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Final Report

DEVELOPMENT OF THE CHEMICAL AND ELECTROCHEMICAL COAL CLEANING (CECC) PROCESS

by

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ABSTRACT

The Chemical and Electrochemical Coal Cleaning (CECC) process developed at Virginia Polytechnic Institute and State University was studied further in this project. This process offers a new method of physically cleaning both low- and high-rank coals without requiring fine grinding. The CECC process is based on liberating mineral matter from coal by osmotic pressure.

The majority of the work was conducted on Middle Wyodak, Pittsburgh No.8 and Elkhorn No. 3 coals. The coal samples were characterized for a variety of physical and chemical properties. Parametric studies were then conducted to identify the important operating parameters and to establish the optimum conditions. In addition, fundamental mechanisms of the process were studied, including mineral matter liberation, kinetics of mineral matter and pyrite dissolution, ferric ion regeneration schemes and alternative methods of separating the cleaned coal from the liberated mineral matter. The information gathered from the parametric and fundamental studies was used in the design, construction and testing of a bench-scale continuous CECC unit. Using this unit, the ash content of a Middle Wyodak coal was reduced from 6.96 to 1.61% at a 2 lbs/hr throughput. With an Elkhorn No. 3 sample, the ash content was reduced from 9.43 to 1.8%, while the sulfur content was reduced from 1.57 to 0.9%.

The mass balance and liberation studies showed that liberation played a more dominant role than the chemical dissolution in removing mineral matter and inorganic sulfur from the different bituminous coals tested. However, the opposite was found to be the case for the Wyodak coal since this coal contained a significant amount of acid-soluble minerals.

EXECUTIVE SUMMARY

A novel coal cleaning technique, the Chemical and Electrochemical Coal Cleaning (CECC) process, has been developed at Virginia Polytechnic Institute and State University (Yoon and Paul, 1987; Paul, 1988). This process is unique in its ability to liberate mineral matter from coal without comminution to ultrafine sizes. The CECC process relies on treating coal with an electrocatalyst, such as ferric ions, which creates osmotic pressure inside the pores and crevices of coal and results in fractured liberation of the mineral matter. The primary objective of the present work was to develop the CECC process.

The fundamental test work was conducted on coal samples from the Middle Wyodak and Pittsburgh No. 8 seams. Initially, Upper Freeport coal was selected as one of the samples to be tested; however, this coal did not respond well to the CECC process due to its highly oxidized state. Limited batch tests were also conducted on Widow Kennedy, Elkhorn No. 3, and Illinois No. 6 coals. The Elkhorn No. 3 coal replaced the Pittsburgh No. 8 coal in the continuous test work (Subtask 6.2).

This project started with the acquisition, preparation (Task 2) and characterization (Task 3) of the coal samples. Parametric batch test work (Task 4) was conducted on the Middle Wyodak and Pittsburgh No. 8 coals in order to model the effects of particular parameters on the CECC process. The process conditions were then optimized on the basis of the results of the parametric tests. Studies were also conducted to investigate the various fundamental aspects of this process. Based on the information collected, a bench-scale continuous unit was designed and constructed (Task 5). Finally, continuous testing of the CECC process (Task 6) was conducted using a bench-scale unit.

In Task 2, test-size samples of each of the selected coals were created by crushing, screening, riffling, and coning. Once prepared, the samples were stored under nitrogen until needed.

In Task 3, sample characterization was conducted on representative head samples of the Middle Wyodak, Upper Freeport and Pittsburgh No. 8 coals. Proximate and ultimate analyses were carried out for the three coal samples, as well as for the Elkhorn No. 3 coal. Mineral matter composition, based on ash analysis, was also determined for these four coal samples. The surface area analyses of the Middle Wyodak coal showed it to be higher than that of the Upper Freeport coal. Pore size distribution measurements showed the total pore volume of the Middle Wyodak coal to be about twice that for the Upper Freeport coal. Fourier Transform Infrared (FTIR) Spectroscopic and Scanning Electron Microscopic (SEM) analyses were also used to characterize the coal surfaces. The X-ray Diffraction (XRD) analysis of the head sample of the Middle Wyodak coal was used to determine the distribution of the mineral matter. Using image analysis, the size distribution of the mineral matter was obtained.

Based on information derived from the project, "Advanced Systems for Producing Super-Clean Coal," (Contract No. DE-AC22-86PC91221), the most critical CECC operating parameters found were as follows: acid concentration, percent solids, ferric ion concentration and temperature. In Task 4, these four operating parameters were studied in a series of statistically designed parametric tests conducted on the Middle Wyodak and Pittsburgh No. 8 coals.

In the parametric testing of the Middle Wyodak coal, statistical analysis of the results indicated that of the four parameters studied, only the effects of acid concentration and temperature were significant in the mineral matter removal by the CECC process. An increase in temperature or acid concentration improved the rejection of mineral matter, while an increase in the ferric ion concentration or percent solids had little effect on ash rejection. The average ash rejection (by weight) obtained in these tests was 66.4%, while sulfur rejection was negligible. The poor sulfur rejection was attributed to adsorption of sulfuric acid by coal.

The results of the batch tests for the Middle Wyodak coal also showed that dissolution, rather than liberation, played a major role in the ash removal. Verified by complete mass balance studies, the predominance of dissolution was attributed to the presence of significant amounts of acid-soluble carbonates and carboxylates of Ca and Mg in this particular coal sample. The XRF and chemical analysis of the feed, as well as elemental analysis of the solution obtained after the CECC treatment, confirmed the presence of carbonates and carboxylates of Ca and Mg.

The parametric test data for the Pittsburgh No. 8 coal indicated that mineral matter removal increased with a decrease in percent solids or ferric ion addition. The opposite was observed when acid concentration or temperature was decreased. Statistically, there was a strong interaction between the effects of acid concentration and ferric ion addition. Mineral matter rejection was favored at low ferric ion addition and high acid concentration. The low ferric ion addition required for this coal was attributed to the additional ferric ions generated from the dissolution of ferruginous minerals (e.g., pyrite). The large amounts of ferric ions present in the system require corresponding amounts of counter ions, hence the need for higher acid concentrations. The parametric tests showed ash and sulfur rejections (by weight) of as high as 56 and 33%.

The mass balance in these tests indicated that liberation played the dominant role in the removal of mineral matter and pyritic sulfur from Pittsburgh No. 8 coal. This was opposite to what was observed for the Middle Wyodak coal since the Pittsburgh No. 8 sample did not contain a significant amount of acid-soluble minerals. For the other samples tested, such as the Upper Freeport, Widow Kennedy and Elkhorn No. 3 coals, the mass balance studies also suggested that liberation was more responsible for the ash rejection in the CECC process.

The optimum operating conditions for the processing of the Middle Wyodak and Pittsburgh No. 8 coals were determined using response surface analyses of the parametric test data. At these statistically determined optimum conditions, the predicted % ash rejections for the Middle Wyodak and Pittsburgh No. 8 coals were 65.5 and 54.7%, respectively. Tests conducted at the predicted optimum conditions for these two coal samples validated the reliability of the statistical analyses.

After the optimum conditions of the CECC process were established and validated, mechanistic studies were carried out (Subtask 4.3). Since the CECC process is capable of removing mineral matter by both dissolution and electrochemically induced liberation, the leaching kinetics of some of the mineral matter species present in the Middle Wyodak and Pittsburgh No. 8 coals were studied. Samples of the solutions were taken from these tests and analyzed for Fe, Ca, Mg, Al and Si. For the Middle Wyodak coal, the dissolutions of the mineral matter containing these species were significant, except for the Si-containing minerals. The rate constants for the dissolution of Ca, Mg, Fe, Al and Si were determined to decrease in the following order: Ca > Mg > Fe > Al > Si. The kinetics of the release of Ca into solution was more than 3 times higher than those for the other species, presumably because Ca is present in the Middle Wyodak coal as acid-soluble carbonates and exchangeable cations.

Investigation of the leaching kinetics of the different soluble mineral matter present in the Pittsburgh No. 8 coal showed that the amounts of the different species dissolved, except Fe, were much lower than those from the Middle Wyodak coal. This was expected since the Pittsburgh coal had a much higher pyrite content than the Middle Wyodak sample. The results of the leaching studies agreed well with the conclusion drawn from the parametric tests that liberation, not dissolution, is the major mechanism responsible for mineral matter rejection from the Pittsburgh No. 8 coal.

In the mechanistic studies, the regeneration of the ferric ions by alternative methods was investigated. The use of *Thiobacillus ferrooxidans* bacteria and air oxidation to regenerate ferric ions was considered in this phase of the project. The conditions for the optimum cleaning of the Middle Wyodak and Pittsburgh No. 8 coal samples by the CECC process using the bacterial regeneration scheme were determined using parametric tests and response surface analyses of the results. The variables studied were pH, temperature, substrate concentration, inoculum concentration and lead time. Validation tests conducted at the determined optimum conditions for both coal samples showed good agreement with the predicted values.

For both coal samples, the results showed that slightly acidic conditions and low substrate concentrations resulted in higher mineral matter rejection. This was expected since the growth of the bacteria is known to be more favorable under less acidic conditions. The effects of all five parameters were found to be significant for both coal samples.

Using bacteria to regenerate the ferric ions, the parametric test data showed that the removal of mineral matter was not as high as that obtained using the electrochemical reactor. This may be attributed to a number of factors such as the higher pH and lower temperature used in the bacterial regeneration scheme. The kinetics and efficiency of ferric ion regeneration using the bacteria were probably not as good as those in the electrochemical regeneration scheme; however, the sulfur removal obtained for the Pittsburgh No. 8 coal was greater in the bacterial tests. This may be attributed to bacterial desulfurization since the coal samples were in direct contact with the bacteria in the parametric tests.

The use of air oxidation for ferric ion regeneration was also investigated. Using an apparatus specially designed for these tests, ferric ions were regenerated separate from the coal reactor. The mineral matter and sulfur rejection observed in these tests were also not as good as those obtained in the electrochemical regeneration scheme. The electrochemical scheme, having been shown to be better for the CECC process, was used in the design of the continuous unit.

Liberation of mineral matter and pyrite by the CECC process was studied using image analysis. The feed and processed samples were analyzed for the amount of free coal, free mineral matter, free pyrite and locked composite particles. The liberation study for the 65 x 325 mesh Pittsburgh No. 8 coal showed that the amounts of mineral matter and pyrite liberated by the CECC process increased significantly with processing time; however, a significant fraction of the liberated mineral matter was larger than 325 mesh. This finding provides an explanation for the poor result obtained with this sample when a 325 mesh screen was used to remove the liberated mineral matter. Thus, other methods of removing the liberated mineral matter, such as flotation, were considered.

Liberation studies on the 65 x 150 mesh Elkhorn No. 3 coal showed that the amounts of mineral matter and pyrite liberated by the CECC process increased with time. The free mineral matter underwent some reduction in size during the CECC treatment and the majority of the liberated mineral particles in this sample were finer than 150 mesh. This is opposite to what was found for the Pittsburgh No. 8 coal, which may explain the better response of the Elkhorn No. 3 coal to CECC treatment.

Two major problems were encountered in the CECC process, namely: i) the electrocatalytically induced liberation of mineral matter did not occur when oxidized coal was the substrate, and ii) screening was not effective for separating the coarse liberated mineral matter from some of the coals tested. The performance of the CECC process is affected significantly by the degree of oxidation of the feed because the liberation mechanism is based on the incipient oxidation of the coal. This was the main reason why Pittsburgh No. 8 coal was used, instead of Upper Freeport coal, as the second coal for the fundamental test work. For all of the coals studied, the higher the degree of surface oxidation of the feed sample, the lower the ash and sulfur rejection. The second problem, as discussed above in the liberation studies, required the use of alternative methods of recovering the clean coal. Tests conducted using flotation, instead of wet-screening, to separate the clean coal from the liberated mineral matter showed significantly improved results.

The data collected in the batch tests were used in the design of the reactor and CECC circuit (Task 5). The bench-scale CECC continuous unit was designed for processing 1-3 lbs/hr of coal. An electrochemical regeneration scheme was incorporated into the reactor design, which consisted of five banks. This design gave it enough flexibility to handle different retention times.

The continuous bench-scale unit was operated at 2 lbs/hr in the shakedown tests and continuous test work (Task 6). Shakedown testing showed that the continuous unit was able to reduce the ash content of a fresh Middle Wyodak coal sample from 5.37% to as low as 1.16%.

The continuous testing of the CECC bench-scale unit was conducted on the Middle Wyodak and Elkhorn No. 3 coal samples. The Pittsburgh No. 8 coal was replaced in the continuous test work due to problems with removing coarse liberated mineral matter and with the samples being oxidizidation. The CECC unit was run under the optimum conditions established for these coal samples in Task 4. For the Middle Wyodak coal, the ash content was reduced from 6.96% to as low 1.61%, corresponding to an ash rejection (by weight) of about 83%. The ash and sulfur contents of the Elkhorn No. 3 coal were reduced from 9.43% and 1.57% to 1.8% and 0.9%, respectively, with yields ranging from 72 to 75%. The average ash and sulfur rejections were calculated to be around 84% and 47%. The CECC continuous unit was used to treat -325 mesh Elkhorn No. 3 coal samples and gave ash and sulfur rejection values of as high as 77% and 66%. In these tests, the clean -325 mesh coal particles were separated from the liberated mineral matter through microbubble column flotation, instead of wet-screening.

