N. Dakota	2.62		8	6.53	0.22
Blank		Cd (Acetate)	1105	7.11	
N. Dakota	2.52		44	6.56	0.38
West Ky.	2.49		114	4.91	0.35
East Tx.	2.49		77	5.63	0.37
Blank		Pb (Acetate)	1069	5.98	
N. Dakota	2.34		4	6.72	0.22
West Ky.	2.50		5	4.83	0.20
East Tx.	2.48		2	5.75	0.21
Blank		U (Nitrate)	1013	2.53	
N. Dakota	2.50		70	6.04	0.16
West Ky.	2.48		8	4.29	0.17
East Tx.	2.49		5	5.53	0.17

N. Dakota: Beulah Zap Lignite, Mercer Co., North Dakota, West Ky.: Carlisle Co., Kentucky. East Tx.: Atascosa Co., Texas.

Table 2. Effect of Coal Rank on Uranium Ion Exchange Capacity

Coal	Dry, Ash Free Oxygen Content (wt.%)	Dry Mass (g)	Residual U (ppm)	Exchange Capacity (meq/g)
N. Dakota Leonardite	25.4	0.52	21.5	0.72
West Ky. Lignite	21.0	0.53	556	0.28
Illinois Bituminous	8.3	0.55	878	0.02

Coal stirred with 50.0 mL of 905 ppm uranium (uranyl nitrate) solution for 10 min, solution filtered and the supernatant sampled for residual metal analysis.

The ion exchange capacity of low rank coals compares favorably with conventional synthetic ion exchange resins in terms of milli-equivalents of adsorbed metal/unit cost of resin. However, the capacity of low rank coals on a per gram basis of the coal (meq/g) is much lower than that for synthetic resins. Hence a larger, albeit cheaper, mass of coal must be used to achieve the capacity of synthetic resins. A number of chemical modifications to increase the inherent exchange capacity have been reported for low rank coals. Some of the more successful reactions include sulfonation, nitration, and alkalization . These reactions increased the ion exchange capacity of the coals, on average, by a factor of 10.

Physical cleaning of lignite reduces the mineral content of coal (primarily pyrite). In a wet process the coal feed is deslimed and the dense fractions are removed by hydroclyclones, spirals or shaker tables, or froth flotation depending on the particle size range of the feed. Presently, Grand Forks Activation Technologies (GFAT) is working on a project to provide technical data and an engineering evaluation for the production of an enhanced physically cleaned lignite from the Beulah Mine in North Dakota. This includes a contract to Barr Engineering Company for selecting and sizing equipment as well as performing vendor testing of the proposed equipment. This work has/is being co-funded by the Knife River Coal Mining Company and the North Dakota Industrial Commission and a DOE-SBIR grant to GFAT. The economics of this plant would be enhanced if fines could be marketed as a value added product rather being treated as reject material. Lignite that has been water processed and sized would be preferable for water use in water treatment. During the physical cleaning process, rough edges would be removed and narrow particle size ranges could be obtained enabling more uniformity in the product. Tests using physically cleaned fractions of lignite should be more accurate and increase confidence that large quantities of known lignite water treatment material can be obtained. It would be easy at this stage of the design work to provide for the correct screening and cleaning procedures to produce products of different size ranges for use in water treatment.

Metal ions can be removed from environmental water with a pH over 4 using lignite. However, the acidity of the mine water poses a problem when utilizing a weak cation exchange material since metal cations are not appreciably adsorbed if the pH is under 4. It may be possible to neutralize the water by using an excess of a high sodium lignite for both acid neutralization and metals removal. However, this would add additional sodium ions to the water. Sodium ions would also be added if sodium hydroxide were used in neutralization. Calcium oxide (lime or hydrated lime) could be used in neutralization with no increase in sodium content of the water. Calcium hydroxide would also interact with sulfate ions to form relatively insoluble calcium sulfate which would precipitate from solution decreasing the ionic strength of the water. However, calcium oxide is relatively expensive, and calcium carbonate will also neutralize solutions. Dolomite could be used but would first need to be crushed to a fine size since calcium sulfate forming of the surface of large particles would decrease its efficiency. A material which is available is landfill sludge from the treatment of water. City water treatment facilities using lime produce quantities of calcium carbonate sludge which is loaded to dump trucks and disposed of in land fills. For the western states, a better source of calcium may be the sugar beet plants in North Dakota and Minnesota. They have stockpiled spent calcium carbonate on-site and now have hundreds of acre feet of semi-dry material. They also use coal for process heat (1 million tons/year) which is delivered by rail. It may be possible to transport calcium carbonate to the western states in a the same cars reducing transportation costs. The use of a low-value landfill sludge to neutralize acidic mine water is part of the proposed concept.

