DOE/PC/91334--T64

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TECHNICAL REPORT

December 1, 1991 through February 29, 1992

Project Title:	Dewatering Studies of Fine Clean Coal
Principal Investigator:	Dr. B.K. Parekh, University of Kentucky Center for Applied Energy Research
Project Monitor:	Dr. Dan Banerjee, CRSC

ABSTRACT

Physical cleaning of ultra-fine coal using an advanced froth flotation techniques provides a low ash product, however, due to high surface area of particles the amount of water associated with clean coal is high. Economic removal of water from the froth will be important for commercial applicability of advanced froth flotation processes. The main objective of the present research program is to study and understand the dewatering characteristics of ultra-fine clean coal and to develop process parameters to effectively reduce the moisture to less than 20 percent in the clean coal product. The research approach under investigation utilizes synergistic effects of metal ions and surfactant to lower the moisture of clean coal using a conventional vacuum dewatering technique. The studies have identified a combination of metal ion and surfactant found to be effective in providing a 22 percent moisture filter cake.

During the second quarter, adsorption studies of anionic, non-ionic and cationic surfactants onto clean coal in the presence and absence of copper ions were conducted. Copper ions enhanced the adsorption of both anionic and cationic surfactants while they had minimal effect on the adsorption of non-ionic surfactant. Electrophoretic mobility measurements were obtained for coal in the presence of anionic surfactant and copper ions. Metal hydroxide ($Cu(OH)_2$ or $Al(OH)_3$) species influenced the electrokinetic behavior of coal in the presence of anionic and non-ionic surfactants, but not in the presence of cationic surfactant.

Filtration tests were continued using a continuous rotary vacuum drum filter. Results obtained from batch filter leaf tests were comparable to continuous filtration tests. The optimum cake thickness was found to be 5.5 mm. In the presence of 50 ppm copper ions and 0.5 lb/ton anionic surfactant, the moisture was significantly reduced from 35 percent to 26 percent. Preliminary test results from the AC Electro-Coagulation tests indicated faster settling rates and floc growth in coal slurry - which are beneficial for filtration in order to provide low moisture cakes.

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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

Recovery of fine clean coal from waste streams offers an attractive source of low-ash, low-pyritic sulfur clean coal. In the fine state, most of the mineral matter is liberated and could be effectively removed by the newly developed advanced column flotation technology. These fine coal cleaning techniques will be particularly applicable to the Illinois high ash, high pyrite sulfur coals, where ultra-fine grinding is necessary to liberate the mineral matter. However, if the recovered fine clean coal cannot be dewatered to a low (less than 20 percent) moisture level, then acceptance of these newly developed techniques by the coal industry is unlikely.

During the last 15 months of the project, it has been reported that metal ion or surfactant alone does not significantly lower moisture in the filter cake. However, combination of metal ion and surfactant provided a filter cake containing about 22 percent moisture. Studies are being continued to optimize the process conditions, and to apply novel AC Electro-Coagulation technique in continuous vaccum drum filter tests.

This quarter, adsorption studies of anionic (Sodium 2-Ethylhexyl Sulfate [S2ES]), cationic (Cetyl Pyridinium Chloride [CPC]) and non-ionic (Octyl Phenoxy Polyethoxy Ethanol) also known as Triton X-114 [X114]) surfactants onto the clean coal were conducted. Significant adsorption of anionic S2ES occurred in the equilibrium concentration range of 300 to 500 mg/l with an adsorption density of 100 mg/g. Adsorption of S2ES increased significantly in the presence of copper ions at a lower equilibrium concentration (100 mg/l). Adsorption of cationic CPC was enhanced by the presence of copper ions whereas copper ions had no significant effect on adsorption for non-ionic Triton X-114 surfactant.

Results obtained from the continuous vacuum drum dewatering tests were comparable to those obtained from the batch tests. The optimum cake thickness was found to be 5.5 mm which is consistent with results previously reported from batch filter leaf tests. A combination of anionic surfactant (S2ES) and copper ions together reduced filter cake moisture from 35 to 26 percent in the rotary vacuum drum filter or in other words a total moisture reduction of 25 percent was obtained with the surfactant-metal ion pre-treatment.

AC Electro-Coagulation (AC/EC) studies were initiated on Galatia fine clean coal slurry. In this process, when an aqueous suspension of solids is passed between two aluminum plates to which AC power is applied, the fine particles start coagulating as soon as the suspension leaves the cell. The AC/EC process provides an unique technique for applying synergistic effect of charge neutralization and metal ion addition in one stage. Preliminary experiments indicated faster settling rates of slurry and growth of flocs upon AC Electro-Coagulation. Studies are in progress in applying the AC Electro-Coagulation and the continuous vacuum drum filter techniques together.

OBJECTIVES

The main objective of the proposed program is to study and understand the dewatering characteristics of fine clean coal obtained using the advanced column flotation technique from the Kerr-McGee Galatia Preparation Plant's fine refuse stream. The ultimate objective is to develop the process criteria to obtain a dewatered clean coal product containing less than 20 percent moisture utilizing conventional dewatering equipment.

The above-stated objectives will be achieved using five (5) different tasks. Task 1 involving acquisition and characterization of the fine clean coal product obtained from the 'Ken-Flote' column has been completed. Task 2 on the investigation of surface chemical properties of the coal before and after flotation, with and without the presence of various surfactants and metal ions has been completed. Task 3 on laboratory dewatering studies of the clean coal product utilizing information gathered in Task 2 is in progress. Task 4 involving the utilization of the novel AC Electro-Coagulation technique is initiated in this quarter. Task 5 on continuous dewatering tests using a laboratory vacuum drum filter is in progress. Continuation of Task 5 will utilize optimum process conditions identified in Tasks 2, 3 and 4.

INTRODUCTION AND BACKGROUND

Most of the coal presently used by the utility industry is cleaned at preparation plants employing wet processes. Water, while being the mainstay of coal washing, is also one of the least desirable components in the final product. The problem becomes severe as the coal particle size decreases. Most of the advanced physical or chemical coal cleaning processes require ultra-fine grinding of coal for liberation of impurities for their removal to produce an ultra-clean coal product. The clean coal product so obtained requires extensive dewatering before it can be used. Currently available dewatering techniques are inefficient for dewatering of ultra-fine (minus 325 mesh) coal. The coal industry in the U.S. has expressed serious concern about utilizing novel advanced cleaning process, if an efficient and economical dewatering process is not available. Thus, the present research program presents a novel approach for the urgent problem which needs to be solved in a short period of time.

The research project utilizes the basic surface-colloid chemistry principle of lowering the zeta potential of coal particles through adsorption of surfactants and metal ions. Parekh[*] has reported that using metal ions, coagulation of

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[*] Parekh, B.K., 1979, "Role of Hydrolyzed Metal Ions in Charge Reversal and Coagulation Phenomena," Ph.D. thesis, The Pennsylvania State University.

ultra-fine particles could be achieved effectively at the zero-point of charge of the metal ion/solid system. Usually, three charge reversal points (or points-of-zero charge) are observed for each metal ion/solid system (Figure 1). The last charge reversal point (CR3) was found to be the most effective for coagulation of particles. The zero-point of charge could also be achieved using only the surfactants. The research program will utilize the synergistic effect of metal ion, surfactant, and pH in a single stage to improve the dewatering characteristics of fine coal utilizing a conventional vacuum dewatering technique.

