DOE/PC/91334--T50

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DE92 018289

TECHNICAL REPORT

December 1, 1991 Through February 29, 1992

Project Title: The Effects of Moderate Coal Cleaning on the Microbial Removal of Organic Sulfur

Principal Investigator: Vipul J. Srivastava
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Project Monitor: Dr. Daniel D. Banerjee, CRSC

ABSTRACT

The purpose of this project is to investigate the possibilities of developing an integrated physical/chemical/microbial process for the pre-combustion removal of sulfur from coal. Microorganisms are capable of specifically cleaving carbon-sulfur bonds and removing substantial amounts of organic sulfur from coal; however, the removal of organic sulfur form coal by microorganisms is hampered by the fact that, as a solid substrate, it is difficult to bring microorganisms in contact with the entirety of a coal sample. This study will examine the suitability of physically/chemically treated coal samples for subsequent biodesulfurization. During the current quarter, chemical comminution and combined chemical treatment/explosive comminution experiments have been performed to generate coal samples with increased surface area and porosity. Ammonia vapor was found to be the most effective chemical comminution agent and the optimum conditions for combined chemical treatment/explosive comminution have not yet been determined.

This project is funded by the U. S. Department of Energy (PETC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared program.

EXECUTIVE SUMMARY

The pre-combustion removal of organic sulfur from coal is a formidable technical challenge. A variety of physical, chemical, and microbiological coal desulfurization processes have been investigated during the past several decades. Efficient and effective methods for the pre-combustion removal of inorganic sulfur, from at least some coals, have been developed; however, no cost-effective method for the pre-combustion removal of organic sulfur from coal currently exists. Biodesulfurization; the removal of organic sulfur from coal using microorganisms such as Rhodococcus rhodochrous IGTS8, is a promising new technology. While the microbial removal of organic sulfur from coal appears to be technically feasible, it is currently too slow to be practical. One of the chief limitations is the relative inaccessibility of solid coal particles to bacteria. It can be readily appreciated that the surface area of a coal sample (particle size and porosity) can greatly influence the effectiveness of a microbial desulfurization treatment. Accordingly, the goal of this project is to examine the suitability of coal samples with increased surface area/porosity due to physical and/or chemical treatments for the subsequent removal of organic sulfur by microorganisms.

Some coal treatment processes designed for the removal of inorganic sulfur from coal exhibit substantial increases in the surface area/ porosity of the product coal. Such coal samples may well be preferred substrates for a microbial process for the removal of organic sulfur from coal as compared with untreated coal. Therefore, the possibility exists that an integrated physical/chemical/microbial process can be developed for the pre-combustion removal of both organic and inorganic sulfur from coal. Chemicals that are capable of comminuting coal, which by definition requires a softening/cleaving of the organic matrix of coal, are of particular interest. The exposure of coal to chemical comminuition agents may well result in coal products that have increased porosity and surface area and; therefore, are better substrates for biodesulfurization. Exposure of coal to ammonia, isopropanol, and methanol in the presence of sodium hydroxide with and without explosive comminution was investigated during this quarter. Ammonia vapor was found to be the most effective chemical comminution agent; however, the optimum conditions for combined chemical treatment/explosive comminution have not yet been determined.

OBJECTIVES

The objective of this research is to provide data relevant to the development of an integrated physical, chemical, and microbiological process for the desulfurization of coal, utilizing existing technologies insofar as is possible. Specifically, the effect of increased surface area and porosity achieved by physical and/or chemical treatments of coal on the subsequent microbiological removal of organic sulfur will be evaluated. Specific tasks scheduled for this reporting period include obtaining and characterizing treated coal samples and initiating biodesulfurization experiments for the microbial removal of organic sulfur.

INTRODUCTION AND BACKGROUND

There are numerous physical, chemical, and microbiological techniques that can effectively remove inorganic sulfur from coal prior to combustion. Moreover, there are physical and chemical techniques for pyrite/ash removal that have been successfully commercialized and are routinely employed in the coal industry. However, while there are technologies capable of removing organic sulfur from coal prior to combustion no commercially viable technology currently exists. The removal of organically bound sulfur from coal by physical/chemical techniques requires harsh conditions as compared with microbiological techniques; therefore, the microbiological approach to the removal of organic sulfur might result in the development of a coal treatment process with more favorable economics than currently available technologies.