Collection and disposal of immobilized metal ions on lignite is beyond the scope of this work, however, would need to be addressed in future work. Possibilities are to selectively recover the metals from the lignite through ion exchange and/or combustion and recovery from the ash. Any combustion process would need to be designed to eliminate any air toxics from the flue gas.

Literature References

1. Knudson, C.L., "Multiple-Use Marketing of Lignite," Final Report to the North Dakota Industrial Commission, Lignite Research Council, LRC-XII-43, (**1993**).

2. Knudson, C.L., Young, B.C., and Musich, M.A., "Physical Cleaning of Lignite." Final Report to the North Dakota Industrial Commission, Lignite Research Council, SFY94-XV-53, (**1994**).

3. Musich, M.A., Young, B.C., and Knudson, C.L., "Upgraded North Dakota Lignite-Production of Test Quantities," Final Report to the North Dakota Industrial Commission, Lignite Research Council, LMFS-94-15, (**1994**).

4. Knudson, C.L., Pedersen, M.P., and Gerlach, T.R., "FBC Compliance Coal Production," Final Report to the DOE SBIR Program-1994, DE-FG02-94ER81773.A000, Grand Forks Activation Technologies. (**1995**).

5. Baltisberger, R.J. and Knudson, C.L., "Investigations of Isothiocyanatopentaaquochromium (III) as a Reagent for the Separation and Identification of Nanogram Quantities of Mercury (I), Mercury (II), and Methylmercury (II)," *Anal Chem,* **1975**, *48*: pp. 1402-1406.

6. Baltisberger, R.J. and Knudson, C.L., "The Differentiation of Submicrogram Amounts of Inorganic and Organ-Mercury in Water by Flameless Atomic Adsorption Specrometry," *Anal Chim Acta,* **1974**, *73*: pp. 265-272.

7. Baltisberger, R.J., Knudson, C.L., and Anderson, M.F., "A Study of the Products of the Reaction of Thiocyanate with Chromium (III) Ion Water/Methanol Solvent Mixtures," *Inorg Chem,* **1974**, *13*: pp. 2354-2360.

8. Lafferty, C.J., Robertson, J.D., Hower, J.C., and Verheyen, T.V., "Ion Exchange Properties of Selected North American Low Rank Coals." 1993 Mar 28; *Preprints of Fuel Chem. Div., Am. Chem. Soc.* Denver; (**1993**): *38*: pp. 468-474.

9. Lafferty, C.J. and Hobday, M.D., "The Use of Brown Coal as an Ion Exchange Material, 1. Basic Parameters and the Ion Exchange Mechanism," *Fuel,* **1990**, *69*: p. 78.

10. Lafferty, C.J. and Hobday, M.D., "The Use of Brown Coal as an Ion Exchange Material, 2. Ionic Selectivity and Factors Affecting Utilization," *Fuel,* **1990**, *69*: p. 84.

11. Lafferty, C.J., "A study of the Ion Exchange Properties of Victorian Brown Coals." Applied Science, Royal Melbourne Institute of Technology:**(1988)**.

12. Lafferty, C.J., Schram, W.H., Hower, J.C., and Robertson, J.D., "An Investigation of the Ion Exchange Properties of Selected North American Low Rank Coals." 1993 Sep 12; *7th International Conference on Coal Science,* Banff, Alberta, Canada; **(1993)**: *1*: pp. 461-464.

13. Robertson, J.D., Lafferty, C.J., and Burberry, K., "The use of Low Rank Coals to remove Radioactive and Heavy Metal Wastes from Aqueous Systems." 1993; *Emerging Technologies in Hazardous Waste Management V,* Atlanta, GA; **(1993)**: *2*: p. 623.

14. Weber, W.W., *Physicochemical Processes for Water Quality Control,* Wiley: New York: **(1972)**.

15. Clark, J.W., Viessman, W., Hammer, M.J., *Water Supply and Pollution Control,* Harper-Row: New York: **(1977)**.

16. Altekar, V.A., Shahani, M.J., and Saha, A.K., *Fuel,* **1974**, *53*: p. 29.

17. Irving, H. and Williams, R.P.J., *J Chem Soc,* **1953**, : p. 3192.

18. Fadl, S.M.M., *Diss Abstr Int,* **1977**, *B39(9)*: p. 4881.

19. Paulson, L.E. and Futch, J.R., *Preprints of Fuel Chem. Div.* **(1979)**: *25*: p. 224.

Subpart 4. Concept Merit & Market Potential

Potential for Reducing Energy Consumed or Wasted

Since this concept is aimed at environmental concerns, it does not reduce energy consumption. However, it is likely a concept that minimizes the expenditure of funds and energy to clean-up acidic, metals contaminated mine water. Primary raw materials costs are in lignite preparation and transportation of processed lignite and calcium carbonate. In fact, slurried lignite used in the process could potentially be processed and combusted (under the proper conditions) to recover metals and to produce process heat.