It was reported by the CAER that metal ions or surfactants alone were not able to significantly reduce the moisture in the filter cake, however, a combination of the two (i.e. metal ion and surfactant) was effective in providing a filter cake containing about 22 percent moisture. During this quarter additional studies related to adsorption of metal ion and surfactant together and alone, and continuous dewatering tests were conducted.

This report describes the experimental results, conclusions and recommendations for the period December 1, 1991 through February 29, 1992.

EXPERIMENTAL PROCEDURES

The adsorption of cationic, anionic and non-ionic surfactants in the presence of copper ions was studied using surface tension measurements obtained with a Fisher Surface Tensiometer Model 20. Solutions of varying surfactant concentrations and 50 ppm copper ions were prepared in distilled water. To determine the amount of surfactant adsorbed on the coal surface, 1.0 g of coal was conditioned with a known amount of surfactant and metal ions for 15 minutes. During the conditioning time, the pH was monitored and remained constant. The conditioned slurry was then filtered and the surface tension of the clear filtrate was measured, from which the surfactant concentration was determined. The difference between the initial surfactant concentration and the filtrate surfactant concentration was the amount of surfactant adsorbed. The filtrate was also analyzed for copper concentration by Atomic Absorption Spectroscopy to ensure that all of the copper ions were adsorbed by the coal and would not affect the surface tension of the filtrate.

Electrophoretic mobility measurements were made on coal in the presence of surfactant alone, metal ions alone and surfactant and metal ions together. The concentration of metal ions and surfactant was maintained at 10^{-4} moles per liter. The suspension of coal particles and metal ions and/or surfactant was conditioned at various pH values for 5 minutes and the electrophoretic mobility was measured using a Zeta Meter Model 3.0.

Continuous filtration testing was conducted using a 6-inch diameter by 3-inch wide vacuum drum filter. The filter tub was fed continuously with a peristaltic pump and the tub overflow returned to the feed sump to ensure a constant tub

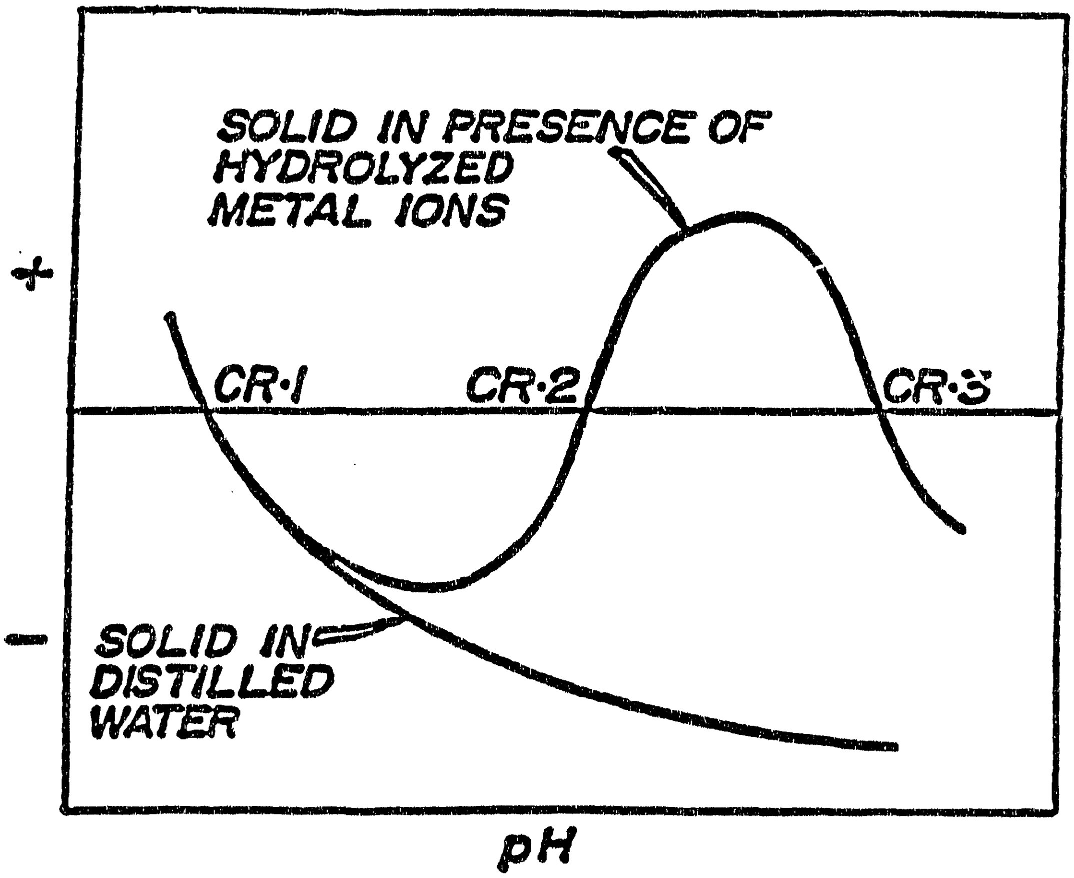


Figure 1. Charge Reversal of Solid with and without the Presence of Metal Ions

level for cake formation. The drum was rotated at the desired speed so that a uniform cake was formed, and the drying cycle time was varied before the dry cake was removed by an advancing knife blade. A continuous filtration test in progress is shown in Figure 2.

AC Electro-Coagulation testing was done to determine the effect of in-line metal ion (aluminum) addition on moisture reduction of filter cakes. A line diagram of laboratory AC/EC apparatus used in the study is shown in Figure 3. The cell consists of two aluminum electrodes (1/8" x 5 1/2" x 60") placed inside a plastic chamber. The distance between the electrodes, which is very important may be varied between 1/4" to 1". The AC/EC apparatus is connected to a central box which monitors voltage and amperage applied to electrodes. The distance between the aluminum plates was kept at 0.5". The volume of AC/EC apparatus is 2.9 liters. The slurry enters at the bottom of the cell and exits at the top. The AC Electro-Coagulator treated slurry starts coagulating as soon as it exits at the top of the cell. The treated slurry was collected in a 1000 ml graduated cylinder and its settling character with time was studied. The particle size distribution of slurry was also measured using the Granulometer (Model 715, Marco Scientific).

RESULTS AND DISCUSSION

The results of the dewatering studies are reported under four different categories.

Adsorption Studies:

The purpose of these studies was to understand adsorption of behavior of metal ions and surfactant alone and together on ultra-fine clean coal. An adsorption isotherm of coal with a cationic surfactant (CPC) and copper (Cu^{+2}) metal ion is shown in Figure 4. Note, that a monolayer coverage of the surfactant alone was formed at an equilibrium concentration of 20 to 50 mg/l with an adsorption density of approximately 20 mg/g of coal. However, when Cu^{+2} ions are present then the surfactant adsorption is significantly enhanced. As can be seen from the figure then even at low equilibrium surfactant concentration, essentially all of the surfactant was adsorbed; monolayer formation and adsorption densities are the same as when surfactant alone was used. However, the shape of the adsorption isotherm in the presence of copper ions indicates a strong affinity for coal surface and strong interaction between the copper ions and surfactant.