IGT has succeeded in developing a bacterial culture, Rhodococcus rhodochrous IGTS8, that specifically cleaves carbon-sulfur bonds in a range of organic substrates and coal. The removal of organic sulfur from coal could be a component of an overall coal preparation process that also involves chemical and physical technologies and will be capable of removing inorganic as well as organic sulfur. One of the chief hurdles or rate-limiting factors in the microbiological removal of organic sulfur from coal is the accessibility of the organosulfur compounds in the coal matrix. In other words, even though a microorganism is capable of cleaving carbon-sulfur bonds, the ability of the microorganism to contact and react with organosulfur compounds will be influenced by the physical structure of the coal (i.e., particle size, pore size distribution, and rigidity/plasticity). These physical characteristics of coal can be altered dramatically depending upon which physical/chemical/microbial treatment technologies are used. This research project will attempt to identify those physical/chemical coal treatment technologies that might be particularly beneficial when used in conjunction with the microbiological removal of organic sulfur in an integrated coal treatment process.

Nearly all Illinois coals contain finely dispersed pyritic granules and classical physical methods for coal cleaning and achieve relatively limited sulfur removal. Therefore, physical coal cleaning alone will not produce a coal with a sulfur content that complies with the New Source Performance Standard for SO_2, and additional techniques such as microbiological treatments to remove organic sulfur are needed. This project will seek to identify those physical/chemical coal treatment technologies that simultaneously render the coal amenable to the removal of organic sulfur by microbial techniques, as well as allow for the efficient separation/removal of pyritic sulfur. This research, then, will contribute to the development of a combined physical/chemical/ microbiological coal treatment process for the removal of both organic and inorganic sulfur, thereby allowing extended utilization of Illinois coals.

EXPERIMENTAL PROCEDURES

The explosive comminution reactor consists of an upper chamber having a volume of 308 mls connected to a lower chamber having a volume of 3900 mls. The reactor is illustrated in Figure 1. During operation, IBC-107 coal samples (usually 10 grams) are added to the upper chamber through a quarter inch openning. To insure that coal can be readily added to the upper chamber of the reactor and so that coal can pass from the upper to the lower chamber, which are connected by a quarter inch valve, all coal is sieved either to -10 + 12 mesh or to -12 + 80 mesh prior to use. A liquid, 25 mls per 10 g sample of coal, is also added to the upper chamber along with the coal. The liquids used are water, an aqueous solution of 0.1N NaOH, methanol containing 0.1N NaOH, or isopropanol containing 0.1N NaOH. (It is necessary to add small amounts of water to methanol or isopropanol in order to prepare 0.1N NaOH solutions). The upper chamber is then pressurized either to 800 or 1200 psi, using nitrogen, and is either operated at ambient temperature or at 240°F. The lower chamber is evacuated to a pressure of 5 microbes Hg by means of a vacuum pump. Both the upper and lower chambers are equipped with pressure gauges to allow the accurate establishment of appropriate pressure/vacuum for each run. Each chamber is also fitted with valves that allows the reactor to be a closed system (unconnected to pressure and vacuum lines after appropriate conditions have been achieved) during each explosive comminution run. The upper chamber is equipped with electric heating tape connected to a rheostat, insulation, and a thermocouple to allow temperature to be controlled and monitored. The upper and lower chambers are connected by an electronic valve that has a one quarter inch opening. This valve allows uniform/reproducible conditions to be used in the release of pressure in each explosive comminution run.

Coal characterization includes weight, and particle size distribution measurements (performed on dry coal samples). Coal weights (dried to a constant weight at 90°C) are obtained so that product recoveries can be calculated. All of the coal used in chemical/explosive comminution runs is sized to -12 + 80 mesh, and after each comminution run the recovered coal is dried and sieved through 10, 12, and 80 mesh screens. Particle size reduction alone does not permit rapid biodesulfurization as prior experiments employing -200 mesh coal have shown. Accordingly, in this study chemically treated and physically/chemically treated coal samples with particle sizes greater than 80 mesh will be used in biodesulfurization experiments. In this way the effects of altering/softening the organic matrix of the coal upon subsequent biodesulfurization efficiency can be examined directly with minimal interference due to the mere reduction of the particle size of coal.