Thus, the CECC process offers a new method of cleaning coal efficiently. It is one of the few processes that can be used for upgrading both low and high rank coals. The technique can be used for producing superclean coals containing less than 2% ash containing less than 2% ash and very little inorganic sulfur. This can be achieved without pulverizing the coal to micron sizes, which offers two main advantages as compared to other advanced physical coal cleaning processes. One is the elimination of the cost of grinding the coal to micron-sizes, and the other is that the clean coal produced by this process can be used for producing highly-loaded coal water mixture (CWM) fuel.

There may be two other added benefits of the process, which were not explored in the present work. One is that clean coal produced by this process should have higher ash fusion temperature than those produced by the advanced physical coal cleaning processes since the acid-to-base oxide ratio of the product coal is increased by the acid treatment. The other is the CECC process may be removing substantial amounts of trace elements from the coal since it involves a leaching-type process.

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INTRODUCTION

The Chemical and Electrochemical Coal Cleaning (CECC) process is an advanced physical coal cleaning process that can achieve mineral liberation with a minimum amount of grinding. This process is considered to liberate mineral matter from coal by an osmotic pressure mechanism. Previous work (Paul, 1988; Paul and Yoon, 1990) has shown that the CECC process can reduce the ash content of a variety of subbituminous and bituminous coals.

In the CECC process, coal is electrolyzed in a mildly acidic medium containing 1 millimolar or less ferric ions, differentiating this process from ferric ion leaching processes where much higher ferric ion concentrations are used. Due to the acidic environment, the minerals present in coal are positively charged. Coal acquires a positive charge as well, partly due to H^+ adsorption, but mainly due to the superficial oxidation of the coal surface resulting from the electron loss caused by the reduction of the ferric ions to ferrous ions on the coal surface (Dhooge and Park, 1983; Anthony and Linge, 1983). When both coal and mineral matter are positively charged as such, counter ions congregate in the vicinity of their surfaces, setting up electrical double layers. Inside the small crevices or pores on the coal surface, the double layers will overlap each other. This overlap reduces the aqueous chemical potential inside the pore below that of the solution outside and creates an osmotic pressure (Schofield, 1946; Usui and Hachisu, 1984; Koval'chuk and Shilov, 1987). The mineral matter trapped inside the pore can be liberated by the osmotic pressure, as theoretical computations have shown that this pressure ranges from 0.7 to 7 atm between surfaces that are 100 to 1000 Å apart (Paul samples.

and Yoon, 1990). Further the osmotic pressure helps initiate or propagate cracks along the coal maceral-mineral boundaries to promote selective breakage, as evidenced by Scanning Electron micrographs of the treated coal (Paul, 1988; Basilio *et al.*, 1992).

Most of the liberated mineral particles are much smaller than their parent coal particles and can be separated by a simple size-based separation technique such as screening. The ferric ions used in the process can be regenerated by several different methods such as aeration, microbial oxidation and electrochemical oxidation.

The objectives of the present work were to: (a) study the mechanisms by which the Chemical and Electrochemical Coal Cleaning (CECC) process removes mineral matter and pyritic sulfur from coal, (b) learn more about the operating parameters of the process, (c) collect engineering information for scale-up of the process, and (d) test the CECC process on a bench-scale continuous operation.

TASK 1 - PROJECT PLANNING

The Cost, Management and Work Plans were approved by the DOE Technical Project Officer. A key activity in this task was the selection of the coals for testing. Since one of the major objectives of this project was to develop an understanding of the mechanisms governing the operation of the process, coals were selected on the basis of the researchers' familiarity and experience with them. The DOE had requested that Pittsburgh No. 8, Illinois No. 6 and/or Upper Freeport coals be considered in the test program. After careful review of all test data, Middle Wyodak and Widow Kennedy coals were initially selected for use in the batch testing program and the Upper Freeport, Illinois No. 6 and Pittsburgh No. 8 coals for use in the continuous test program (Task 6).

This decision was based on past experience. The Middle Wyodak and Widow Kennedy coals had shown mineral matter reductions ranging from 40 to 60 percent. In view of these substantial ash reductions and the researchers' familiarity with these samples, it was decided to base most of our developmental research work on these coals. By contrast, very few test data were found for the three coals recommended by DOE. Tests conducted on these coals indicated that the Upper Freeport coal responded fairly well to the CECC process with ash reductions of about 35%, whereas, the Illinois No. 6 and Pittsburgh No. 8 coals yielded ash reductions that were generally less than 20%. However, a Pittsburgh No. 8 sample from Pennsylvania showed ash reductions after CECC treatment ranging from 20 to 50%.

After discussions with DOE, the Widow Kennedy coal was replaced as a primary sample by the Upper Freeport coal. As will be shown in Task 4, the Upper Freeport coal, which was severely oxidized, did not respond positively to CECC treatment. This sample was then replaced by the Pittsburgh No. 8 coal, which was used in the Batch Tests (Task 4). There were, however, some problems found in the CECC treatment of the Pittsburgh No.8 coal, dealing mainly with the inability of screening to separate the clean coal from the liberated mineral matter. With the approval of DOE, the Pittsburgh No. 8 coal was replaced in the Continuous Test Work (Subtask 6) with Elkhorn No. 3 coal. This is discussed in more detail in Tasks 4 and 6.

TASK 2 - SAMPLE ACQUISITION, PREPARATION AND STORAGE

At the start of the project, a 55-gallon drum of Middle Wyodak coal was obtained from the Kerr-McGee Coal Corporation in Gillette, Wyoming. As outlined in the Work Plan, the coal was crushed to 12-mesh topsize in a hammermill and split into four parts: A1 (reserve sample), A2 (batch testing sample), B1 (retesting sample), and B2 (continuous unit test sample). Each split was analyzed for sulfur and ash content, and the representativeness of each sample determined. Results of the sampling work, which are summarized in Table I, indicate very excellent agreement of sulfur and ash values within the different sample splits. Individual sulfur and ash deviations from the sample average appear to be very good.

Table I. Ash and sulfur analyses for sample splits of the Middle Wyodak coal.

Sample No.	Ash (%)	Sulfur (%)	Ash Deviation from Average (7.770%)	Sulfur Deviation from Average (0.472%)
Sample A1	7.931	0.483	0.161	0.011
Sample A2	7.955	0.465	0.185	0.007
Sample B1	7.593	0.473	0.177	0.001
Sample B2	7.603	0.470	0.167	0.002

A statistical analysis of the results indicates that the ash and sulfur values are within the 95% confidence level with ash values falling between 7.80 and 8.64 and sulfur values between 0.44 and 0.59. Since the sulfur and ash analyses confirmed that crushing and splitting had been properly implemented, the samples were crushed to the required test-sample size, as described in the work plan.

For Middle Wyodak, the total weight of the four splits was 123.7 kg. Split A1 accounted for 36.7 kg; split A2, 30.7 kg; split B1, 28.2 kg and split B2, 28.1 kg. As discussed in the Work Plan, split A1 was designated as the reserve sample for the project, split B1 for use in Task 4 as part of the validation test work (Subtask 4.2), and split B2 was targeted for use during the Continuous Unit Operation phase (Task 6). Of the four samples, splits A1, B1, and B2 were stored in bulk under nitrogen. Although an earlier plan had specified that split B1 was to be further crushed and riffled into test samples, this sample was instead stored under nitrogen at a larger top size to help retard oxidation, since it was not planned for use until Subtask 4.2, approximately one year into the project. Completed work-up of the B1 split was rescheduled closer to the date that the sample would be used in Subtask 4.2.

Split A2 of the Middle Wyodak coal was targeted for use in the Parametric Test work (Subtask 4.1). As outlined in the Work Plan, this sample split was further crushed to 65-mesh top-size and riffled into four lots labeled A2d ("d" for dry), A2w ("w" for wet), A2c ("c" for clean) and A2s ("s" for stored). The A2d sample was dry-screened to provide 65 x 200-mesh, 200 x 325-mesh and 325-mesh x 0 material; the A2w sample was wet-screened to provide the same splits. The A2c sample was to be cleaned by a specific gravity or flotation method before CECC treatment. But since this work was not scheduled until the end of the Parametric Testing phase (Subtask 4.1), the precleaning step was postponed until the sample was ready for testing in order to help prevent sample degradation via oxidation. The A2s sample was stored to be used in the case that more sample was needed. Table II provides an overview of the samples collected as part of this work-up effort.

Table II. Tabulation of the samples collected through work-up of the Middle Wyodak coal.

Split	Sample	Mesh size	Amount collected	Processing Technique
A2			30.7 kg	Sample further crushed to 65-mesh topsize and worked up as follows:
	A2d		7.5 kg	Dry screened to provide the following:
		65 x 200-mesh	5.7 kg	
		200 x 325-mesh	1.6 kg	
		325-mesh x 0	0.2 kg	
	A2w		6.3 kg	Wet-screened to provide the following:
		65 x 200-mesh	3.2 kg	
		200 x 325-mesh	0.9 kg	
		325-mesh x 0	2.2 kg	
	A2c		8.2 kg	Stored in bulk under nitrogen.
	A2s		8.7 kg	Stored in bulk under nitrogen.
B1			28.2 kg	Stored in bulk under nitrogen.
B2			28.1 kg	Stored in bulk under nitrogen

Through the efforts of the DOE COR, a 55-gallon drum of Upper Freeport coal was obtained from Praxis Engineers. As outlined in the Work Plan, this coal was crushed to 12-mesh topsize in a hammermill and split into four parts: A1, A2, B1 and B2. Sulfur and ash analyses were conducted on each split to determine the representativeness of the four splits. Results of the sampling work are summarized in Table III.

Statistical analysis of the results indicates that the sulfur and ash values all lie within the 95% confidence level with sulfur falling between 2.521 and 2.579% and ash between 17.363 and 17.488%. Since all of these values lie within the 95% confidence interval, these analytical results indicate good representativeness within the samples. This confirms that the crushing and splitting were properly implemented and thus that the samples were crushed to the required test-sample size.

Table III. Ash and sulfur analyses for sample splits of the Upper Freeport Coal.

Sample No.	Ash (%)	Sulfur (%)	Ash Deviation from Average (17.43)	Ash Deviation from Average (2.55)
Sample A1	17.45	2.54	0.184	0.013
Sample A2	17.39	2.57	0.212	0.018
Sample B1	17.40	2.56	0.126	0.010
Sample B2	17.47	2.53	0.128	0.023

For the Upper Freeport coal, the total weight of the four splits was 144.75 kg. Split A1 accounted for 36.62 kg; split A2, 39.09 kg; split B1, 34.18 kg and split B2, 34.87 kg. As with the Middle Wyodak coal, three of these splits A1, B1 and B2 were stored in bulk under nitrogen for later use. Split A2, however, was crushed and screened into test-size samples for immediate use.

TASK 3 - SAMPLE CHARACTERIZATION

Ultimate and proximate analyses were conducted on samples of Middle Wyodak and Upper Freeport coal, as shown below in Tables IV and V, respectively. These included a head sample and a sample of the four main splits for each coal.

A sample of Middle Wyodak coal was dry-ground to 65-mesh topsize in a ball mill and the 65 x 325 mesh fractions were collected by dry-screening. The samples were riffled into 100-g lots, sealed in air-tight plastic bags, and stored in a freezer. The ash and sulfur analyses for the different fractions are given in Table VI.

Table IV. Ultimate analysis of the Middle Wyodak coal (dry basis).

Analysis	Head Sample	Split A1	Split A2	Split B1	Split B2
Carbon	68.33				
Hydrogen	4.66				
Oxygen	18.17				
Nitrogen	1.10				
Sulfur (total)	0.42	0.49	0.56	0.54	0.56
Sulfate	0.01				
Pyritic	0.19				
Organic	0.22				
Ash	8.18	8.17	7.91	8.79	8.06
Moisture	24.62	19.03	25.10	27.22	26.95
Btu/lb	11722	11459	11473	11309	11491

Table V. Results of ultimate and proximate analyses of Upper Freeport coal.

Analysis (%)	Head Sample	Split A1	Split A2	Split B1	Split B2
Dry-loss	0.81	1.08	1.18	1.11	1.20
Carbon	70.29				
Hydrogen	4.45				
Oxygen	5.45				
Nitrogen	1.33				
Sulfur (total)	2.58	2.62	2.89	2.68	2.84
Sulfate	0.05				
Pyritic	1.93				
Organic	0.60				
Ash	17.79	17.55	17.60	17.50	17.37
Btu/lb	12503	12518	12676	12688	12530

The ash analyses for mineral matter of the Middle Wyodak and Upper Freeport coal head samples are given in Tables VII and VIII. The majority of the mineral matter

Table VI. Ash and sulfur analyses for sized fractions of Middle Wyodak coal.

Fraction (mesh)	Weight (g)	Weight (%)	Cum. Wt. (%)	Ash (%)	Cum. Ash (%)	S (%)	Cum S. (%)
65 x 200	19.53	53.2	53.2	5.95	5.95	0.50	0.50
200 x 325	5.88	16.0	69.2	6.85	6.16	0.47	0.49
-325	11.30	30.8	100.0	9.54	7.20	0.45	0.48
composite	36.71	100.0					

Table VII. Coal ash analysis for mineral matter of Middle Wyodak coal.