Potential for Minimizing Waste Stream Contaminants

The implementation of this concept has an excellent chance to remove cationic metals contaminants from waste water streams. It utilizes low cost lignite as a weak acid ion exchange material that is readily available close to mining operations. The concept also would potentially use waste calcium carbonate which is available in acre feet quantities. Both feed stocks are available at low cost with transportation likely being the most expensive cost. Lignites have been demonstrated to remove metals if the pH of the solution is above 4 while calcium carbonate is known to neutralize acidic solutions and to precipitate sulfates decreasing the ionic content of the solution. (Any base such as sodium hydroxide would increase the pH but would also increase the salt content of the solution.) While it is true that carbon dioxide would be released during acid neutralization using calcium carbonate, it would be much less than the total carbon dioxide produced during the production of an agent such as calcium oxide produced from dolomite. Also, the calcium carbonate from water treatment is finely divided with a high surface area which will mean it will react rapidly and more to completion. In general, this is a concept to use waste materials (fines from a physical cleaning plant and waste calcium landfill sludge from water treatment) to treat acidic, metals contaminated mine water to produce clean water.

Potential for wide Scale Use

The ion exchange properties of lignites sampled from the Beulah Zap formation in North/South Dakota have been reported by other researchers **(19)** and the proposers **(8,12,13)**. The Beulah lignite displays good ion exchange characteristics due to the high levels of organically associated sodium (sodium carboxylates) naturally present in the coal. Such high levels of sodium are deleterious to the use of these lignites for combustion as it causes premature boiler fouling and slagging. The high organic sodium levels however result in a potentially increased solution pH when the coal is mixed with water, resulting in a greater extent of dissociation of the carboxyl sites and hence an increased ion exchange capacity. However, there are other sources of lignite/leonardite which could be utilized:

> Jackson Group, Texas. Part of the Gulf Coast lignite deposit, samples of this coal have also displayed relatively high ion exchange capacities, again due to the high levels of organic sodium associated with the coal **(8,13)**.

Claiborne Deposit, Kentucky. Also part of the extreme northern member of the Gulf Coast deposit, samples of this lignite are currently being excavated as part of a clay mining operation being carried out in Carlisle County Kentucky, by the Kentucky-Tennessee Clay Company. The KTCC has provided samples in the past to CAER.

Lignite from the Beulah Mine located in North Dakota has been selected for use in this first engineering and economical evaluation of the concept since it presently is being studied in the work presently being performed by GFAT and thus will reduce the cost of developing this proposed concept. Wet landfill sludge can be obtained from numerous water treatment plants. However, sugar beet plants in North Dakota and Minnesota have been stockpiling waste calcium carbonate and have hundreds of acre feet of semidry material. They also burn coal from Montana and return shipment of calcium carbonate in the same rail cars may reduce transportation costs.

Reasons Why Concept should be Funded

The time is right for the proposed integrated concept. The technology has been demonstrated and what is needed is some testing, fine-tuning, and an economic assessment so mining and environmental companies can see the benefits of this concept and join in commercialization. With the development of the concept and preparation and publication of a Tech-Brief the potentials for scale-up are excellent. Cost-share at the demonstration stage is very likely from coal mining companies and state agencies.

Subpart 5. Previous Work of Proposing Organization

Current Stage of Development

This proposal represents the current stage of development of the concept to utilize lignite to remove metal ions from waste water. It brings together talented personnel with varied backgrounds and with the expertise to develop the information required for further development and commercialization.

Knife River Coal Mining Company has committed funding to the project (contingent on this proposal being funded and on obtaining State funding). Also, since this project meets the goals and objectives required to obtain funding from the North Dakota Lignite Research Council, it is likely that additional funding would be obtained to develop the proposed concept (contingent on this proposal being funded).