Adsorption of isotherms of an anionic surfactant (S2ES) alone and with copper ions are shown in Figure 5. Note, that in this case also the presence of copper ions enhanced adsorption of S2ES, but not to the extent shown with CPC in Figure 3. For S2ES surfactant adsorption on coal occurred only at high equilibrium concentration of more than 100 mg/l. A significant adsorption

Figure 2. Filtration of Fine Clean Coal Slurry Using a Laboratory Vacuum Drum Filter

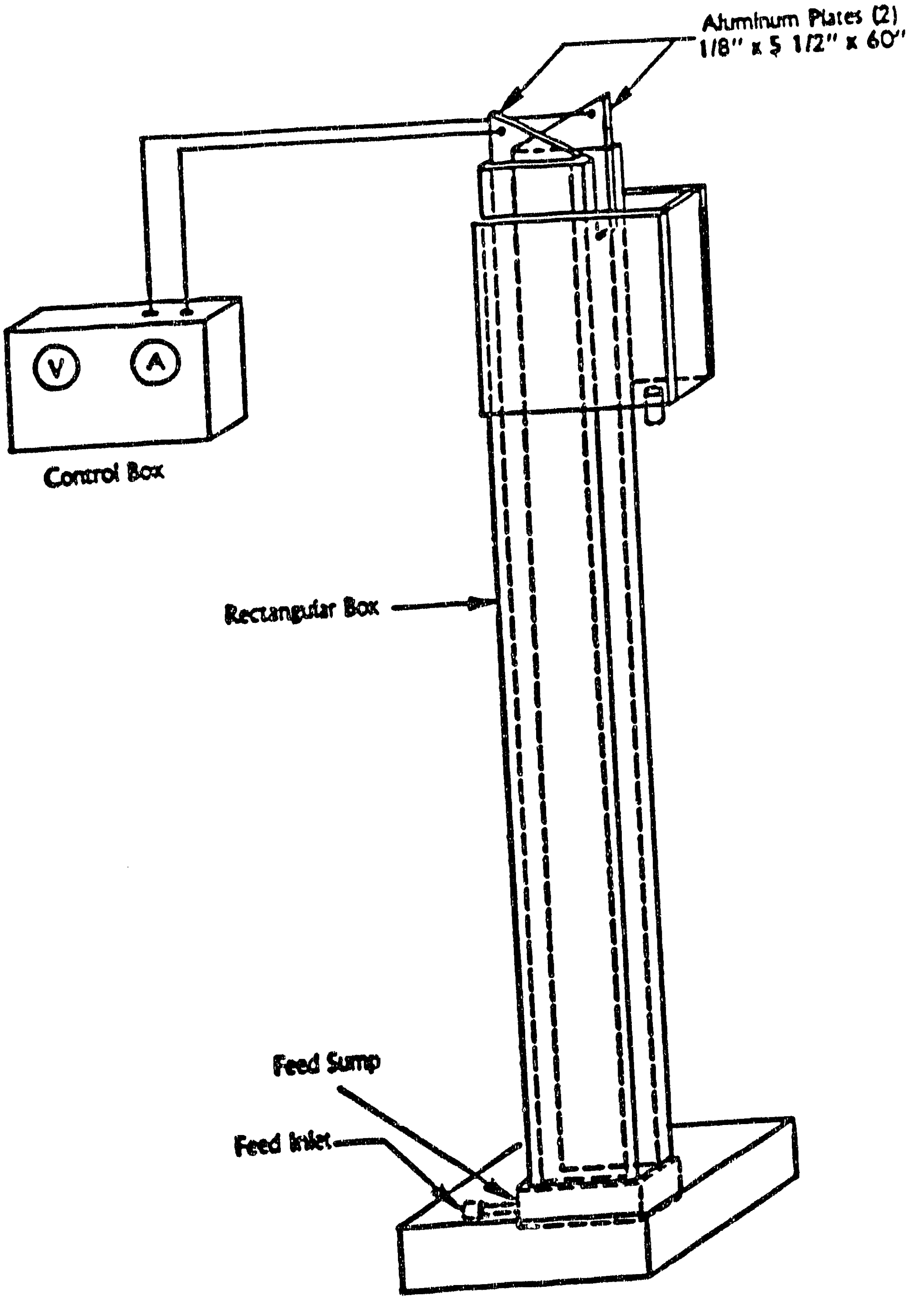


Figure 3. Schematic Diagram of a Laboratory AC Electro-Coagulator

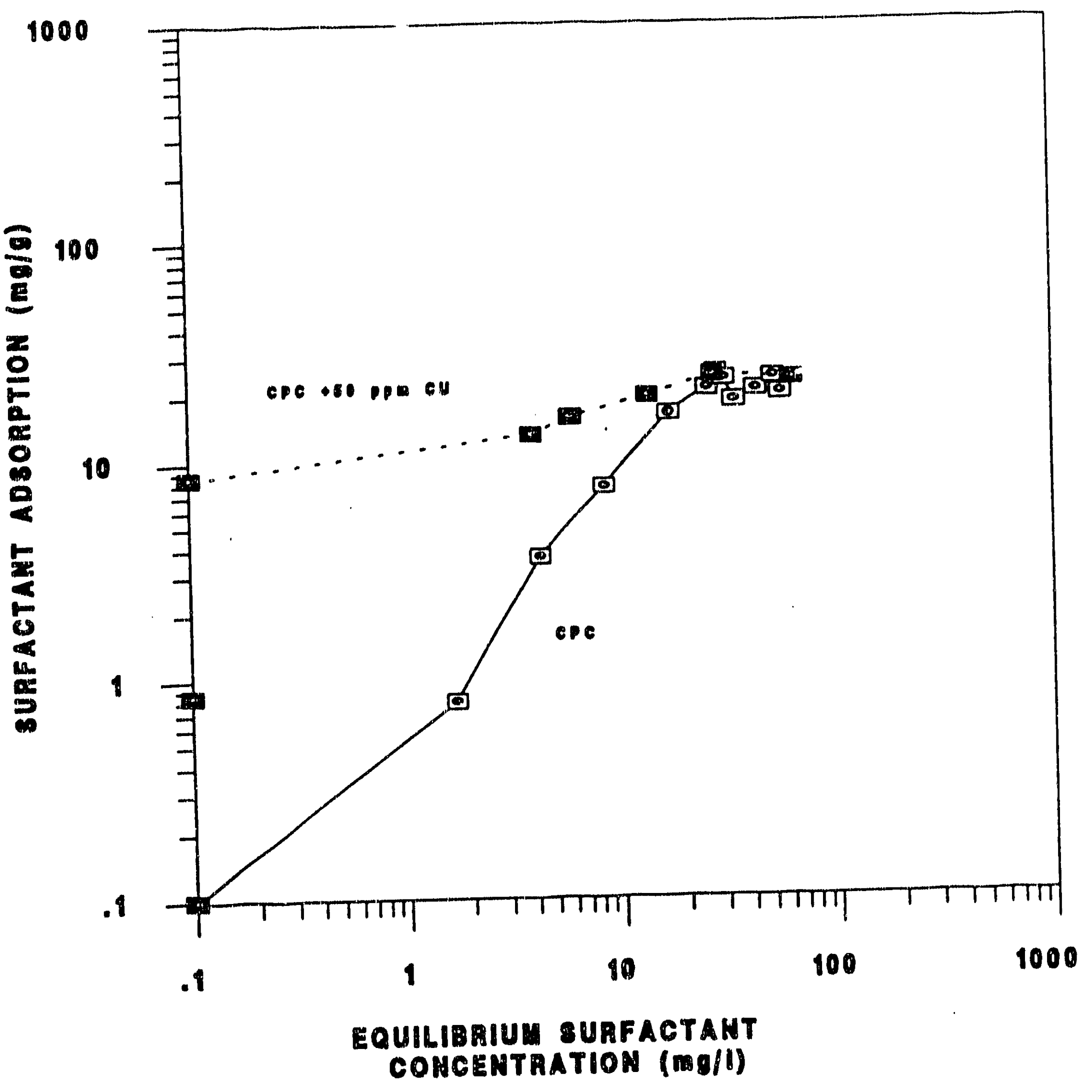


Figure 4. Adsorption Isotherms for Cationic Cetyl Pyridiniuim Chloride (CPC) Alone and Together with Copper Ions on Galatia Fine Clean Coal

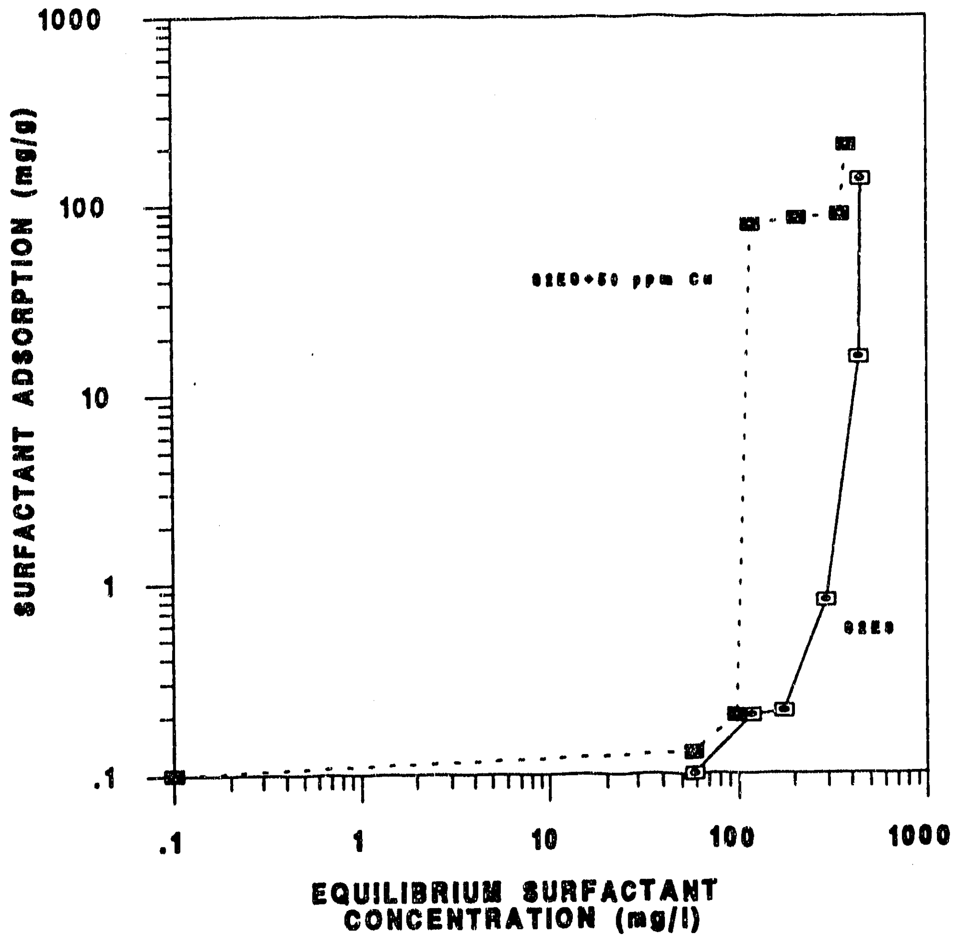


Figure 5. Adsorption Isotherms for Anionic Sodium 2-Ethylhexyl Sulfate (S2ES) Alone and Together with Copper Ions on Galatia Fine Clean Coal

occurred in the equilibrium concentration range of 300 to 500 mg/l, with no evidence or monolayer formation. However, in presence of copper ions, S2ES adsorption is significantly increased even at lower (<100 mg/l) equilibrium concentration and a monolayer formation was observed at the adsorption density of 100 mg/g and an equilibrium concentration of 100 mg/l.

For the non-ionic (X144) surfactant (Figure 6), copper ions had no significant effect on adsorption of X144. As can be seen from the figure that X144 surfactant showed a much stronger affinity for the coal surface, with monolayer formation at equilibrium concentration of 1 mg/l. At higher concentration of 10 mg/l formation of another monolayer occurred. Presence of copper ions did not show any significant differences, except that the second layer formation was shifted to a higher equilibrium concentration of 100 mg/l.