Mineral Analysis	% Weight (Ignited Basis)
Silicon (SiO_2)	38.62
Alumina (Al_2O_3)	14.81
Titania (TiO_2)	1.39
Ferric Oxide (Fe_2O_3)	6.68
Lime (CaO)	20.52
Magnesia (MgO)	4.68
Potassium Oxide (K_2O)	0.37
Sodium Oxide (Na_2O)	0.60
Sulfur Trioxide (SO_3)	8.87
Phosphorus Pentoxide (P_2O_5)	1.07
Strontium Oxide (SrO)	0.31
Barium Oxide (BaO)	0.42
Manganese Oxide (Mn_3O_4)	0.02

found in the Middle Wyodak coal was oxides of Si, Ca and Al. For the Upper Freeport coal, the mineral matter was mostly oxides of Si, Al and Fe. The amount of Fe oxide present in the Middle Wyodak coal is much smaller than in the Upper Freeport sample. However, there is a significant amount of acid-soluble Ca and Mg oxides in the subbituminous coal.

FTIR spectroscopic analyses of the Middle Wyodak and Upper Freeport coal head samples were carried out using diffuse reflectance infrared spectrometry (DRIFTS). The spectra were recorded using a Perkin Elmer Model 1710 FTIR spectrometer equipped with a mercury cadmium telluride (MCT) detector. A Barnes Analytical/Spectra-Tech

Table VIII. Coal ash analysis of Upper Freeport coal.

Mineral Analysis	%Weight (Ignited Basis)
Aluminum (Al_2O_3)	24.59
Barium (BaO)	0.13
Calcium (CaO)	0.96
Iron (Fe_2O_3)	20.45
Magnesium (MgO)	1.03
Manganese (MnO_2)	0.02
Phosphorus (P_2O_5)	0.39
Potassium (K_20)	2.60
Silicon (SiO_2)	47.83
Sodium (Na_2O)	0.26
Strontium (SrO)	0.04
Sulfur (SO_3)	0.55
Titanium (TiO_2)	1.15

DRIFTS accessory was used in these measurements. The 10% coal samples in KBr were ground together in a Wig-L-Bug for 2 minutes and their spectra measured by averaging 100 scans at 4 cm^{-1} resolution. Spectral-grade KBr, ground for 2 minutes, was used as the reference material.

Figure 1 shows the diffuse reflectance spectra obtained for the head samples of the Middle Wyodak and Upper Freeport coal. The trends in the spectra were typical of those found in the absorption spectra for these types of coals in KBr pellets. The intensity of the broad phenolic O-H stretching bands above 3100 cm^{-1} decreased as the coal rank increased. The band observed at 3050 cm^{-1} is due to the aromatic C-H stretching

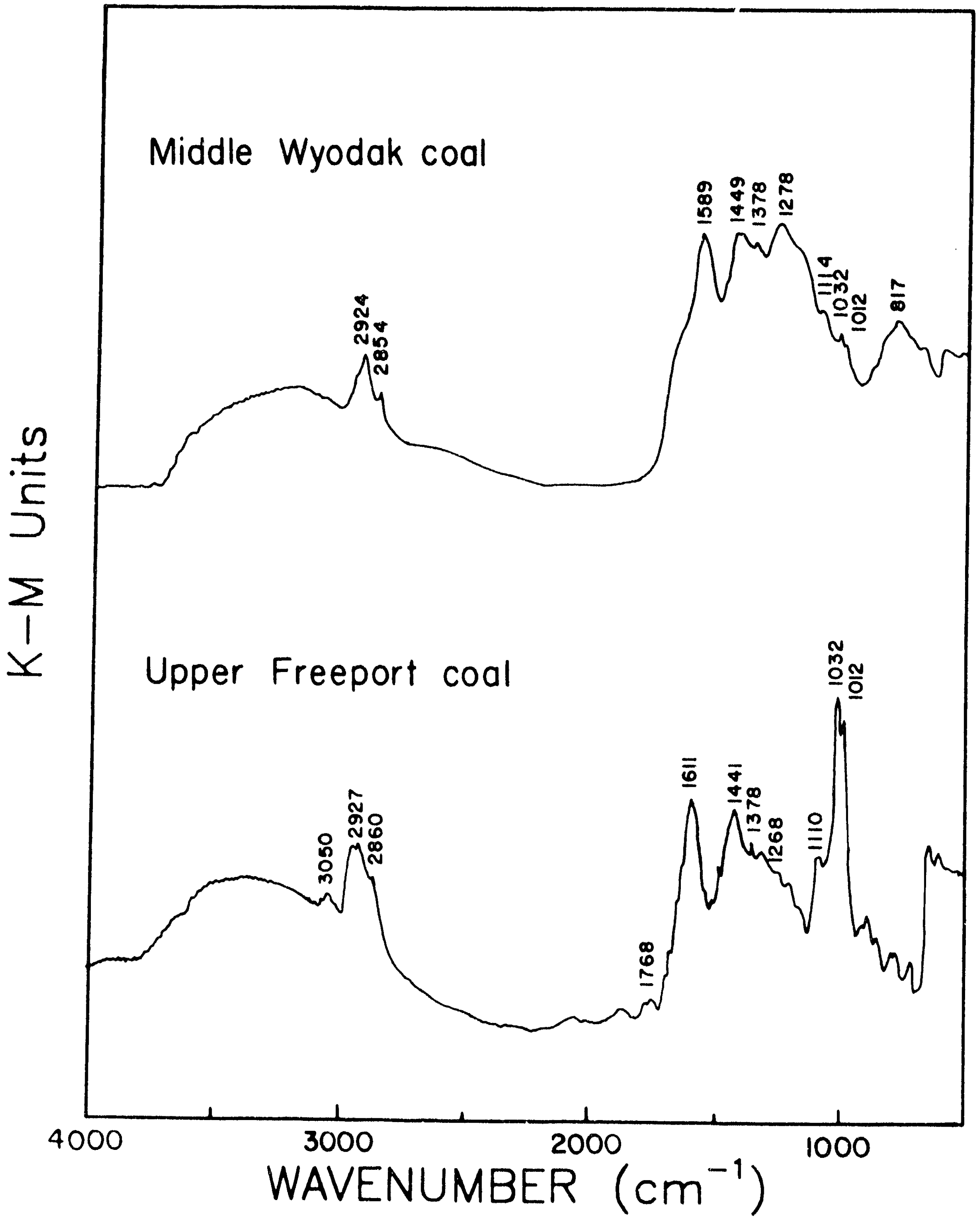

Figure 1. Diffuse reflectance spectra of 10% Middle Wyodak coal in KBr (a) and 10% Upper Freeport coal in KBr (b).

vibrations, while the absorption peaks found at 2960, 2925 and 2854 cm^{-1} may be attributed to aliphatic C-H vibrations. The signal intensity ratio of the aromatic C-H stretching band to the aliphatic C-H vibrations is known to increase with coal rank. This was also observed in the spectra of the two head samples.

The band observed at 1589 cm^{-1} for the Middle Wyodak coal may be attributed to the carboxyl group vibrations. This band was not present in the spectrum for the Upper Freeport coal. However, bands are observed at 1611, 1768 cm^{-1}, as well as sharp bands that appear between these two bands. These may be attributed to carbonyl vibrations, which are indicative of the oxidation of this coal sample. There are also sharp peaks at 1032 and 1012 cm^{-1}, which were more significant in the spectrum for the Upper Freeport coal sample. These two absorption peaks are due primarily to the presence of clay minerals. The ash analysis of these two samples verified this observation. The results showed that DRIFTS is useful for coal surface characterization. This technique was used later to characterize the changes in the surface of some of the treated coal samples in Task 4.

The head sample of the Middle Wyodak coal was also characterized using X-ray diffraction (XRD) analysis. Since this technique could not be used on pure coal samples because the minerals present in the coal were too dilute to be directly identified, the analyses were done on the low-temperature ash (LTA). The results showed that the dominant minerals present in the Middle Wyodak coal samples are kaolinite (density = 2.63 g/cc) and quartz (density = 2.65 g/cc).

Based on this information and the data from the X-ray fluorescence (XRF) analysis of the low-temperature ash, the distribution of the mineral matter present in the Middle Wyodak coal was estimated. Table IX shows that about 67% of the minerals present in the coal is kaolinite and quartz. These values were obtained by assuming that all of the Al found in the coal was in the form of kaolinite, while the rest of the Si not found in the kaolinite was in quartz. It is interesting to note that 16.95% Ca and 5% Mg were also present in the coal sample. Extended X-ray absorption fine structure (EXRAFS) spectroscopic analysis by other researchers showed that these elements are present in coal as exchangeable cations. It is believed that they are molecularly dispersed throughout the coal maceral as the salt of carboxylic acids. The amount of pyrite was calculated from the amount of pyritic sulfur present in the coal, while the remaining Fe was assigned to FeO OH.

Table IX. Distribution of mineral matter in Middle Wyodak coal.

Mineral	Weight Percent
$Al_4Si_4O_{10}$	42.31
SiO_2	25.84
FeS_2	3.88
$FeO \cdot OH$	5.80
Ca^{2+}	17.12
Mg^{2+}	5.05

Scanning electron microscopy (SEM) was also used to characterize the surface of the two head samples. Figure 2 shows the SEM photomicrographs of the Middle Wyodak and Upper Freeport coal samples. Pyrite grains are visible in the Upper Freeport coal sample, but not in the Middle Wyodak coal in this particular photomicrograph.

The size distribution of the mineral matter present in a 28 x 0 mesh fraction of the Middle Wyodak coal head sample was determined using a Zeiss SEM-IPS image analyzer interfaced with a Cambridge Stereoscan 120 SEM. Back-scattered electron images were collected from the polished cross-sections of coal particles embedded in epoxy resin. The mineral matter was discriminated from the coal based on gray level, which is proportional to the average atomic number of an individual mineral. Pyrite shows the highest gray level, followed by other minerals such as clay and quartz, and then by coal.

Assuming that the mineral matter present in the Middle Wyodak coal is pyrite, kaolinite and quartz, the area of each mineral particle was measured using the image analyzer. These data were then converted to mass using densities of 5.01 and 2.65 g/cc for pyrite and the other minerals, respectively. The results presented in Figure 3 show the mass percent passing a given particle size for pyrite and total mineral matter (which includes quartz, kaolinite and pyrite). The 80% passing size of pyrite and the total mineral matter found in the 28 x 0 mesh size Middle Wyodak coal were approximately 45 and 125 microns. Surface area and pore size distribution measurements were carried out for the Middle Wyodak and Upper Freeport coal samples obtained in Task 2. The measurements were done by the Micromeritics Instruments Corporation using the head

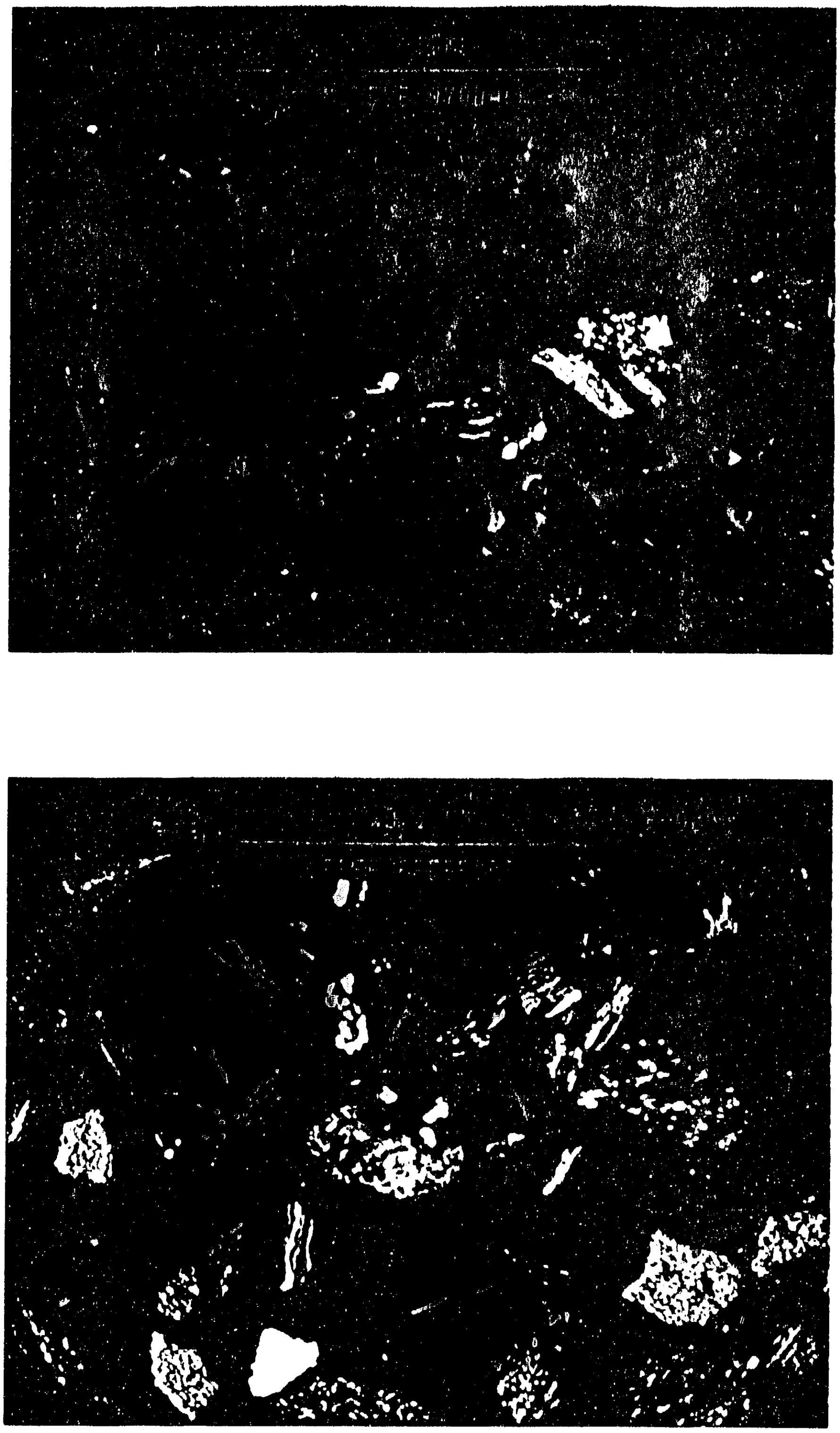

Figure 2. Scanning electron photomicrographs of 65 x 200 mesh fraction of Middle Wyodak coal (top) and 100 x 200 mesh fraction of Upper Freeport coal (bottom).