Chemical treatments alone were performed by exposing 10 g samples of either -10 + 12 mesh or -12 + 80 mesn IBC-107 coal samples to 25 mls of water containing 0.1N NaOH, isopropanol containing 0.1N NaOH, or methanol containing 0.1N NaOH. Coal was also exposed to ammonia vapor in a sealed container. Chemical treatments were performed at ambient temperatures and pressures and

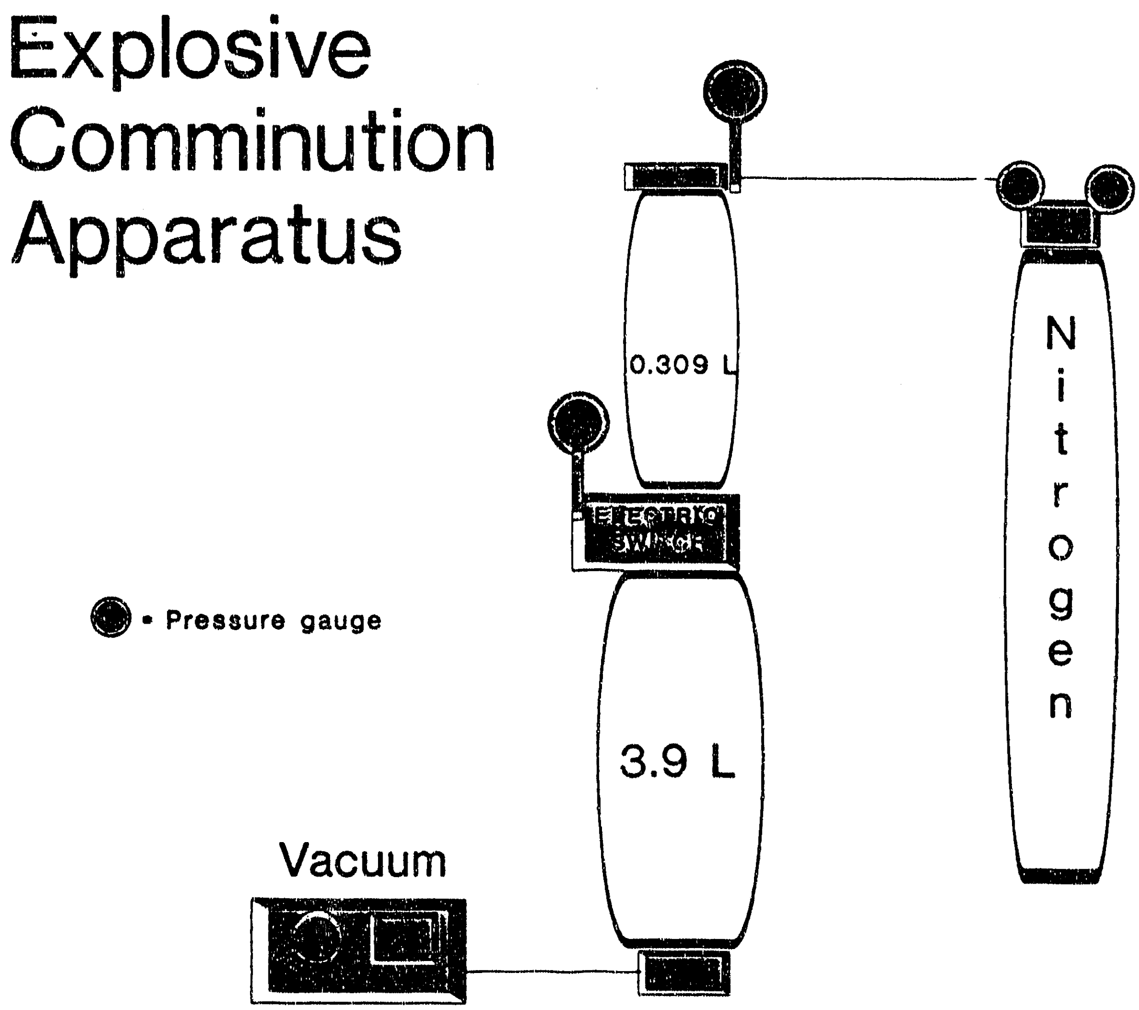

Figure 1. LABORATORY-SCALE REACTOR FOR THE EXPLOSIVE COMMINUTION OF COAL

were of one week duration without shaking/agitation. After chemical exposure, the coal samples were dried to constant weights at 90°C and sieved.