In summary, adsorption studies showed that copper ions enhanced the adsorption of both cationic and anionic surfactants and had minimal effect on the non-ionic surfactant. The most significant adsorption enhancement was observed with the cationic surfactant.

Electrophoretic Mobility Measurements:

Electrophoretic mobility measurements were obtained on clean coal in the presence of surfactant and copper ions alone and with copper ions surfactant mixture. The results for the S2ES/copper system are shown in Figure 7. For surfactant alone, the coal was negatively charged throughout the pH range suggesting that S2ES was adsorbed to a limited extent. In the presence of copper ions, the electrophoretic mobility changed significantly with a point-of-zero charge (PZC) occurring at pH 7 which corresponds to charge reversal (CR2) or the pH of formation of $Cu(OH)_2$. Another charge reversal point would occur near pH 10.5 which is charge reversal (CR3) or the PZC for $Cu(OH)_2$. In the presence of copper ions and surfactant, the electrophoretic mobility was essentially the same in the pH range where $Cu(OH)_2$ was present. This suggests that when $Cu(OH)_2$ was present, it dominated the surface properties of the coal. Below pH 5, Cu^{2+} is the dominant copper species and copper ions as well as surfactant molecules compete for adsorption sites. Essentially the same results were obtained for X114 and copper indicating similar dominance by $Cu(OH)_2$. For the CPC/copper system, $Cu(OH)_2$ had no effect on the electrophoretic mobility and the surfactant dominated.