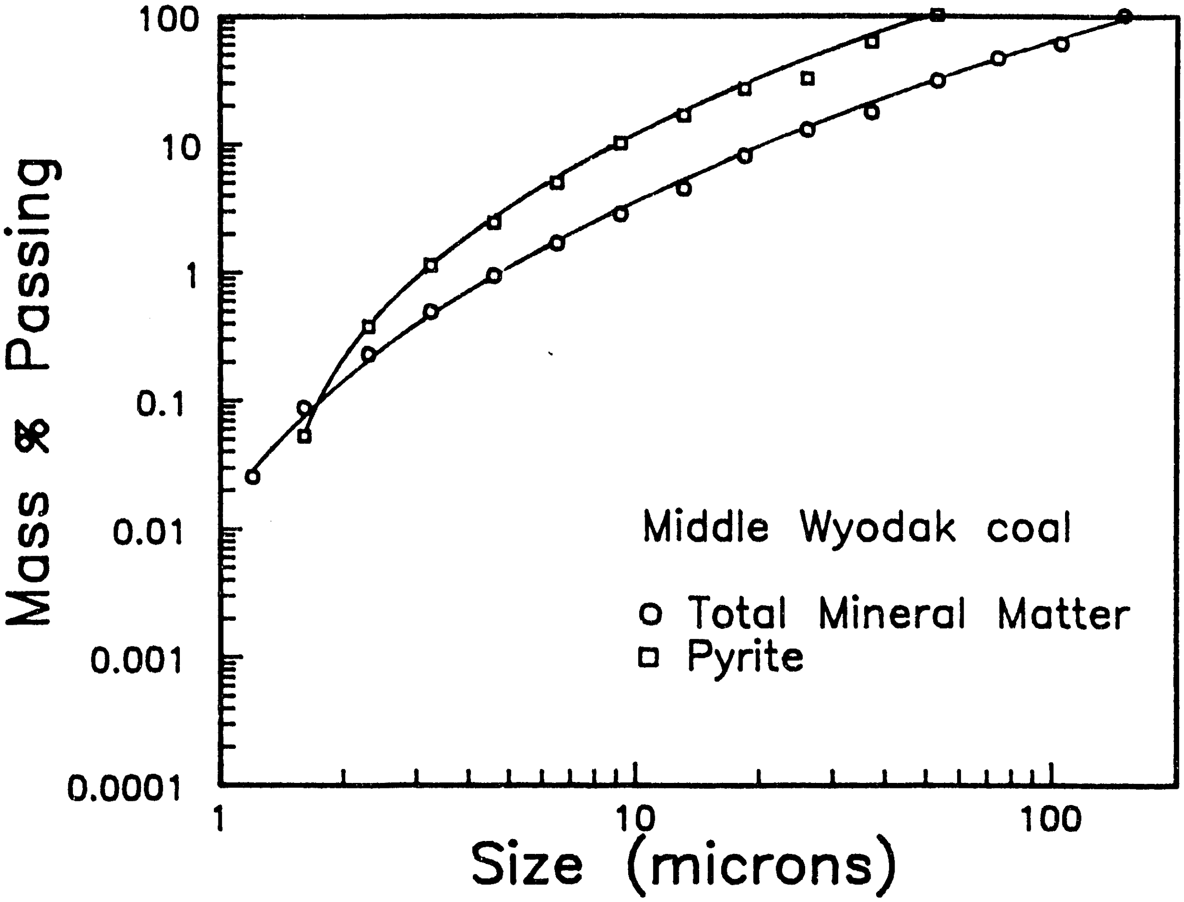

Figure 3. Particle size distribution of pyrite and total mineral matter present in a 28 x 0 mesh fraction of Middle Wyodak coal.

samples from the two coal seams. Table X shows the results of the BET and Langmuir surface area and pore distribution analyses. The surface area, pore volume and pore distribution were determined by the static-volumetric method using nitrogen gas.

The BET surface areas of the Middle Wyodak and Upper Freeport coal were determined to be 2.43 and 1.68 m^2/g, respectively. The total pore volume for the Middle Wyodak coal was about twice that for the Upper Freeport coal. The average Barrett-Joyner-Halenda (BJH) adsorption pore diameter for the Middle Wyodak coal is also larger than that for the Upper Freeport coal. The complete adsorption and desorption pore distributions for the two coal samples are given in Appendix 1.

Table X. Surface area and pore distribution analysis.

	Middle Wyodak	Upper Freeport
BET surface area (m^2/g)	2.43	1.68
Langmuir surface area (m^2/g)	3.47	2.37
BJH cumulative adsorption pore volume (cm^3/g)*	0.014	0.007
BJH cumulative desorption pore volume (cm^3/g)*	0.014	0.007
BJH adsorption average pore diameter (Å)	266.28	210.11
BJH desorption average pore diameter (Å)	181.10	186.75

*pore volume of pores between 17 and 3000Å

Due to the poor response of the Upper Freeport coal to CECC treatment, as shown in Task 4, the second coal sample studied in this project was changed to a Pittsburgh No. 8 coal. The Upper Freeport sample obtained in Task 2 was found to be severely oxidized, and thus not amenable to CECC processing. As is discussed later, the use of oxidized feed sample is detrimental to the CECC process since the process is based on the incipient oxidation of the coal surface to start the osmotic pressure build-up.

Ultimate analysis of the head sample of the Pittsburgh No. 8 coal was conducted and the results shown in Table XI. This particular coal sample is found to have a lower mineral matter content than the Upper Freeport coal, but a slightly higher sulfur content.

Table XI. Results of the ultimate analysis of Pittsburgh No. 8 coal.

Analysis (%)	
Dry-loss	3.25
Carbon	75.44
Hydrogen	4.24
Oxygen	10.29
Nitrogen	1.46
Sulfur (total)	1.47
Sulfate Sulfur	0.57
Pyritic Sulfur	0.88
Organic Sufur	0.02
Ash	7.10
Btu/lb	13,825.00

It is interesting to note that the organic sulfur content of the Pittsburgh No. 8 coal is almost half of the total sulfur content. The analysis for the mineral matter composition of this coal sample is given in Table XII. The majority of the mineral matter found in this coal were oxides of Si, Al and Fe. There is also a significant amount of oxides of Ca and S (as SO_3) present in this sample. From this ash analysis, the maximum amount of mineral matter that may be considered as soluble in the acidic conditions used in the CECC reactor is about 34%.

Table XII. Coal ash analysis of Pittsburgh No. 8 coal.

Mineral Analysis	% Weight (Ignited Basis)
Aluminum (Al_2O_3)	18.44
Barium (BaO)	0.11
Calcium (CaO)	6.36
Iron (Fe_2O_3)	19.69
Magnesium (MgO)	1.05
Manganese (MnO_2)	0.05
Phosphorus (P_2O_5)	0.60
Potassium (K_2O)	1.61
Silicon (SiO_2)	42.54
Sodium (Na_2O)	0.48
Strontium (SrO)	0.14
Sulfur (SO_3)	6.29
Titanium (TiO_2)	0.95

The ultimate analysis results for the head sample of the Elkhorn No. 3 coal are given in Table XIII. This coal sample was used to replace the Pittsburgh No. 8 coal in the Continuous Test Work (Task 6). Details concerning the reason for the shift to the Elkhorn No. 3 coal are given in Tasks 4 and 6. The assay showed that the ash and sulfur contents were 7.1 and 1.47%. The ash and sulfur content of this run-of-mine sample from the Consolidated Coal Company was lower than for any of the bituminous coal samples analyzed. The pyritic sulfur content of the Elkhorn coal is about 60% of the total sulfur content. The results of the analysis of the ash for mineral matter are given in Table XIV. The majority of the mineral matter present in the Elkhorn coal were oxides

Table XIII. Results of the ultimate analysis of Elkhorn No. 3 coal.

Analysis (%)	
Dry-loss	3.25
Carbon	75.44
Hydrogen	4.24
Oxygen	10.29
Nitrogen	1.46
Sulfur (total)	1.47
Sulfate Sulfur	0.57
Pyritic Sulfur	0.88
Organic Sufur	0.02
Ash	7.10
Btu/lb	13,825.00

Table XIV. Coal ash analysis of Elkhorn No. 3 coal.

Mineral Analysis	% Weight (Ignited Basis)
Aluminum (Al_2O_3)	24.47
Calcium (CaO)	1.72
Iron (Fe_2O_3)	23.27
Magnesium (MgO)	1.69
Phosphorus (P_2O_5)	0.08
Potassium (K_2O)	2.96
Silicon (SiO_2)	41.91
Sodium (Na_2O)	0.53
Sulfur (SO_3)	2.18
Titanium (TiO_2)	1.19

of Si, Al and Fe, which accounted for almost 90% of the mineral matter content. The amount of soluble oxides of Ca and Mg is negligible, which would suggest that any mineral matter removal via dissolution in the CECC process would be insignificant.

TASK 4 - BATCH TESTING

Batch tests were carried out to study the effect of different parameters on the CECC process. A statistically designed parametric test program was used to determine the optimum operating conditions and validation tests were conducted afterwards. Mechanistic studies were also conducted to investigate the leaching kinetics of mineral matter and pyrite, methods of ferric ion regeneration, ash liberation, and the effect of size distribution and EDTA addition on the CECC process.

A standard electrochemical reaction vessel (Figure 4) was used in the experiments, which consisted of pre-soaking coal overnight (about 15 hours) in sulfuric acid, followed by 1-5 hours of electrolysis at an applied potential of 1.0 V (SCE). After electrolysis, the coal was separated into different size fractions by wet-screening. Each fraction and the coal feed were analyzed for sulfur and ash using a sulfur determination unit and a multi-sample thermogravimetric analyzer.