Physically cleaned lignite produced in prior work funded by KRCMC, DOE-METC, and NDIC is available for use in testing reducing coal preparation cost to this project. GFAT is presently working with KRCMC in the development of a physical cleaning demonstration unit (over 150,000 tons/year). The economics of this plant would increase dramatically if the minus 1/4" material of physically cleaned, sized lignite had a value added market. Drying and briquetting of minus 1/4" material is too expensive except as a premium, smallboiler fuel based on present economic evaluations. However, physically cleaned coal lumps (1/2" x 1/4") can be more easily used as a boiler fuel. The success of this proposed concept could result in the success to this on-going project.

Work from which Proposed Concept Arose

The prior research by Dr. Chris Lafferty at the University of Kentucky combined with processing development studies performed at the University of North Dakota Energy & Environmental Research Center (EERC) and on-going plant design efforts at GFAT is the primary work from which this concept originated.

Previous Technical Progress

The prior work by Dr. Lafferty and others demonstrates that lignites can be used as a weak cation exchange medium to remove metals from water. The on-going work of Dr. Baldwin adds contacts with mining companies as well as chemical engineering expertise. The on-going work of GFAT on the design and potential construction of a physical cleaning plant for lignite adds the potential to have uniform lignite feedstock for ion exchange in large tonnage quantities.

Previous State or Federal Contracts and/or Grants

The development of elements of this concept were initiated by work funded to the EERC with Dr. Knudson as the Principal Investigator and in follow up work to the EERC to produce ton quantities of physically cleaned lignite.

> "Physical Cleaning of Lignite": ($60,000 to EERC); Funded by NDIC-LRC No. SFY-XV-53, KRCMC, and U.S. DOE-METC; P.I.: C.L. Knudson.
>
> "Upgraded North Dakota Lignite -- Production of Test Quantities": ($40,000 to EERC); Funded by NDIC-LRC No. LMFS-94-15, KRCMC, and U.S. DOE-METC; P.I.: M. Musich.

The work has continued through Grand Forks Activation Technologies with support from the North Dakota Industrial Commission, Lignite Research Council (NDIC-LRC) and Knife River Coal Mining Company (KRCMC) as follows:

> "Production of Enhanced Physically Cleaned Lignite": ($100,000 to GFAT); Funded By NDIC-LRC, No. FY95-XVIII-57 and KRCMC; P.I.: C. L. Knudson; Sep 94, on-going.
>
> "Equipment, Engineering & Economic Evaluation for a Lignite Production Facility": ($102,649 to GFAT) NDIC-LRC, No. FY95-XIX-59, KRCMC, and GFAT; P.I.: C.L. Knudson; June 95, on-going.

Prior work performed at CAER has been internally funded:

> "Development of a Novel Coal Based Water Treatment Process": ($40,000, internally funded by CAER); co-P.I.'s: C. Lafferty and J. D. Robertson; Sep 1992 to Present.

The total dollar value invested in this concept by the proposers (GFAT and CAER) is nominally $243,000.

Subpart 6. Work Plan

Work Plan Summary

The work plan integrates the skills and talents of the proposing organizations to provide the best possibility of developing a commercial process. In the development of this concept, Dr. Baldwin will provide initial samples of environmental or mine water to GFAT where acid neutralization testing will be performed. GFAT will provide lignite samples and pH moderated water samples to CAER for testing. Data will be collected at GFAT, combined into an economic evaluation, and assembled into the reports and presentation material.

Task 1. Definition of Potential Sites for Metals Removal

Task Leader: Dr. Robert Baldwin

A listing of potential sites for remediation will be developed as well as available analyses of the water for remediation. At least, one representative sample will be selected, procured, and provided to GFAT for testing.

Task 2. Lignite Preparation/Mine Water Acid Neutralization.

Task Leader: Mr. Mel Pedersen

GFAT presently has lignite samples available for use in this work from prior physical cleaning pilot tests performed at EERC under subcontract. Various size fractions of the physically cleaned lignite will be evaluate for settling properties and bed flow properties. Sized samples for use in ion exchange tests (batch and column) will be prepared and provided to CAER.

Ca-sludge (landfill sludge) from water treatment processes (city water treatment plants and/or sugar beet plant stockpiles) will be tested in the acid neutralization of mine water provided through Task 1. Neutralized (at least above pH 4) and precipitated sludge as well as untreated water will be provided to CAER for ion exchange evaluations.

Task 3. Lignite Ion Exchange with Mine Water and Simulated Water.