RESULTS AND DISCUSSION

All of the coal used in chemical comminution and chemical/explosive comminution experiments was sized to either -10 + 12 mesh or to -12 + 80 mesh. IBC-107 coal, as received, was sieved through 10, 12, and 80 mesh screens and the percent weight distribution of these size classes is shown in Table 1. Thus it can be seen that the majority of IBC-107 coal (72%) falls within the -10 to +80 size fractions that are used in further experiments reported here. After sieving, the coal was riffled into 10 gram samples.

The effect of combined chemical treatment and explosive comminution was investigated. Previous work reported last quarter regarding coal swelling as a consequence of exposure to water, methanol, isopropanol, and ammonia with and without 0.1N NaOH indicated that isopropanol containing 0.1N NaOH seemed to be the best chemical agent and ammonia had the least effect in those preliminary studies. Accordingly, isopropanol and methanol containing 0.1N NaOH were used predominantly in experiments performed during this quarter. Explosive comminution experiments were performed using 10 g samples of -12 + 80 mesh IBC-107 coal at two different temperatures (70°F and 240°F), two pressures (800 psi and 1200 psi), and three chemicals (water, isopropanol and methanol each containing 0.1N NaOH). Dry coal samples were added to the upper chamber of the reactor shown in Figure 1 and 25 mls of the appropriate chemical solution was added. The system was then pressurized and brought to the appropriate temperature for 5 minutes to allow the coal and the chemical solution to interact before the valve was opened initiating the explosive reaction. The results of these tests are shown in Table 2. There did not appear to be any significant difference between treatments employing 800 psi or 1200 psi; however, the differences between 70°F and 240°F were dramatic. The amount of coal that could pass through a 80 mesh screen roughly doubled when the temperature was increased from 70°F to 240°F. The observation that the aqueous solution resulted in a higher percentage of coal particles in the -80 mesh size range than either isopropanol or methanol may indicate that the swelling/expansion of the organic matrix of the coal is greater with isopropanol and methanol.

The effect of chemical treatment alone was assessed by exposing -10 + 12 mesh and -12 + 80 mesh IBC-107 coal samples to water, isopropanol, or to methanol solutions containing 0.1N NaOH for one week at ambient temperatures and pressures without agitation. A coal sample was also exposed to ammonia vapors for one week. The samples were then dried and sieved. The results are shown in Table 3. These data show that an aqueous solution of .1N NaOH causes the greatest amount of coal swelling and the least amount of comminution. Ammonia vapor appears to be the best chemical comminution agent in these tests followed by methanol and isopropanol in that order. The superiority of methanol and isopropanol solutions as comminution agents in comparison with aqueous 0.1N NaOH is clearly seen only with -10 + 12 mesh coal as the starting material.

Table 1. SIZE CHARACTERIZATION AND FRACTIONATION OF IBC-107 COAL

Mesh Size	% Weight of Coal
+10	21.3%
-10 + 12	17.1%
-12 + 80	55.2%
-80	6.4%

Table 2. EXPLOSIVE COMMINUTION OF CHEMICALLY TREATED IBC-107 COAL

	Sample			Product				
Mesh Size	Chemical Treatment	Temperature	Pressure	+10 Mesh	-10 + 12 Mesh	-12 + 80 Mesh	-80 Mesh	% Recovery
-12 + 80	H_2O .1N NaOH	70°F	800 psi	0.1%	0.8%	65.0%	34.1%	99.0%
-12 + 80	H_2O .1N NaOH	70°F	1200 psi	0%	0.2%	66.7%	33.1%	95.7%
-12 + 80	H_2O .1N NaOH	240°F	1200 psi	0%	0%	35.5%	64.5%	92.4%
-12 + 80	Isopropanol .1N NaOH	70°F	800 psi	0%	0.1%	63.4%	36.5%	95.6%
-12 + 80	Isopropanol .1N NaOH	70°F	1200 psi	0%	0.3%	62.1%	37.6%	86.8%
-12 + 80	Isopropanol .1N NaOH	240°F	1200 psi	0%	0%	41.7%	58.3%	91.1%
-12 + 80	Methanol .1N NaOH	240°F	1200 psi	0%	0%	54.5%	45.5%	93.4%