Subtask 4.1 - Parametric Testing

The generally accepted operating parameters for the CECC process include acid concentration, acid type, reaction time, ferric ion concentration, temperature, applied potential, coal particle size and percent solids. However, based on information collected in the project entitled: Advanced Systems for Producing Super-Clean Coal (Contract No. DE-AC22-86PC91221), percent solids, ferric ion concentration, sulfuric acid concentration and temperature were determined to be the most critical test variables. Accordingly, the statistical experimental design incorporated only these variables. A

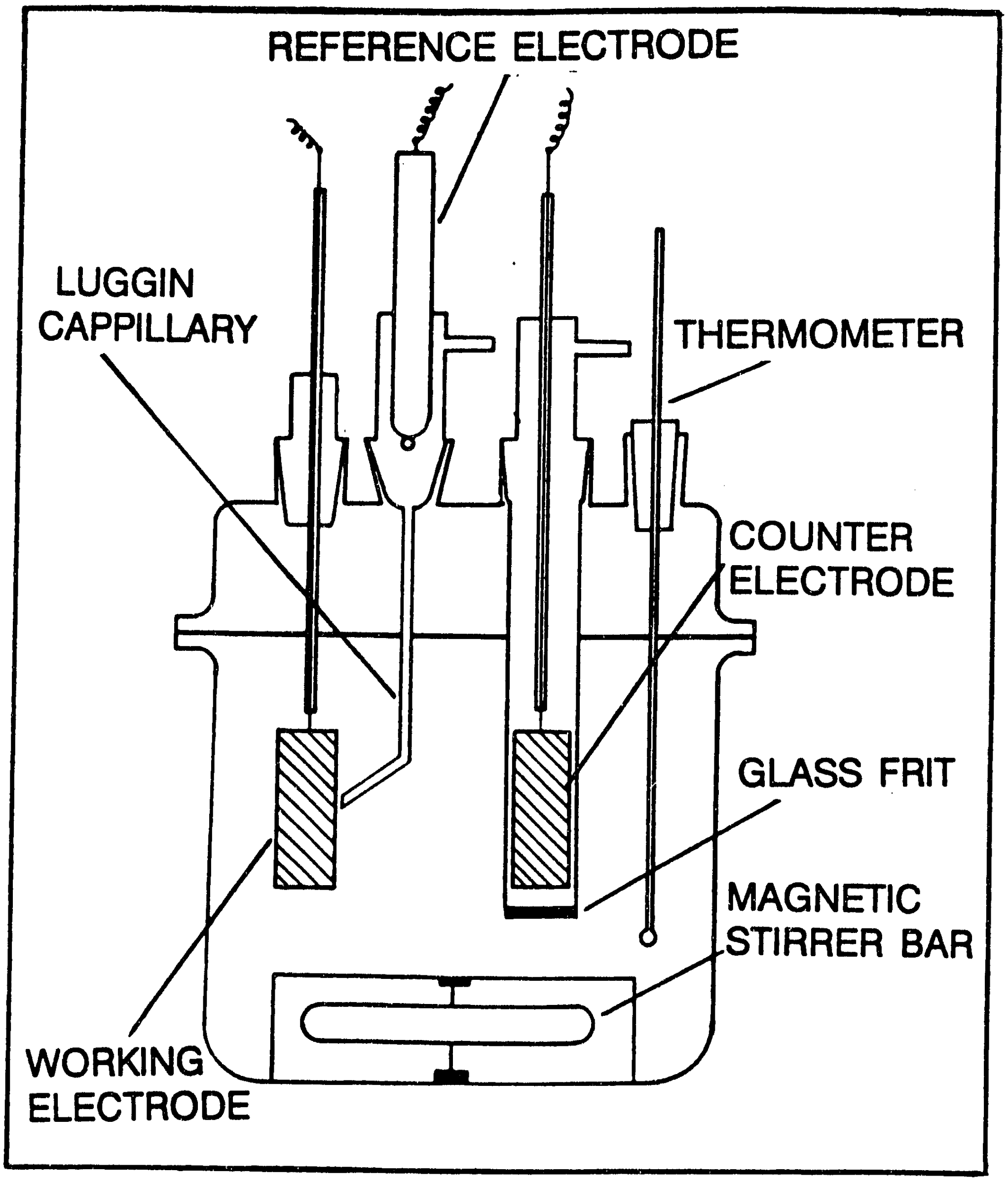

Figure 4. The stirred-tank reaction vessel.

series of parametric batch tests were conducted on a Middle Wyodak and Pittsburgh No. 8 coal to determine the effects of these variables on the CECC process.

The test program used for the parametric batch tests is given in Table XV. A total of 27 tests were carried out, including one test (No. 17 in Table XV) run in triplicate to estimate the experimental error. The % ash rejection obtained for each set of test conditions used for the parametric testing of the Middle Wyodak coal are presented in Table XV. The ash rejection by % weight was calculated in this work according to the following equation:

$$Rejection\ (by\ wt.\%) = 100 - \frac{Yield(wt.\%)\ X\ Product\ Ash\ (\%)}{Feed\ Ash\ (\%)} \qquad [1]$$

Complete test data including sulfur and ash content are given in Appendix 2.

Table XV shows that the % ash rejection increased with increasing temperature and acid concentration. However, the effects of the other parameters and any interaction effects can not be easily discerned from looking at Table XV. To actually determine these effects, a statistical analytical technique called response surface method was used. The RSREG procedure for the Statistical Analysis System (SAS) computer program installed in the IBM 3090/300 mainframe computer at Virginia Tech was used to determine the fit of the parameters to the response surface. The statistical analysis results indicated that the effects of acid concentration and temperature are significant in the removal of ash by the CECC process. However, the effects of ferric ion concentrations and percent solids on the % ash rejection were statistically insignificant. Significant interaction effect was found only between ferric ion and acid concentrations. This is expected since the ferric ions in the system require corresponding counter ions, which are

Table XV. Statistically designed experiment and ash removal results.

Test No.	Percent Solids	Fe^{3+} (M)	H_2SO_4 (M)	Temperature (°C)	Ash Reductio (%)
1	4	10-5	1	40	70.26
2	8	10-5	1	40	71.35
3	4	10-3	1	40	72.39
4	8	10-3	1	40	69.19
5	4	10-5	3	40	72.81
6	8	10-5	3	40	71.30
7	4	10-3	3	40	71.27
8	8	10-3	3	40	70.53
9	4	10-5	1	80	75.87
10	8	10-5	1	80	72.83
11	4	10-3	1	80	74.36
12	8	10-3	1	80	73.58
13	4	10-5	3	80	75.41
14	8	10-5	3	80	74.95
15	4	10-3	3	80	76.70
16	8	10-3	3	80	76.23
17-1	6	10-4	2	60	74.79
17-2	6	10-4	2	60	75.59
17-3	6	10-4	2	60	72.38
18	2	10-4	2	60	73.89
19	10	10-4	2	60	71.24
20	6	0	2	60	72.65
21	6	10-2	2	60	72.75
22	6	10-4	0	60	49.32
23	6	10-4	4	60	69.39
24	6	10-4	2	20	68.94
25	6	10-4	2	100	74.53

supplied by the acid, for maintaining the charging of the surface during the osmotic pressure build-up.

The relative amounts of mineral matter removed by liberation and by chemical dissolution were determined through a mass balance analysis. Using the known weights and assay of the feed, product and refuse, the mass balance of the ash or non-combustible material was determined. Table XVI shows the results of the mass balance calculations for Test No. 17-3. After treatment of this sample, 1.02 g of non-combustible material was left in the product and 0.97 g reported to the refuse. This means that 2.68 g of non-combustible material was removed, of which 1.71 g was removed by dissolution and/or lost during the treatment. Based on the mass balance of the ash, the amount of ash rejection that is attributed to liberation is about 36.2% and the rest is due to chemical dissolution and/or is lost. However, the feed coal was dry-screened and presumably contained fine particulates that were adhering to the coarse particles. Thus, the calculated ash rejection due to liberation probably also included fine liberated mineral matter initially present in the feed. To avoid the ambiguity concerning the actual amount

Table XVI. Results of CECC Test No. 17-3 on Middle Wyodak Coal.

	Feed	Product	Refuse
Weight (g)	49.21	31.02	15.50
Ash (%)	7.51	3.29	6.29
Non-Combustible Material (g)	3.70	1.02	0.97

of mineral matter liberated by the CECC process, the entire set of tests was repeated with wet-screened coal.

For the wet-screened coal, details of the statistical design and actual experimental procedures were the same as those employed for the dry-screened samples. The only difference was in the preparation of the feed sample. A total of 27 tests were performed, the results of which are shown in Table XVII. Complete test data including sulfur and ash content are given in Appendix 3.

The effects of the four parameters can not also be easily discerned from looking at Table XVII, except for that of acid concentration. Using the same statistical analysis technique used for the dry-screened sample, the effects of the different parameters on ash rejection were determined. The results indicate that the effects of acid concentration and temperature are significant in the removal of ash by the CECC process. Within the given ranges of ferric ion concentration and percent solids used in the experiments, the ash rejection was not improved significantly. Interaction effects were observed only for the ferric ion and acid concentrations. These observations are similar to those made for the dry-screened samples. However, the ash rejection for the wet-screened samples was slightly lower. This may be because the additional ash removal brought about by the wet-screening of the -325 mesh size ash particles that were initially present in the dry-screened feed was not significant in the treatment of the wet-screened sample.

The results of the mass balance for Test No. 17-3 on wet-screened coal are shown in Table XVIII. It can be seen that of the total ash removal, 84.5% can be attributed to dissolution (and/or lost) and 15.5% to liberation. These values are based on the

Table XVII. Statistically-designed experiment and ash rejection results obtained with wet-screened Middle Wyodak coal.

Test No.	Percent Solids	Fe^{+3} (M)	H_2SO_4 (M)	Temperature (°C)	Ash Rejection (%)
1	4	10-5	1	40	61.46
2	8	10-5	1	40	60.88
3	4	10-3	1	40	60.57
4	8	10-3	1	40	60.92
5	4	10-5	3	40	60.55
6	8	10-5	3	40	63.17
7	4	10-3	3	40	61.54
8	8	10-3	3	40	64.93
9	4	10-5	1	80	55.08
10	8	10-5	1	80	68.61
11	4	10-3	1	80	67.69
12	8	10-3	1	80	68.97
13	4	10-5	3	80	67.43
14	8	10-5	3	80	66.67
15	4	10-3	3	80	65.69
16	8	10-3	3	80	65.14
17-1	6	10-4	2	60	63.51
17-2	6	10-4	2	60	61.58
17-3	6	10-4	2	60	58.62
18	2	10-4	2	60	63.73
19	10	10-4	2	60	63.55
20	6	0	2	60	63.86
21	6	10-2	2	60	63.21
22	6	10-4	0	60	16.45
23	6	10-4	4	60	63.55
24	6	10-4	2	20	60.82
25	6	10-4	2	100	66.73

Table XVIII. Results of the CECC Test No. 17-3 on wet-screened Middle Wyodak coal.

	Feed	Product	Refuse
Weight (g)	50.18	42.78	5.65
Ash (%)	6.14	2.98	5.02
Non-Combustible Material (g)	3.70	1.02	0.97

assumption that the ash that did not report to the product and refuse was dissolved and/or lost.

It should be noted that the mean particle size of low temperature ash from the 65 x 325 mesh size Middle Wyodak coal sample was found to be between 12 and 14 microns. Thus, any ash liberated by the CECC process could have been lost during filtration; such ash would have been accounted as dissolved material. There is also the problem of recovering any liberated ash particle from the acid solution, which would add to the amount of mineral matter removed that is attributable to dissolution. Note also that the refuse ash is lower than the feed ash. This is because a considerable amount of the coal reported to the refuse by abrasion. Apparently, the stirring action of the magnetic bar broke apart some of the coal particles.

Diffuse reflectance infrared spectroscopic analyses were performed on the feed, product, and refuse of Test No. 17-3 for both dry- and wet-screened samples (Figures 5 and 6). The spectra of the feed samples were similar to that recorded for the head sample; however, the spectra for the product and refuse samples were different. For both coal samples, the intensity of the absorption bands observed at 1744, 1694, and

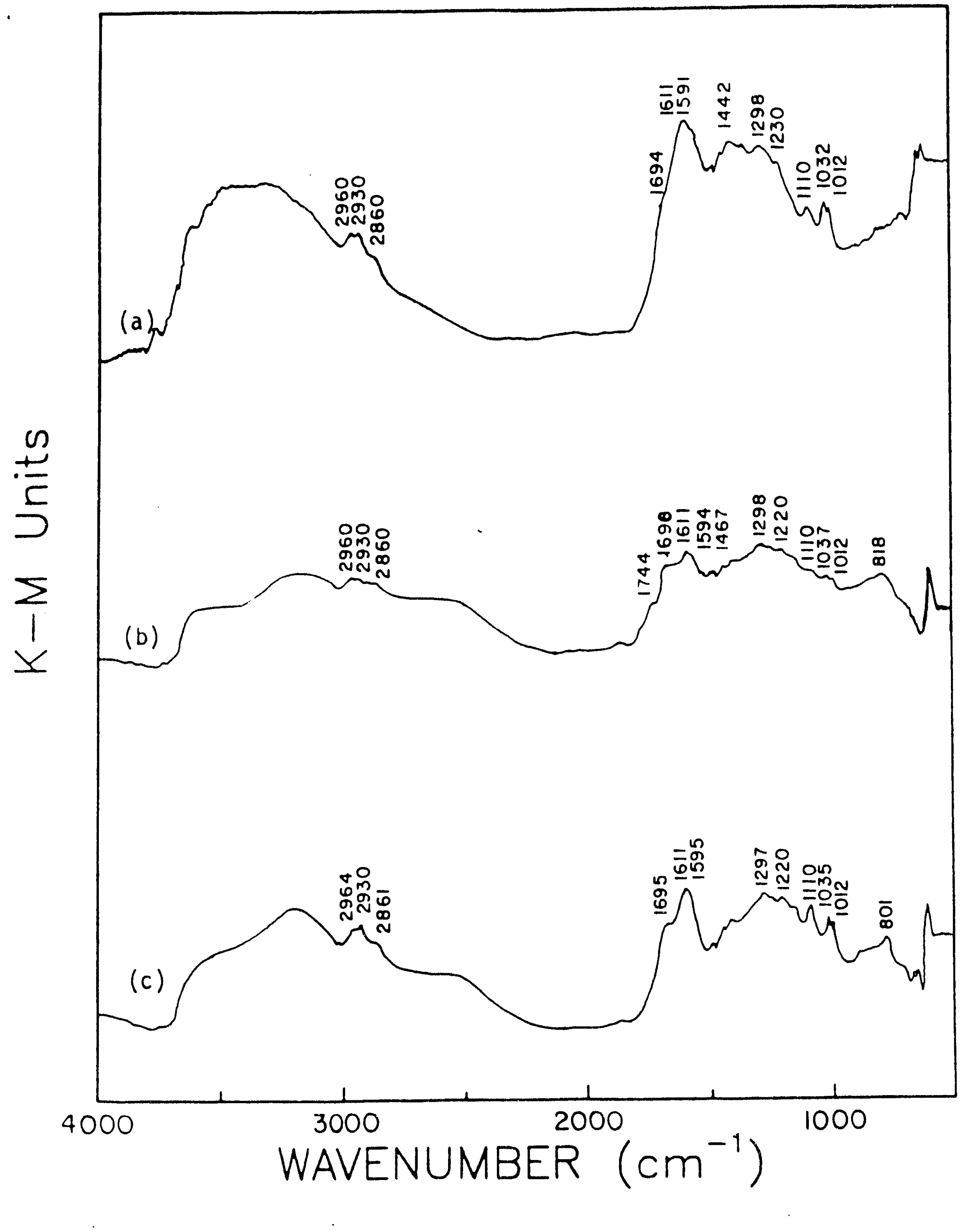

Figure 5. Diffuse reflectance spectra of dry-screened Middle Wyodak coal feed (a), product (b), and refuse (c) samples from parametric Test No. 17-3.