In the presence of aluminum, essentially the same results were obtained where $Al(OH)_3$ determined the electrophoretic mobility of the coal when either anionic or non-ionic surfactant were present. The presence of $Al(OH)_3$ had no effect on the electrophoretic mobility of coal in the presence of CPC. These results illustrate the importance of the metal hydroxide in determining the electrokinetic behavior of coal. When the metal hydroxide species are present, it determines the electrophoretic mobility of the coal even when surfactants are present. This

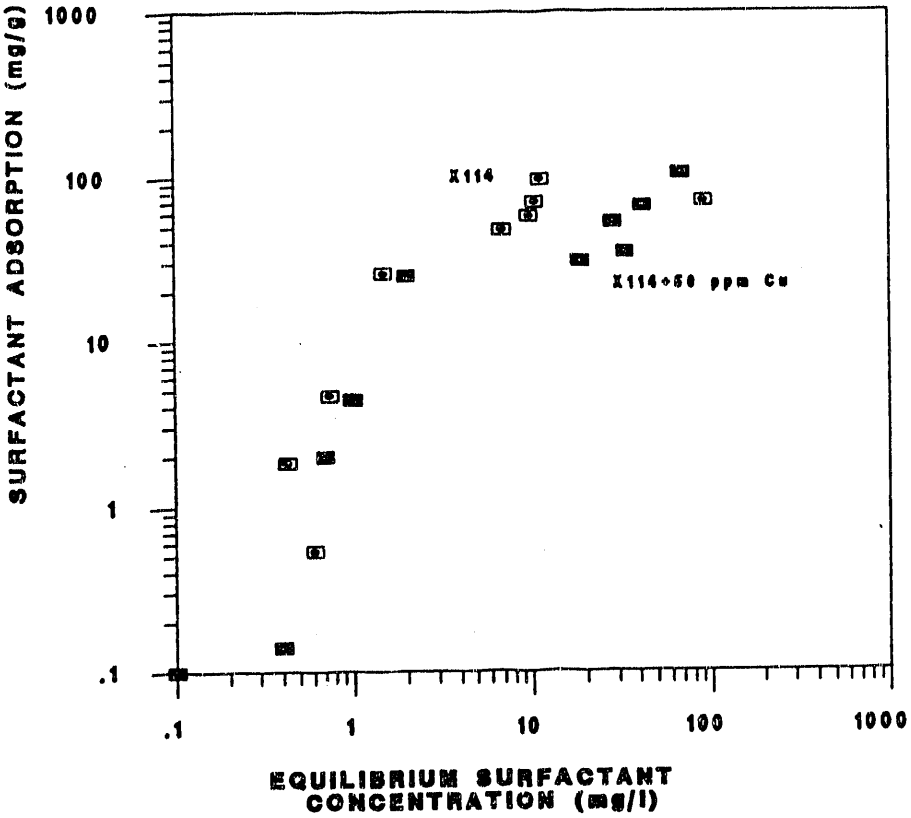


Figure 6. Adsorption Isotherms for Non-Ionic Octyl Phenoxy Polyethoxy Ethanol (Triton X-114) Alone and Together with Copper Ions on Galatia Fine Clean Coal

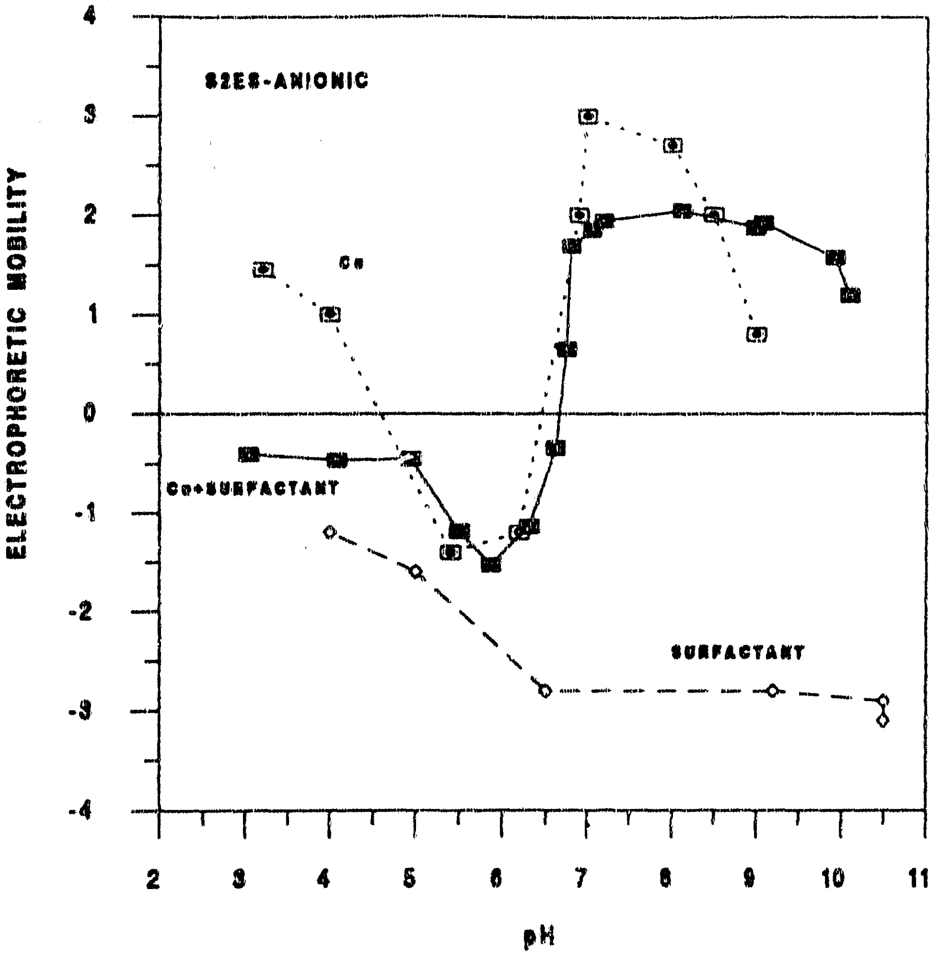


Figure 7. Electrophoretic Mobility Behavior of Anionic Surfactant (S2ES) and Copper Ions Alone and Together with Copper Ions on Galatia Fine Clean Coal at a Concentration of 10^{-4} M/L Each

is not the case for CPC which dominates and diminishes the role of the metal hydroxide in determining electrokinetic behavior.

Continuous Filtration Tests:

The effect of cake thickness on the cake moisture for various filter cycle time using the continuous vacuum drum filter is shown in Figure 8. The results show that for all different filter cycle time the optimum cake thickness is 5.5 mm, which is consistent with the results obtained in batch tests. Increasing or decreasing of cake thickness results in higher cake moisture regardless of the filtration time. It should be noted that these results were obtained at a vacuum of 17 inches of Hg compared to 23 inches of Hg used in batch tests. Efforts are in progress to modify the drum filter to achieve the higher vacuum, which is anticipated to reduce moisture significantly.