Table 3. CHEMICAL COMMINUTION OF IBC-107 COAL

Mesh Size	Chemical Treatment	Temperature	+10 Mesh	-10 + 12 Mesh	-12 + 80 Mesh	-80 Mesh
-10 + 12	H_2O .1N NaOH	70°F	6.3%	70.1%	23.1%	0.4%
-10 + 12	Isopropanol .1N NaOH	70°F	4.5%	62.6%	32.4%	0.5%
-10 + 12	Methanol .1N NaOH	70°F	3.2%	42.1%	53.3%	1.3%
-12 + 80	H_2O .1N NaOH	70°F	0%	3.5%	96.5%	0%
-12 + 80	Isopropanol .1N NaOH	70°F	0%	2.2%	97.8%	0%
-12 + 80	Methanol .1N NaOH	70°F	0%	1.3%	98.3%	0.4%
-12 + 80	Ammonia	70°F	0%	0.2%	88.3%	11.4%

All chemical treatments were performed at atmospheric pressure and were of one week duration with no agitation.

CONCLUSIONS AND RECOMMENDATIONS

Combined chemical treatment and explosive comminution have not revealed significant differences between aqueous solutions and chemical comminution solutions whereas studies with chemical comminution solutions clearly demonstrate their superiority to aqueous solutions. These differing observations probably result from too brief of an exposure period between coal and the chemical solution prior to explosive comminution and because a more detailed analysis of particle size distribution is required. Experiments planned for next quarter will allow longer contact times between coal and chemical solutions, include a more thorough particle size analysis, examine ammmonia vapor in greater detail as a comminution agent, and will produce a large quantity of data concerning the biodesulfurization of coal samples.

PROJECT MANAGEMENT REPORT

December 1, 1991 Through February 29, 1992

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COMMENTS

The project is proceeding as scheduled.

This project is funded by the U. S. Department of Energy (PETC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared program.