Task Leader: Dr. Chris Lafferty

Testing will be performed on samples provided by GFAT on streams that could be produced from a physical cleaning plant presently being designed. The lignite samples will include particle size fractions suitable for use in a settling tank application (minus 1/8" and nominally 20 x 100 mesh) and in a bed application (nominally 1/4" x 1/8"). The sized lignite samples will be tested with at minimum one acid mine water and one known solution of metals. A primary goal is to provide working capacity data to determine the quantity of lignite required to treat a given amount of mine water.

Petrographic characterization of each of the lignite samples will also be performed in order to determine if specific macerals display enhanced cation adsorption capacity. A series of standard adsorption experiments, principally in batch mode, will be conducted on each lignite in order to characterize their ion exchange characteristics and capacity and to assess any variability in the performance as a function of lignite source. Some of the key variables that are known to effect lignite exchange capacity and that will be investigated as part of the study include:

- Cation exchange capacity as a function of solution pH.
- Cation competition effects.
- Anion interference effects.
- Effect of multiple low loading contacts compared to single high loading contacts.
- Column vs Batch adsorption studies.

The metals to be studied for uptake by low-rank coals will include those of major industrial importance, e.g. copper, nickel, lead, zinc and chromium, as well as those species commonly found in the groundwater at contaminated sites. Quantitation of metal adsorption will be performed using a combination of directly and inductively coupled plasma atomic emission spectroscopy (DCP/ICP-AE).

A series of standard leaching procedures, e.g. TCLP (EPA-1311), 24 hr shake test (ASTM-D3987) and Synthetic Leachate Procedure (EPA-1312) will be performed on samples of exchanged lignites to assess the overall stability of the exchanged coals. The results of the leaching tests will be evaluated in terms of their compliance with Environmental Discharge Limits, Drinking Water Standards and Warm Water Aquatic Life Limits.

Task 4. Process Economics, and Reporting.

Task Leader: Dr. Curtis Knudson

The economics of the process will be developed to include feed stock costs production, loading, and transportation costs to a specific remediation site. The quantities of feedstocks required for treatment will be determined from data obtained in Tasks 1 and 2 for a mine site determined in Task 1. The market potential for other remediation sites and the use of feedstocks from other locations will be evaluated. The concept data will be assembled into a technical report using the standard format for use in developing of a one-page "Tech Brief". The Project Manager (and potentially co-Principal Investigators) will attend a commercial planning workshop (CPW) meeting (as required) and participate, gladly, in presentation of concept to potential sponsors on dates and at locations to be determined.

Facilities

GFAT conducts business from its Washington Street location in Grand Forks, North Dakota. A 1550 ft^2 facility is designed as a business office, conference/meeting area, laboratory, and storage area. Approximately 1000 ft^2 are dedicated to daily operations and a meeting/conference area. Office equipment includes a Panasonic facsimile/telephone machine, Canon PC-25 photocopier, Magnavox television/VCR, and a full inventory of office supplies. In addition, GFAT is outfitted with two personal computers: one Packard Bell 486DX - 60 Mhz and one MicroSys 486DX - 60 Mhz. These are complemented with both IBM dot matrix and Epson Action Laser printers, as well as graphics (Corel Draw), word processing (Work Perfect and Microsoft Word), spreadsheet (Lotus), reference handling (Reference Manager), and communication software. GFAT's laboratory is located in a 550-ft^2 area adjacent to its office space. Laboratory equipment includes a dedicated data acquisition computer, Fluke data logger, Cole-Parmer laboratory oven, ThermoLyne 1300 furnace, coal sieves and a stock of laboratory equipment and glassware. The laboratory is equipped with the tanks and equipment to easily prepare up to 20 pound samples of processed coal for use in this study. In prior and on-going work GFAT has subcontracted to EERC (about 8 blocks away) for the preparation of larger samples and for pilot scale work. Additional analytical services can be provided through laboratories at the University of North Dakota Energy & Environmental Research Center (EERC), and Microbeam Technologies, Inc. (MTI), both of Grand Forks.

Activation Technologies
Grand Forks

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June 30, 1995

Ms. Karlene Fine
North Dakota Industrial Commission
600 East Boulevard Avenue
State Capitol, Ground Floor
Bismarck, ND 58505-0001

Dear Ms. Fine:

Subject: Transmittal Letter, Unsolicited Proposal

This transmittal letter represents a binding commitment for Dr. Curtis L. Knudson to complete the project as described in the GFAT Proposal No. 95-1004 submitted to the North Dakota Industrial Commission on July 1, 1995, entitled "Low-Cost Metals Adsorbents From Lignite (NDIC-LRC)".

Enclosed is the $100 application fee.

Curtis L Knudson

Curtis L. Knudson, Ph.D.
President