Continuous filtration tests data using a constant cake thickness of 5.5 mm are shown in Figure 9. This figure also shows cake moisture obtained with Cu^{+2} (open diamond) and Cu^{+2}-S2ES (open triangle) system. For comparison batch filtration test data (open square) are also included. Note that cake moisture obtained for the blank (no metal ion or surfactant addition) are comparative for both continuous and batch tests. These two tests provided a 35 percent moisture filter cake after 6 minutes of filtration time. When 50 ppm of copper ions were added, the filter cake moisture was reduced to 32 percent after 6 minutes of filtration time. However, for the same filtration time when 0.5 lb/ton of S2ES and copper ion (50 ppm) were added together, the moisture was reduced by another 6 percent to 26 percent. In other words, addition of the S2ES and copper ions reduced moisture in the filter cake by 25 percent compared to the blank tests.

AC Electro-Coagulation Studies:

To evaluate effect of in-situ addition of metal ion in coal slurry, studies were initiated using the AC Electro-Coagulator (AC/EC). The AC/EC technique, as mentioned earlier, neutralizes particle charge as well as provide a small amount (~10 to 15 ppm) of aluminum ions. Initial studies were conducted on monitoring the settling rate of the AC/EC treated coal slurry. A clean coal slurry containing about 13 percent solids at natural pH of 7-8 was treated through the AC/EC technique. The slurry residence time in the coagulator was kept at 1 minute and voltage and ampere were varied.

Settling rates of the coal slurry with and without AC/EC treatment are shown in Figure 10. Note, that AC/EC treated slurry using 37 volts and 70 amperes current settled faster than the untreated slurry. The settling rate of the AC/EC treated slurry was 9.0 ml/min compared to 7.5 ml/min of untreated slurry. The particle size data indicated that AC/EC treated slurry had a lower amount of ultra-fine (less than 5 micron) particles compared to the untreated one.

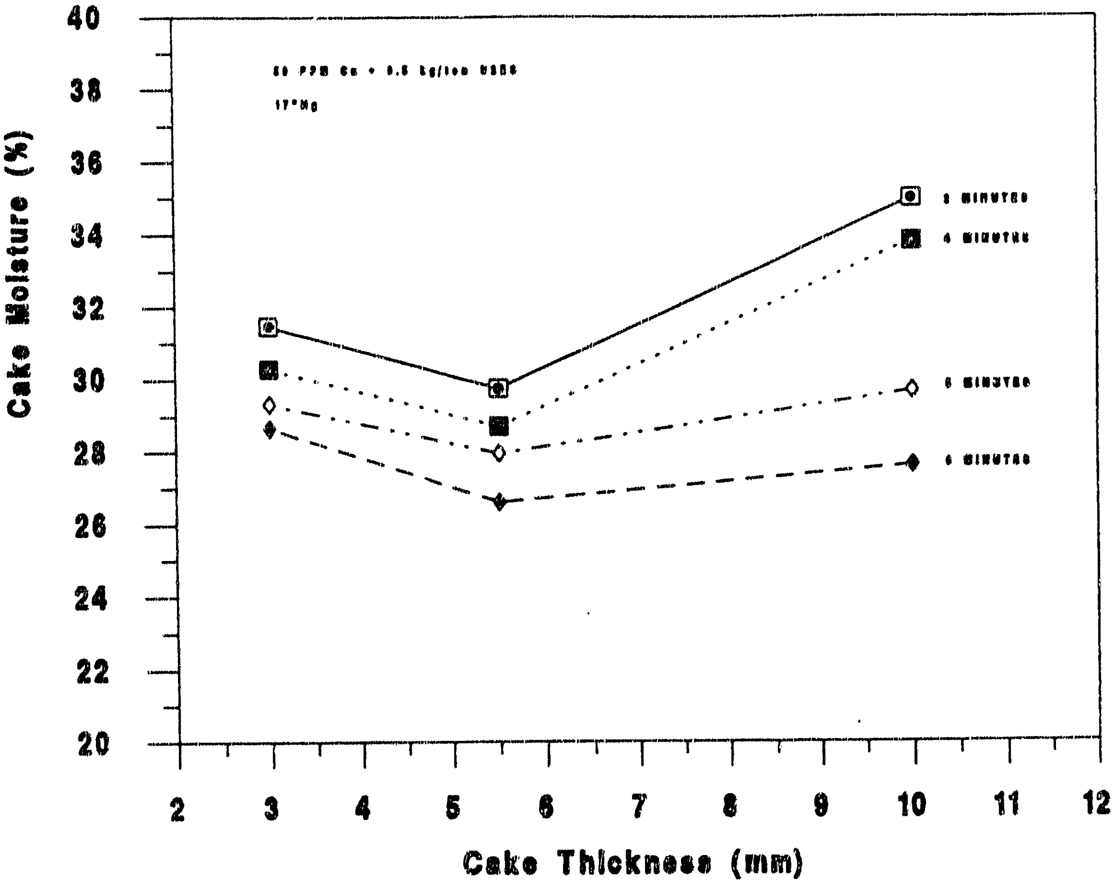


Figure 8. Effect of Cake Thickness on Moisture Content of Filter Cake at Different Dry Cycle Times Using Continuous Vacuum Drum Filter