EXPENDITURES - EXHIBIT B

Projected and Estimated Actual Expenditures by Quarter

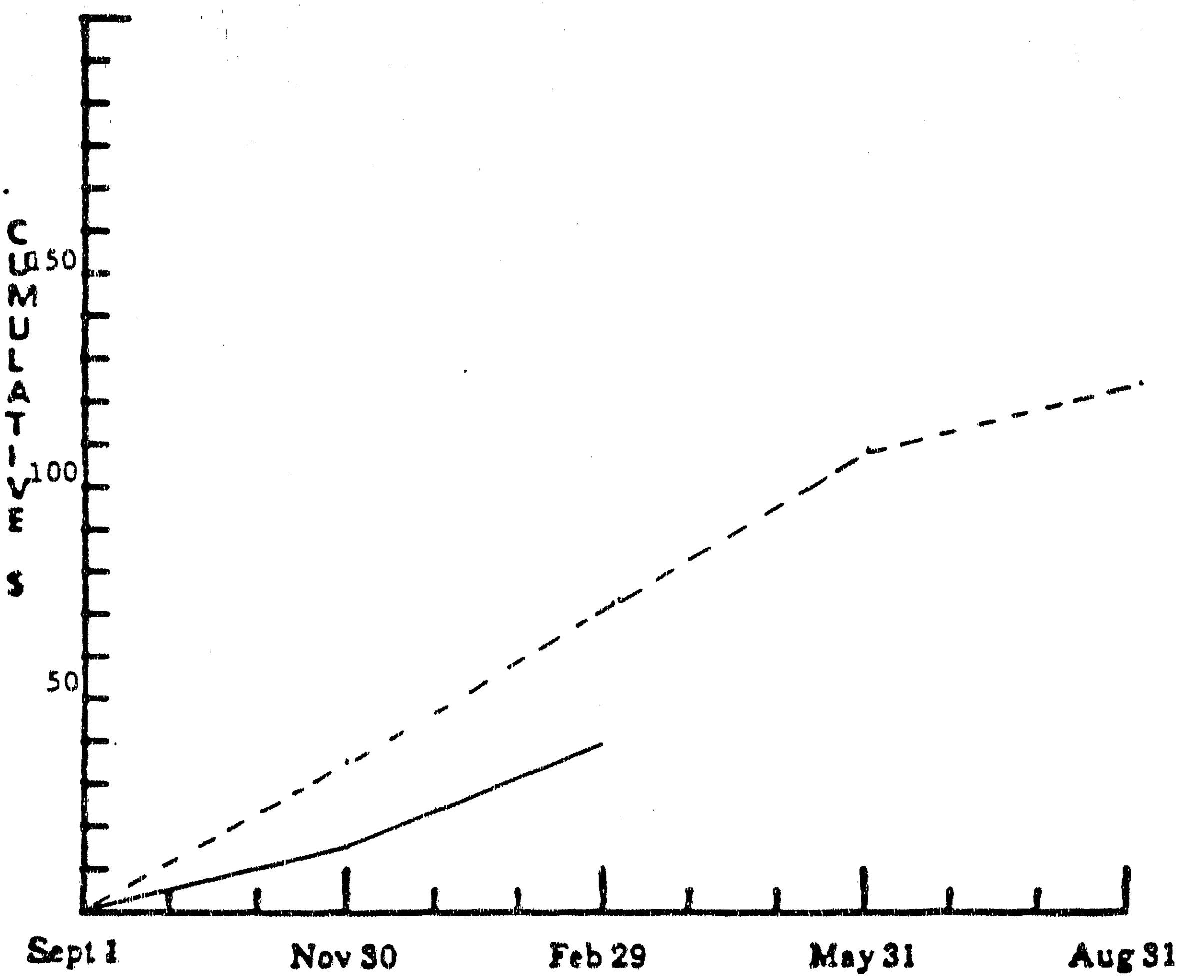
Quarter*	Types of Cost	Direct Labor	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1991 to	Projected	12,000	1,000	-			21,896	34,896
Nov. 30, 1991	Estimated Actual	4,379	500				7,918	12,797
Sept. 1, 1991 to	Projected	24,000	3,000	-			44,003	71,003
Feb. 29, 1992	Estimated Actual	13,000	1,500				23,809	38,309
Sept. 1, 1991 to	Projected	36,000	5,000	1,146			66,340	108,486
May 31, 1992	Estimated Actual							
Sept. 1, 1991 to	Projected	41,346	6,000	1,404			76,276	125,026
Aug. 31, 1992	Estimated Actual							

* Cumulative by quarter

COSTS BY QUARTER - EXHIBIT C

(Example) (In Thousands)

Effect of Moderate Coal Cleaning on Microbial Removal of Organic Sulfur
Your Project Title Here



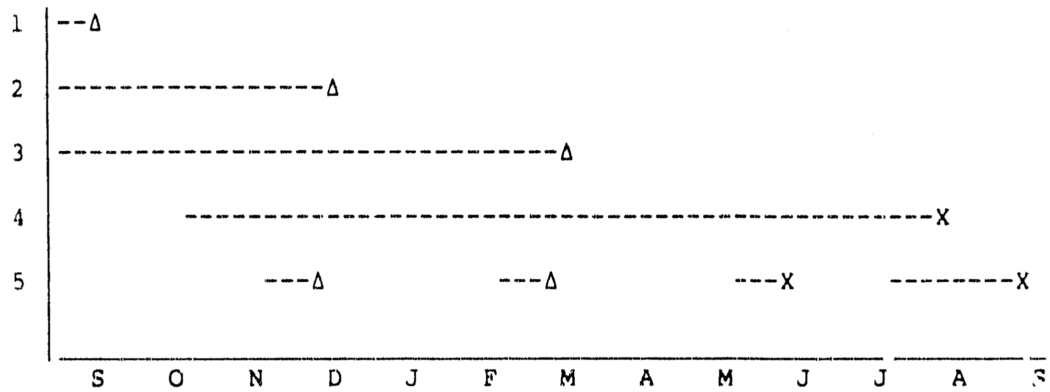
Months and Quarters

0 = Projected Expenditures 125,026

Δ = Actual Expenditures ______

Total CRSC Award $______

SCHEDULE OF PROJECT MILESTONES



1. Coal samples are received from CRSC.

2. Lab-scale device for explosive comminution of coal is constructed.

3. Characterization of chemically treated coal is completed.

4. Characterization of biotreated coal is completed.

5. Preparation of technical and project management reports.

END

DATE FILMED

9/10/92