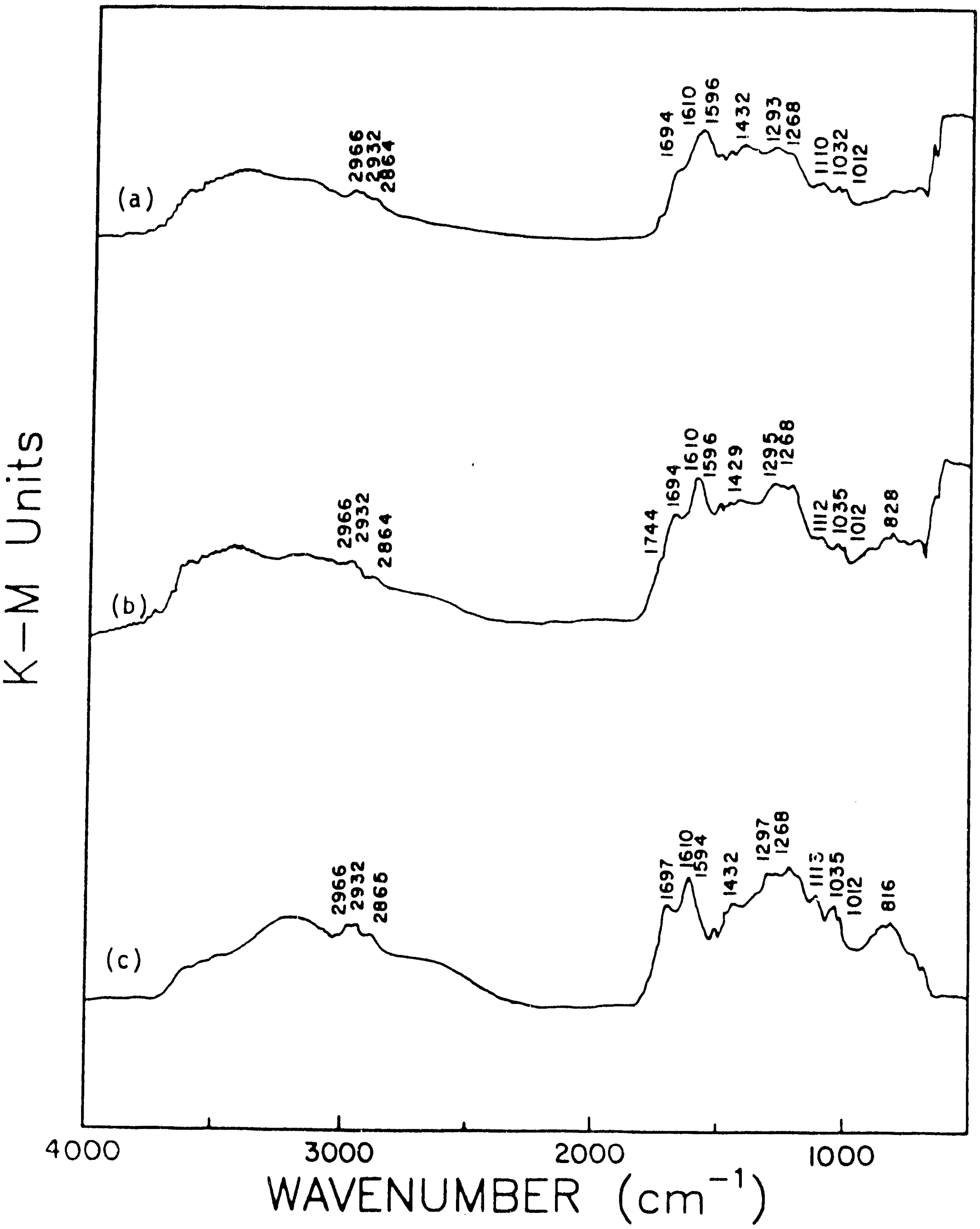

Figure 6. Diffuse reflectance spectra of wet-screened Middle Wyodak coal feed (a), product (b), and refuse (c) samples from parametric Test No. 17-3.

1610 cm^{-1} increased. These bands may be attributed to C=O vibrations. The intensity of the peaks in the 1200-1300 cm^{-1} region, indicative of ether, ester or phenolic C-O vibrations, also increased. These observations indicate that the coal surface oxidized, presumably during the CECC process. The ratios of the signals attributed to the clay minerals at 1032 and 1012 cm^{-1} to those of the C-H vibrations increased in the refuse, indicating an increase in ash content. However, these ratios were significantly lower in the product. This is in agreement with the assay results given in Appendix 3.

The results of the parametric testing of Middle Wyodak coal, as described above, showed that dissolution rather than liberation, played a major role in the mineral matter removal. This could be attributed mainly to the large amounts of exchangeable cations contained in the Middle Wyodak coal sample. The presence of Ca^{2+} and Mg^{2+} ions was verified by XRF and chemical analysis of the feed sample.

Lending support to the idea that ion exchange was primarily responsible for the mineral matter removal, were data from additional tests on the Middle Wyodak coal undertaken to obtain a complete mass balance of this process. The experiments were conducted on wet-screened Middle Wyodak coal employing the same CECC set-up used for the parametric tests. The experimental conditions used were: 6% solids in 2 M H_2SO_4 solution containing 10^{-4} M Fe^{3+} at 60 °C with an applied potential of 1 V (SCE). Table XIX shows the results obtained at different treatment times. The percentages of ash-forming material removed by liberation or dissolution were obtained by a mass balance of the ash found in the feed, product, and reject. It was assumed that any mineral matter not reporting to the product or reject was dissolved and/or lost. When a

Table XIX. Results of CECC tests conducted on wet-screened Middle Wyodak coal.

Reaction Time	Ash Content (% wt)		Ash Rejection (% wt)			Yield (% wt)
	Feed	Product	Total	Liberated	Dissolved	
5 hrs	6.68	3.21	55.46	5.20	94.60	92.70
5 hrs*	6.71	2.49	66.93	10.13	89.87	89.70
5 days**	6.68	2.89	59.28	6.00	94.00	92.50

*Feed size was 65- x 200-mesh, instead of 65- x 325-mesh.
**Without stirring.

feed size of 65 x 200-mesh was used, instead of 65 x 325-mesh, the mineral matter removed after 5 hours of treatment increased; however, the percentage of material removed by liberation was not significantly changed. In order to minimize the breakage of coal by abrasion, a 5-day test without stirring was also conducted. The resultant ash rejection was similar to that found for the 5-hour test with stirring, but the amount of mineral matter removed due to liberation decreased. The longer treatment time may have resulted in the dissolution of some of the liberated mineral matter.

The results of the elemental analysis of the spent solution, which was performed to identify the minerals dissolved by the CECC process, supported our conclusions about the presence of exchangeable cations in the Middle Wyodak coal. A mass balance of the process based on the calculated mineral content of the solution was also calculated from the elemental analysis of the solution. In this experiment, 25.2 g of 65 x 200-mesh Middle Wyodak coal, assaying 8.9% ash, was treated in 0.5 M H_2SO_4 solution containing ferric ions at 60°C. A potential of 1 V (SCE) was applied to the CECC reactor and the sample treated for 8 hours. The results of the analysis of the solution and the corresponding mass balance are given in Table XX. The amount of mineral matter liberated by the CECC process was about 27.9%, which is higher than that determined from the mass balance studies based on the solids. However, the percentage of mineral matter removed by dissolution was still much greater than the amount liberated. It is interesting to note that the spent solution contained about 69% (by weight) Ca and Mg ions.

The mass balance studies were also carried out for samples from other coal seams to determine the extent to which dissolution plays a role in mineral matter removal by the CECC process. The conditions used for these experiments were the same as those used for the Middle Wyodak coal samples. The coal samples tested were Upper Freeport,

Table XX. Mass balance based on the spent solution for the Middle Wyodak coal.

Element	Concentration (mg/l)	Weight (mg)	Mineral	Weight (mg)
K	10.5	7.87	Illite	116.9
Al	91.0	68.25	Kaolinite	252.4
Si	22.8	17.10	Quartz	
Mg	75.2	56.40	Dolomite	428.0
Ca	235.0	176.0	Calcite	103.9
			Bassanite	150.7
Fe	244.0	minimal	Siderite	45.0

Total mineral matter dissolved: 1097 mg
Total mineral matter removed: 1521 mg
% Dissolved: 72.1
% Liberated: 27.9

Pittsburgh No. 8, and Widow Kennedy coal, which all did not contain as many exchangeable cations as the Middle Wyodak coal.

Table XXI shows the amount of mineral matter rejected after CECC treatment and the amounts rejected through liberation and dissolution for wet-screened Upper Freeport coal samples. After 5 hours of treatment, no significant mineral matter removal was observed. Increasing the processing time to 2 days resulted in a mineral matter rejection of only 27.98%, approximately 85% of which was due to liberation. The results of the 5-day test showed an ash rejection of 60.38% with 68% of the mineral matter removal attributed to liberation. However, the yield was only 48.9% with the ash content reduced from 16.39% to 13.71%. The slow kinetics of the process with the Upper Freeport coal may be attributed to the high degree of oxidation of the coal sample used in these tests. The results of the diffuse reflectance spectroscopic analysis for this coal sample did indicate that the coal surface was oxidized (Figure 1). The relatively small surface area, pore volume and pore size of the Upper Freeport coal also probably affected the kinetics of the process.

Table XXI. Results of CECC tests conducted on wet-screened Upper Freeport coal.

Reaction Time	Ash Content (% wt)		Ash Rejection (% wt)			Yield (% wt)
	Feed	Product	Total	Liberated	Dissolved*	
5 hrs	16.55	16.95	---	---	---	97.20
2 days	17.63	15.13	27.98	85.33	14.67	83.90
5 days	16.39	13.71	60.38	68.00	32.00	48.90

*and/or lost

These experiments were repeated for wet-screened Pittsburgh No. 8 coal samples. The results, given in Table XXII, show that the amount of ash-forming material rejected after 5 hours of treatment was much lower than that obtained for the Middle Wyodak coal. However, the percent of material rejected due to liberation was much higher for the Pittsburgh No. 8 coal. This is presumably because the Pittsburgh No. 8 coal sample had a much lower Ca and Mg content. The removal of mineral matter improved significantly in the 3-day test, where a mineral matter rejection of almost 70% was obtained. Of the total amount of mineral matter removed, 52.6% was by liberation, which suggests that the mineral content of the feed sample may dictate whether liberation or dissolution plays the major role in mineral matter removal. Overall, the results for the Pittsburgh No. 8 coal were better than those for the Upper Freeport coal.

Similar experiments were also conducted for the wet-screened Widow Kennedy coal, the mass balance for which is given in Table XXIII. For this coal, the mineral matter removal by the CECC process was not as significant as for the other coals. Even after 5

Table XXII. Results of CECC tests conducted on wet-screened Pittsburgh No. 8 coal.

Reaction Time	Ash Content (% wt)		Ash Rejection (% wt)			Yield (% wt)
	Feed	Product	Total	Liberated	Dissolved*	
5 hrs	10.04	9.14	16.21	50.00	50.00	92.00
3 days	10.61	5.84	69.86	52.60	47.40	54.80
5 days	10.86	5.38	66.92	46.22	53.78	67.40

*and/or lost

Table XXIII. Results of CECC tests conducted on wet-screened Widow Kennedy coal.

Reaction Time	Ash Content (% wt)		Ash Rejection (% wt)			Yield (% wt)
	Feed	Product	Total	Liberated	Dissolved*	
5 hrs	24.42	25.11	---	---	---	91.63
3 days	25.35	21.25	27.32	94.60	5.40	86.70
5 days	29.02	21.48	32.52	32.93	67.07	91.17

*and/or lost

days of treatment, the mineral matter rejection remained very low. As for some of the other coals, the poor performance of the CECC process for this coal sample may be attributed to the sample's high degree of oxidation, which seems likely since the Widow Kennedy sample used in these experiments was stored in a laboratory freezer for about 5 years. Evidence for this hypothesis can be derived from previous CECC research at Virginia Tech (A. D. Paul, 1988, Ph.D. dissertation) that showed excellent mineral matter rejection with fresh Upper Freeport and Widow Kennedy coal samples.