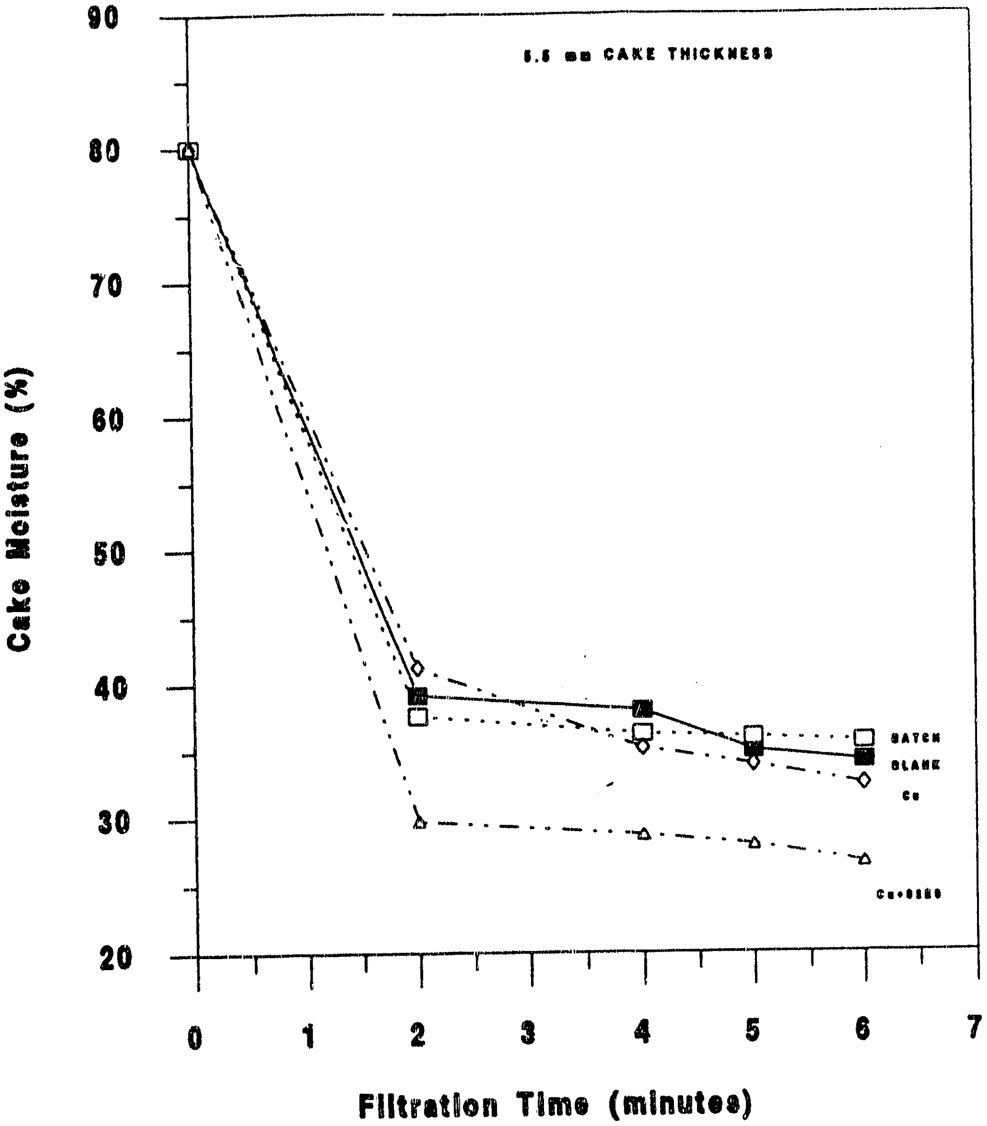


Figure 9. Continuous Filtration Test Results with and without Reagents in Baseline Batch Filtration Data Included for Comparison

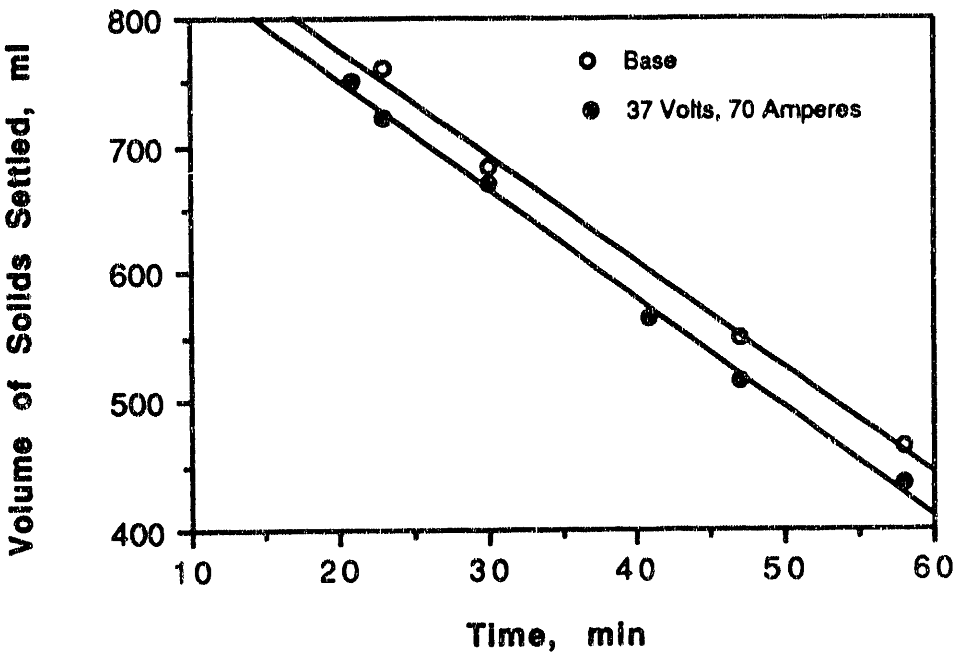


Figure 10. Comparison Between Settling Rates of Coal Slurries in a Graduated Cylinder - Treated with and without AC Electro-Coagulation (Sample Size: 1000 ml)

CONCLUSIONS AND RECOMMENDATIONS

- Adsorption studies showed that copper ions enhanced the adsorption of both cationic and anionic surfactants and had minimal effect on the adsorption of non-ionic surfactant. The most significant adsorption enhancement was observed for cationic surfactant.

- When metal hydroxide ($Cu(OH)_2$ or $Al(OH)_3$) is present with surfactant, the electrokinetic behavior of coal is determined by the metal hydroxide species. This is true for non-ionic and anionic surfactant, but not for cationic surfactant (CPC). CPC dominates and diminishes the effect of metal hydroxides for changing the electrophoretic mobility of coal.

- Continuous filtration tests showed that copper ions alone improve filtration by reducing cake moisture form 35 to 32 percent moisture. The addition of 0.5 lb/ton S2ES with copper ions further reduced the cake moisture to 26 percent.

- Continuous filtration tests confirm that the optimum cake thickness for reducing cake moisture is 5.5 mm.

- Faster settling rates and floc growth were observed for fine clean coal slurries treated with AC Electro-Coagulator. This behavior is beneficial for filtration, which may provide low moisture cakes.

FUTURE WORK

- Semi-continuous dewatering tests with rotary vacuum drum filter will be continued using the optimum amount of reagents found to be effective in batch filter leaf tests.

- Tests with AC Electro-Coagulator will be continued. Further tests on filtration will be conducted after AC/EC treatment. AC/EC apparatus operating parameters will be identified in order to obtain low moisture cakes.

PROJECT MANAGEMENT REPORT

Dec. 1, 1991 through Feb. 29, 1992

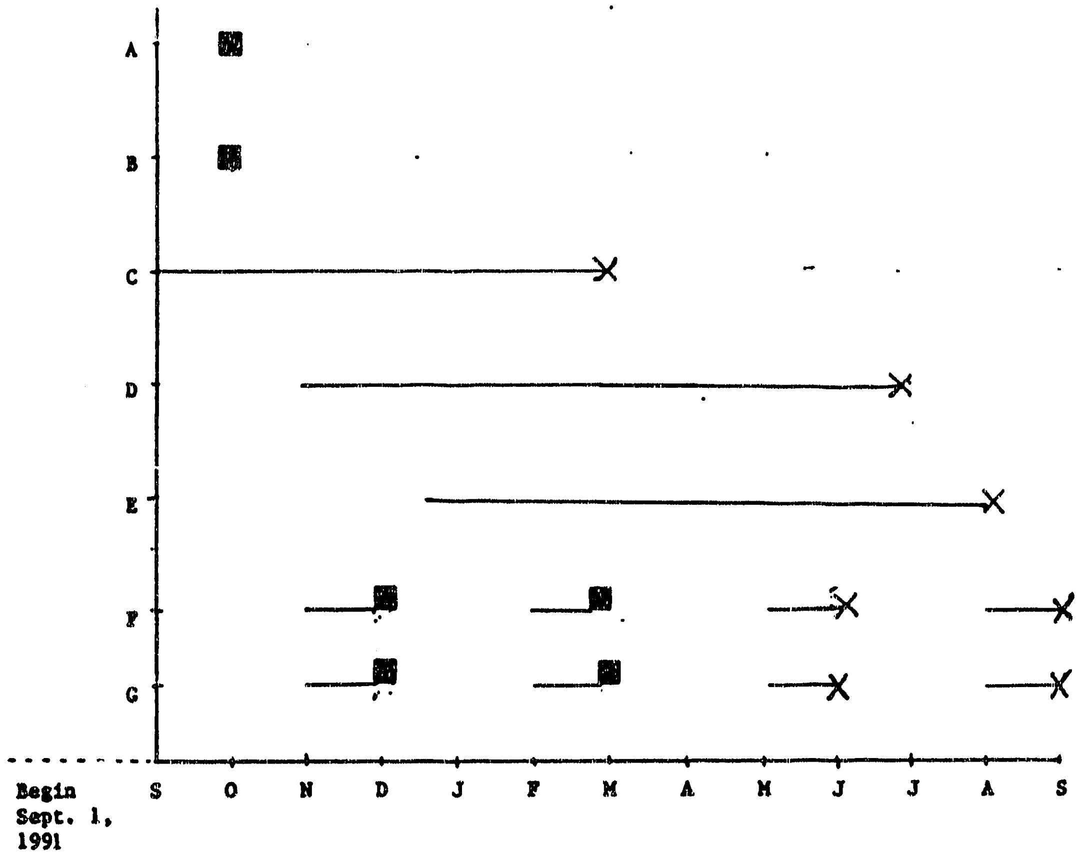
Project Title:	Dewatering Studies of Fine Clean Coal
Principal Investigator:	Dr. B.K. Parekh University of Kentucky Center for Applied Energy Research
Project Monitor:	Dr. Dan Banerjee Center for Research on Sulfur in Coal