Batch testing of a relatively unoxidized 65 x 325 mesh Upper Freeport coal sample was conducted to verify the effect of the oxidation state of the feed on the CECC process. The test conditions used were: 4% solids, 3 M H_2SO_4 solution containing 10^{-5} M Fe^{3+} and temperature of 80°C. Table XXIV shows the results obtained for this Upper Freeport run-of-mine coal sample from the Helen Mine, Indiana County, Pennsylvania. The feed had a relatively high ash content due to the method by which this sample was mined. After 17 hours of CECC treatment, the mineral matter rejection was 48.74% with a yield of 76.29%. However, the resulting product still had an ash content of about

Table XXIV. Results of CECC tests conducted on Upper Freeport coals.

Reaction Time	Ash Content (%wt)			Ash Rejection (%wt)			Yield (% wt)
	Feed	Product	Reject	Total	Liberated	Dissolved*	
17 hrs	44.04	29.59	77.21	48.74	62.80	37.20	76.29

*and/or lost

29.59%. A second stage of CECC processing or longer treatment time is expected to further reduce the ash content.

The results of these batch tests are better than those obtained previously using the highly oxidized Upper Freeport coal samples (Sample A-2 from Task 2). For these samples, the total mineral matter rejection after 48 hours of processing was only about 28% with a yield of 84%. It should also be noted that the response of the oxidized Widow Kennedy sample was not as good as those obtained in previous work with relatively fresh samples. These results suggest that the degree of oxidation of the feed sample does affect the coal response to the CECC treatment. The apparent sensitivity of the CECC process to the oxidation state of the feed sample may result from something inherent in the CECC process, which is based on the incipient oxidation of the coal surface. The oxidation of the sample prior to treatment probably results in the passivation of the sample's surface, thus inhibiting the charging mechanism involved during the osmotic pressure build-up on the coal during the CECC treatment.

Due to the poor response of the Upper Freeport coal to CECC treatment, the parametric testing of this coal sample was discontinued. Pittsburgh No. 8 coal was selected, with approval from DOE, to replace the Upper Freeport coal for the parametric tests.

For the parametric testing of Pittsburgh No. 8 coal, the same statistical design and experimental procedures described for the Middle Wyodak were used. The various experimental conditions used for each test are also given in Table XXV. The tests were conducted on 65 x 325 mesh wet-screened samples with a treatment time of about 5 hours. Since tests conducted on wet-screened Middle Wyodak coal samples gave a more accurate indication of the mineral matter removal by the CECC process, the tests for the Pittsburgh No. 8 coal were limited to wet-screened feed samples. Also, HCl was used in these experiments since residual H_2SO_4 was found in the Middle Wyodak coal sample even after repeated washing. This apparent adsorption of H_2SO_4 presumably resulted in the higher sulfur content of the CECC product. A total of 27 tests were done on the Pittsburgh No. 8, as shown in Table XXV, where it can be seen that the average % ash and % sulfur rejections for these parametric tests were around 38.08% and 18.20%.

Results indicate that percent solids and ferric ion concentration most probably affect the mineral matter removal by the CECC process. It can be seen that maximum mineral matter rejection can be obtained at conditions where the percent solids and ferric ion concentration are low. On the other hand, an increase in the acid concentration causes a significant increase in mineral matter rejection, but only a modest increase in sulfur removal. The effect of temperature is not as significant as that of the other parameters. The removal of mineral matter and sulfur, though, was observed to be favored at higher temperatures.

Table XXV. Ash and sulfur rejection results obtained from the parametric tests conducted on wet-screened Pittsburgh No. 8 coal.

Test No.	Percent Solids	Fe^{+3} (M)	HCl (M)	Temperature (°C)	Ash Rejection (%)	Sulfur Rejection (%)
1	4	10^{-5}	1	40	51.70	31.58
2	8	10^{-5}	1	40	38.74	9.01
3	4	10^{-3}	1	40	38.85	12.48
4	8	10^{-3}	1	40	34.39	12.23
5	4	10^{-5}	3	40	56.09	33.08
6	8	10^{-5}	3	40	31.12	10.32
7	4	10^{-3}	3	40	45.02	33.26
8	8	10^{-3}	3	40	40.40	19.93
9	4	10^{-5}	1	80	40.84	20.37
10	8	10^{-5}	1	80	38.73	28.46
11	4	10^{-3}	1	80	37.61	19.70
12	8	10^{-3}	1	80	38.17	18.52
13	4	10^{-5}	3	80	46.38	22.93
14	8	10^{-5}	3	80	35.15	28.66
15	4	10^{-3}	3	80	44.14	21.43
16	8	10^{-3}	3	80	42.75	19.26
17-1	6	10^{-4}	2	60	34.75	15.44
17-2	6	10^{-4}	2	60	31.10	8.88
17-3	6	10^{-4}	2	60	34.68	9.86
18	2	10^{-4}	2	60	40.49	21.59
19	10	10^{-4}	2	60	28.23	14.15
20	6	10^{-6}	2	60	33.58	7.45
21	6	10^{-2}	2	60	24.65	11.27
22	6	10^{-4}	0	60	13.27	9.08
23	6	10^{-4}	4	60	50.14	17.21
24	6	10^{-4}	2	20	30.84	13.83
25	6	10^{-4}	2	100	46.36	21.46

The amount of mineral matter rejection was lowest in the case where there was no acid added to the system (Test No. 22). When the ferric ion addition was 10^{-2} M (Test No. 21), the percentage of ash rejection was only 24.65%. Decreasing the ferric ion addition to 10^{-6} M did not substantially improve the mineral matter removal. However, the % ash rejection was at a maximum at low ferric ion addition and high acid concentration (Test No. 5). This would indicate that there is a strong interaction between these two parameters in the CECC processing of the Pittsburgh No. 8 coal. Even though an increase in the ferric ion concentration is theoretically expected to favor an increase in the osmotic pressure, there should be a corresponding amount of counter ions present, provided by the acid, to effectively increase the osmotic pressure in the coal pore structures.

The presence of ferric ions is also known to cause the oxidation of the coal and pyrite present in samples. This is beneficial to the CECC process but may hinder the mineral matter removal at some critical ferric ion concentration. There is presumably a limit on the amount of ferric ions that can be present during effective removal of mineral matter and sulfur from the coal. This limit is most probably determined by the number of counter ions present in the system and by the ferric to ferrous ion ratio. Since the CECC process is dependent on the electrocatalytic role of the Fe^{3+}/Fe^{2+} couple, an increase in the ferrous ion concentration will affect the coal oxidation through reversal or retardation of the ferric reduction reaction:

$$Fe^{3+} + e \rightarrow Fe^{2+} \qquad [2]$$

The kinetics of the forward reaction is known to decrease by the decrease in the ferric to ferrous ion ratio. Accumulation of the ferrous ions could also interfere with the free migration of the ferric ions to the reaction sites on the coal surface. Excessive amounts of ferric and/or ferrous ions can result in the chemisorption of these ions on the coal surface.

In these tests, 6 to 12 mM ferric ions, depending on the % solids, are expected to be present in the system without any further external addition of ferric ions. This value is based on the complete dissolution of the pyrite present in the Pittsburgh No. 8 coal sample, which contains about 1.47% pyritic sulfur. The addition of ferric ions to the CECC reactor, plus the production of ferric ions through pyrite dissolution, may have resulted in an excess of these ions being present in the batch tests. At relatively high concentrations of ferric ions, the formation of jarosite is favored in the acidic conditions used in this process. Jarosite precipitation on the coal surface will interfere with the charging of the coal surface, thus preventing the osmotic pressure build-up required to remove the mineral matter. It should also be pointed out that in coal treated with ferric chloride solutions, considerable amounts of ferric ions have been found to lodge in the coal structures (Beall *et al.*, 1983, Fuel, 62:289-291). This may also account for the decrease in the mineral matter removal by the CECC process.

The mass balances for the parametric test results are given together with the ash analysis of the feed, product, and reject in Table XXVI. The lowest product ash content obtained from the parametric test was 4.95% (Test No. 5), while the amount of mineral matter removed that could be attributed to liberation ranged from about 32 to 69% with

Table XXVI. Ash analysis results of the CECC parametric tests conducted on wet-screened Pittsburgh No. 8 coal.

Test No.	Ash Content (% wt)			Ash Rejection (% wt)			Yield (% wt)
	Feed	Product	Reject	Total	Liberated	Dissolved*	
1	10.60	5.68	39.03	51.70	60.30	39.70	90.13
2	10.60	6.85	69.00	38.74	32.34	67.66	94.79
3	10.60	7.00	44.53	38.85	44.53	55.47	92.59
4	10.60	7.49	33.89	34.39	43.59	56.41	92.85
5	10.60	4.95	51.30	56.09	45.61	54.39	94.03
6	9.67	7.34	43.01	31.12	43.92	56.08	95.17
7	9.65	7.61	36.67	45.02	53.16	46.84	90.08
8	9.88	6.30	46.36	40.40	61.70	38.30	93.47
9	10.27	6.70	47.57	40.84	67.36	32.64	90.68
10	10.27	6.81	41.61	38.73	64.73	35.27	92.40
11	10.89	7.44	38.52	37.61	63.41	36.59	91.31
12	10.12	6.82	37.89	38.17	56.03	43.97	91.75
13	9.92	5.82	31.70	46.38	50.01	49.99	91.58
14	9.91	7.17	29.27	35.15	68.11	31.89	89.63
15	10.60	6.65	34.61	44.14	57.08	42.92	89.04
16	10.60	6.71	36.35	42.75	57.16	42.84	90.44
17-1	9.65	6.73	36.35	34.75	42.49	57.51	93.56
17-2	9.99	7.26	49.13	31.10	51.13	48.87	94.81
17-3	9.99	7.26	49.13	31.10	51.13	48.87	94.81
18	9.65	6.50	31.88	40.94	40.86	59.14	87.69
19	9.65	7.55	54.15	28.23	64.86	35.14	91.73
20	9.47	6.66	48.55	33.58	51.61	48.39	94.45
21	9.93	7.45	58.27	24.65	69.26	30.74	95.77
22	9.93	8.87	39.89	13.27	44.78	55.22	97.09
23	10.30	5.91	54.80	50.14	64.99	35.01	86.88
24	10.27	7.45	40.18	30.84	37.19	62.81	95.34
25	10.27	6.23	36.83	46.35	58.80	41.20	88.44

* and/or lost

an average of about 53.5%. The percentages of mineral matter removed by liberation for this coal are higher than those obtained for the Middle Wyodak coal samples. It should be remembered that the Middle Wyodak coal contained large amounts of soluble and/or exchangeable cations.

Based on the mass balance, the mineral matter removed that could be attributed to liberation was higher for the case where the ferric ion addition was maximal (Test No. 21) than for that where it was minimal (Test No. 20). Similar trends were also observed for the other three parameters. It is interesting to point out that the effect of increasing ferric ion addition on the total mineral matter removal is opposite to that observed for the mineral matter liberation. This would support the explanations given above concerning the effect of ferric ion concentration on osmotic pressure build-up and mineral matter rejection. On the other hand, the effect of increasing acid concentration and temperature on mineral matter liberation are the same as those seen for total mineral matter removal.

Table XXVII shows the sulfur analysis results for the different batch tests and the mass balance of the sulfur. The lowest product sulfur content obtained was about 1.95%. The mass balance for sulfur showed that the amount of sulfur removal attributable to liberation ranged from 45 to 76% with an average of about 62.5%. This would indicate that liberation, rather than pyrite dissolution is playing a major role in sulfur removal.

Treating precleaned coal by the CECC process was also studied. Several tests were conducted with Middle Wyodak coal samples that were precleaned by conventional froth flotation. The wet-screened 65- x 325-mesh feed samples were floated in a 5-liter Denver flotation cell using 1 kg/ton each of kerosene and MIBC. After flotation for 1

Table XXVII. Sulfur analysis results of the CECC parametric tests conducted on wet-screened Pittsburgh No. 8 coal.

Test No.	Sulfur Content (% wt)			Sulfur Rejection (% wt)			Yield (% wt)
	Feed	Product	Reject	Total	Liberated	Dissolved*	
1	2.74	2.08	7.56	31.58	73.98	26.02	90.13
2	2.74	2.63	6.24	9.01	68.50	31.50	94.79
3	2.74	2.59	6.32	12.48	76.13	23.87	92.59
4	2.74	2.59	3.81	12.23	53.40	46.40	92.85
5	2.74	1.95	10.17	33.08	59.51	40.69	94.03
6	3.12	2.94	5.29	10.32	62.64	37.36	95.17
7	3.01	2.23	7.78	33.26	64.22	35.78	90.08
8	2.79	2.39	6.38	19.93	60.91	39.09	93.47
9	2.79	2.45	7.15	20.37	74.71	25.29	90.68
10	2.79	2.16	7.10	28.46	55.32	44.68	92.40
11	3.15	2.77	5.98	19.70	64.97	35.03	91.31
12	2.68	2.38	4.44	18.52	51.09	48.91	91.75
13	2.84	2.39	5.39	22.93	60.19	39.81	91.58
14	2.99	2.38	6.48	28.66	61.31	38.69	89.63
15	2.89	2.55	5.72	21.43	71.27	28.73	89.04
16	2.89	2.58	5.57	19.26	71.30	28.70	90.44
17-1	3.12	2.82	6.58	15.44	45.89	54.11	93.56
17-2	3.08	2.96	-**	8.88	-	-	94.81
17-3	3.08	2.94	-**	9.86	-	-	94.43
18	3.12	2.79	-**	21.59	-	-	87.69
19	3.12	2.92	6.15	14.15	45.45	54.55	91.73
20	2.98	2.92	-**	7.45	-	-	94.45
21	2.99	2.77	-**	11.27	-	-	95.77
22	2.99	2.80	-**	9.08	-	-	97.09
23	2.97	2.83	-**	17.21	-	-	86.88
24	3.12	2.82	-**	13.83	-	-	95.34
25	3.12	2.77	5.91	21.46	67.07	32.93	88.44

* and/or lost

** not enough sample for sulfur analysis minute, the product was filtered and dried. The precleaned samples were then treated in the CECC cell under the conditions employed for Tests No. 9, 12 and 17 of the parametric test design (Table XV). These tests were those that gave the lowest, highest and average mineral matter rejections, respectively, for the Middle Wyodak coal. The ash content of the feed sample was reduced from 6.74% to 6.21% by conventional flotation with a yield of around 82.2%.