COMMENTS

The project is progressing on schedule. At present, we do not anticipate any problems in the tasks proposed for the research program.

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.

SCHEDULE OF PROJECT MILESTONES



Hypothetical Milestones:

- A. Acquisition and Characterization of Samples (Task 1)
- B. Surface Chemical Studies (Task 2)
- C. Dewatering Studies (Task 3)
- D. AC Electro-Coagulation Studies (Task 4)
- E. Continuous Dewatering Tests (Task 5)
- F. Technical Report prepared and submitted
- G. Project Management reports prepared and submitted

Comments:

This is a 24-month research project. Task 1 and 2 were completed last year. Additional studies have been planned for Task 3.

YEAR 2: SEPTEMBER 1, 1991 TO AUGUST 31, 1992

EXPENDITURES - EXHIBIT B

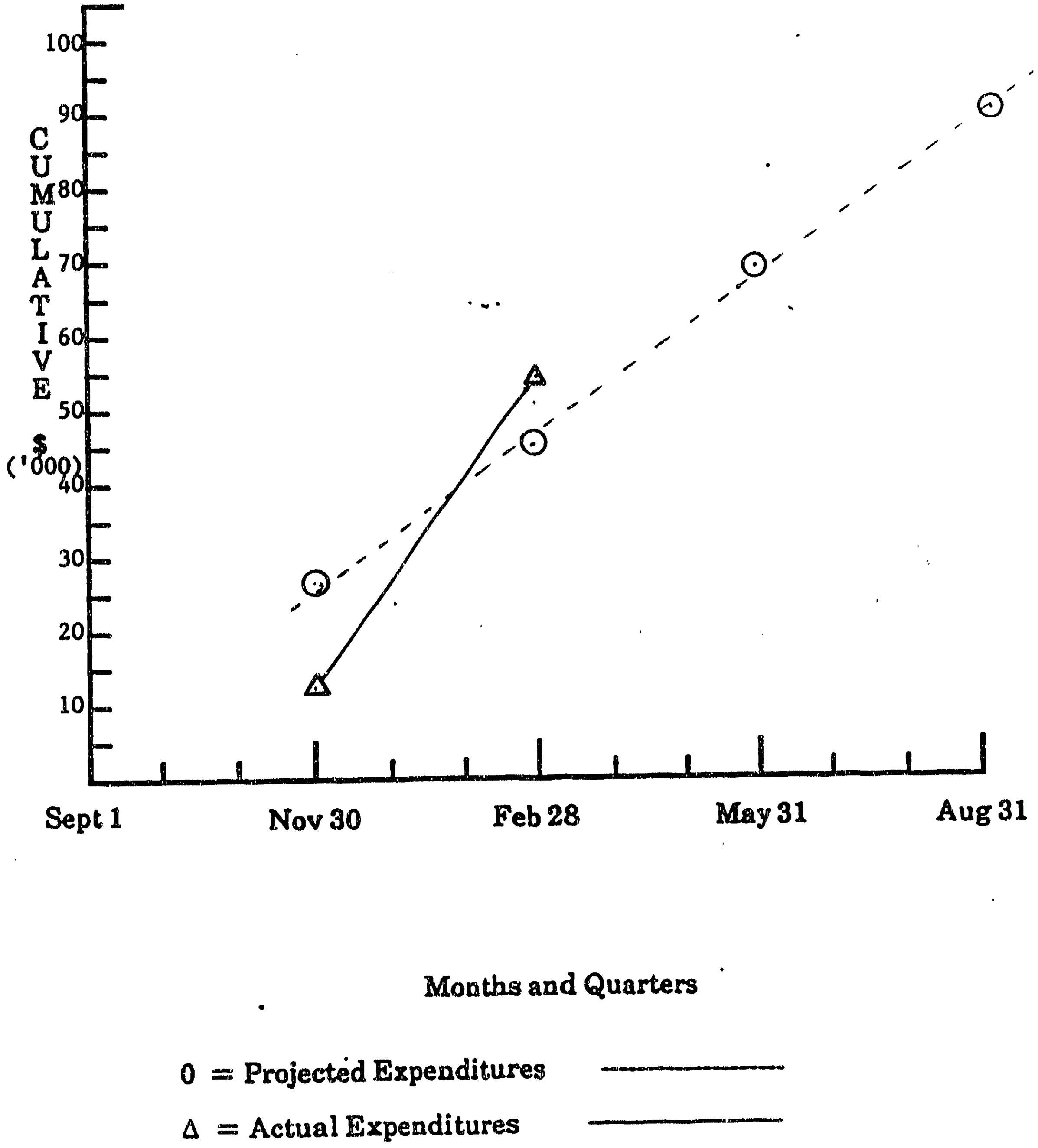
Projected and Estimated Actual Expenditures by Quarter

Quarter *	Types of Cost	Direct Labor	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
ept. 1, 1991 to ov. 30, 1991	Projected	$15,712	$1,390	$ 500	-0-	$ 500	$ 4,476	$22,579
	Estimated Actual	6,983	1,017	735		250	1,676	10,661
ept. 1, 1991 to eb. 28, 1992	Projected	31,424	2,780	1,500	-0-	1,000	8,952	45,658
	Estimated Actual	33,270	3,922	2,358		1,000	9,732	50,282
ept. 1, 1991 to ay 31, 1992	Projected	47,136	4,170	3,000	-0-	1,500	13,428	69,237
	Estimated Actual							
ept. 1, 1991 to ug. 31, 1992	Projected	62,850	5,560	4,200	-0-	2,000	17,906	92,516
	Estimated Actual							

* Cumulative by quarter

COSTS BY QUARTER - EXHIBIT C

Dewatering Studies of Fine Clean Coal



Total CRSC Award $ 92,516 Year 2

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