However, the entire set of precleaning experiments was later repeated since some of the original samples obtained after the CECC treatment were lost during the wet-screening. The ash content of the feed sample for the new tests was reduced from 6.66% to 5.79% after flotation. From this second set of experiments, Table XXVIII gives the results for three tests done under different conditions. The specific conditions used for each test were the same as those given in Table XXV. The product ash contents after CECC treatment are slightly lower than those obtained without precleaning. However, the percentages of mineral matter rejected in all three tests are still lower than those

Table XXVIII. Results of CECC tests conducted on precleaned Middle Wyodak coal.

Test No.	Ash Content (% wt)			Ash Rejection (% wt)	Yield (% wt)
	Feed	Product	Reject		
9	5.79	2.81	6.10	54.12	94.54
15	5.79	2.63	5.16	56.68	95.38
17	5.79	2.59	7.49	57.21	95.65

observed previously. These results, therefore, do not justify precleaning the Middle Wyodak coal by froth flotation prior to CECC treatment. This was somewhat expected since this coal sample is a subbituminous coal with poor response to flotation.

The effect of precleaning the Pittsburgh No. 8 coal prior to CECC processing was also studied. A series of CECC batch tests was conducted on wet-screened coal samples that were precleaned by conventional froth flotation. The 65 x 325 mesh samples were floated in a 5-liter Denver batch-type flotation cell under the same flotation conditions used for the Middle Wyodak coal samples. The flotation product was dried and treated in the CECC reactor under the conditions used for Test Nos. 5, 13 and 17 of the parametric test design given in Table XXV. After flotation the ash content of the flotation feed sample had been reduced from 10.12% to about 8.10% with a recovery of about 96%.

Precleaning was also found to be unjustified for the Pittsburgh #8 coal. The results of the CECC tests for the precleaned Pittsburgh No. 8 coal samples are given in Table XXIX. Test No. 5 gave the best % ash rejection of the three tests, which was also observed in the batch tests conducted without precleaning. However, the product ash contents and the % ash rejections for the precleaned samples after CECC treatment were not as good as those obtained without precleaning. The sulfur removal was also lower with the precleaned samples. The poor mineral matter and sulfur removal may have been due to the oxidation of the coal sample during the precleaning stage. In the coal precleaning, the sample may have become oxidized after the flotation and subsequent oven-drying that precedes CECC treatment. It has already been shown that the use of

Table XXIX. Results of CECC tests conducted on precleaned Pittsburgh No. 8 coal.

Test No.	Ash Content (% wt)		Ash Rejection (% wt)	Sulfur Content (% wt)		Rejection (% wt)
	Feed	Product		Feed	Product	
5	8.37	6.53	19.16	2.806	2.763	5.21
13	8.05	6.97	14.62	2.841	2.728	5.95
17	8.01	6.81	20.32	2.829	2.737	6.77

oxidized feed sample resulted in the poor performance of the CECC process. These results, therefore, suggest that precleaning of the Pittsburgh No. 8 coal by conventional froth flotation prior to CECC processing would probably not be beneficial, which is similar to what was suggested for the Middle Wyodak coal. The only significant benefit achieved by precleaning the Pittsburgh No. 8 coal is higher coal recovery, which was observed for all three tests.

Subtask 4.2 - Determination of Optimum Conditions and Validation

In order to determine the optimum conditions for the CECC processing of Middle Wyodak and Pittsburgh No. 8 coal, statistical analyses of the parametric test results for these coal were conducted using response surface methodology. This methodology involves finding a suitable approximating function and determining the values of the independent variables in order to determine an optimum response. It should be pointed out that although this technique is not used primarily for understanding the mechanism of the process, it may in some cases prove useful in determining the underlying mechanism.

Analysis of the data for the wet-screened Middle Wyodak coal indicates that good choices for high response lie along the <0.16, 0.17, 0.12, 0.37> vector. The values given in this vector are in design units, -2, -1, 0, 1, 2, for the % solids, ferric ion concentration, acid concentration and temperature, respectively. All points along this vector have a predicted mean response of between 62 and 69% ash rejection. In terms of actual parameter value, this vector would correspond to the following conditions (Table XXX): 6.86 % solids, $10^{-3.54}$ M Ferric ions, 2.32 M H_2SO_4 and 80°C.

Table XXX. Optimum conditions determined for the CECC treatment of Middle Wyodak coal.

Operating Parameters	Middle Wyodak
% Solids	6.86
Fe^{3+} Addition (M)	$10^{-3.54}$
Acid Concentration (M)	2.32
Temperature (°C)	80°C
Predicted % Ash Rejection	65.5

Since these conditions were not actually tested, validation tests were conducted at these optimum conditions. Test Nos. 1 and 2 (Table XXXI) show that the ash rejection using these optimum conditions is within the range of the predicted mean response. However, the obtained ash rejection values are lower than the maximum value observed in the parametric tests. Consequently, an additional test was conducted using another set of conditions that were further up the statistically determined vector. The conditions used for this experiment (Test No. 3) were as follows: 7.76 %solids, $10^{-3.66}$ M Ferric ions, 2.26 M H_2SO_4, and 94.8°C. 66.94% of the mineral matter was removed, which is higher than in the two previous tests. These results indicate that the statistically determined vector is a good approximation of the optimum condition required to process the Middle Wyodak coal.

Table XXXII shows the conditions that would give the optimum mineral matter rejection for Pittsburgh No. 8 coal based on the statistical analysis of the data. In the optimization of the response model, the stationary or optimum point found was a saddle

Table XXXI. Results of CECC tests conducted on wet-screened Middle Wyodak coal using the statistically-determined optimum conditions.

Test No.	Ash Content (% wt)			Ash Rejection (% wt)	Yield (% wt)
	Feed	Product	Reject		
1	6.66	2.69	11.16	62.29	93.37
2	6.92	2.84	20.31	62.69	90.91
3	6.92	2.61	11.29	66.94	87.71

Table XXXII. Optimum conditions determined for the CECC treatment of Pittsburgh No. 8 coal.

Operating Parameters	Pittsburgh No. 8
% Solids	6.0
Fe^{3+} Addition (M)	10^{-5}
Acid Concentration (M)	5.0
Temperature (°C)	68.0°C
Predicted % Ash Rejection	54.71

point. Ridge analysis, a statistical technique for analyzing this type of response surface, was used to determine the actual optimum point, which is given by the following conditions: 6% solids, 10^{-5} M Fe^{3+} addition, 5 M acid, and a temperature of 68°C. Given these optimum conditions for the CECC processing of the Pittsburgh No. 8 coal, the % ash rejection is predicted to be around 54.7%, which is lower than the predicted optimum for the Middle Wyodak coal. It can be seen that only a small amount of ferric addition is required for treating the Pittsburgh No. 8 coal, lower than that required for the Middle Wyodak coal. The percent solids and temperature requirements are also lower for the Pittsburgh No. 8 coal. However, the acid concentration needed to process this coal is higher than the optimum acid requirements for the Middle Wyodak coal. This may be because additional ferric ions come from the coal itself, requiring more counter ions. Also, a smaller amount of exchangeable ions and soluble minerals is present in the Pittsburgh No. 8 coal than in the Middle Wyodak coal.

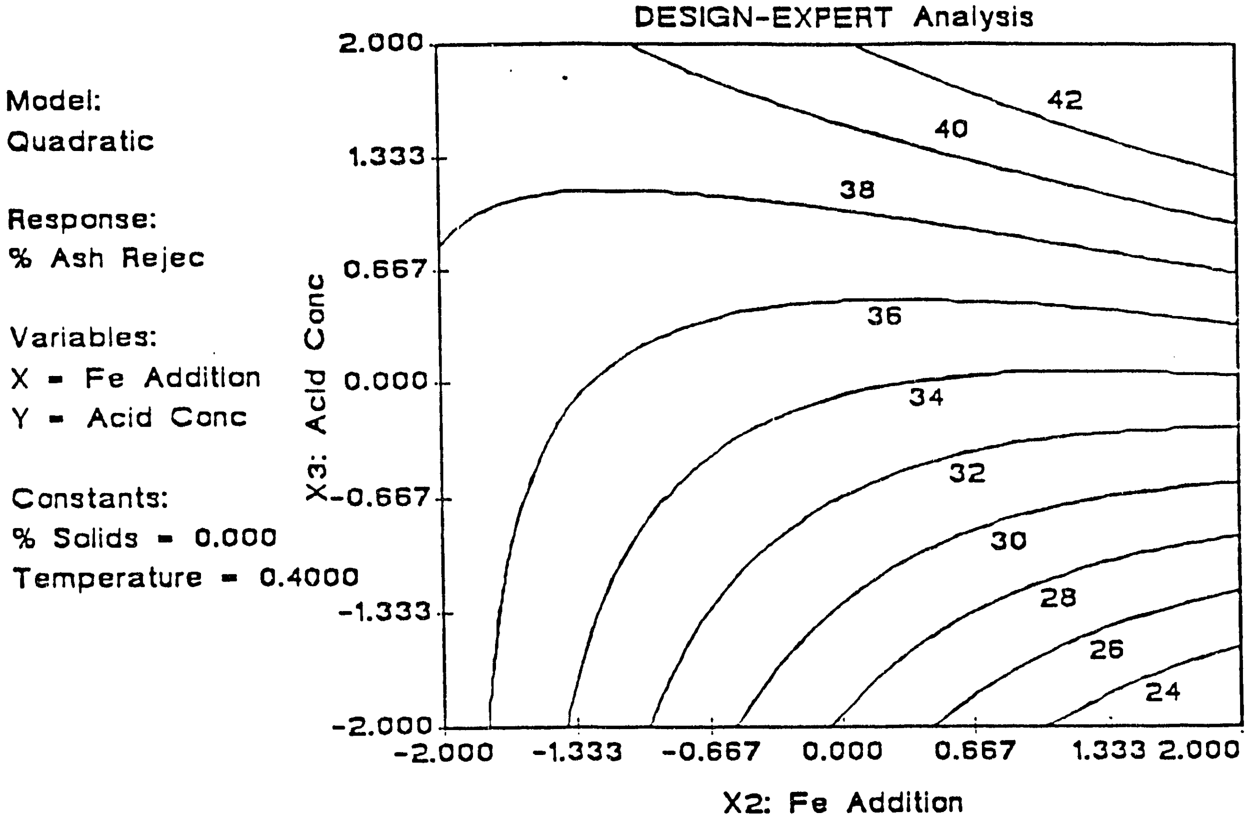

Figure 7. The effect of Fe^{3+} and acid concentration on the % ash rejection for the Pittsburgh No. 8 coal. The variables are given in coded form where the minimum value is -2 and the maximum value is +2.

Figure 7 shows the change in % ash rejection as a function of ferric ion addition and acid concentration. This response surface was obtained from the statistical model fitted for the parametric data. The percent solids and the temperature were held at the determined optimum values of 6% ($X_1 = 0$) and 68°C ($X_4 = 0.4$). This response surface is a rising ridge surface where the determined stationary or optimum point is a saddle point. This means that the actual stationary point is remote from the experimental region, as shown in Figure 7 where the optimum acid concentration of 5 M is outside the response surface plot. It can be seen that to obtain high % ash rejection, an increase in ferric ion addition must be accompanied by a corresponding increase in acid concentration of the system. This agrees with the suggestion that the presence of the ferric ions in the CECC process requires a corresponding number of counter ions for the effective removal of mineral matter.

Since the optimum conditions for Pittsburgh No. 8 coal listed in Table XXXII were not actually tested, validation tests were conducted at these conditions. Table XXXIII shows the results of the validation tests conducted for the Pittsburgh No. 8 coal samples. The mineral matter removal obtained for Test Nos. 1-3 is much lower than that predicted by the response model, and the % ash rejections for these tests is not within the range of the predicted mean response. This poor response may be attributed to the surface oxidation of the feed sample. The feed samples for the validation tests came from the same batch used for the parametric tests. Although these samples were stored in the freezer, oxidation had presumably occurred since these samples had been in storage since last year. In fact, a repeat test carried out using the condition set for Test No. 17

Table XXXIII. Results of CECC tests conducted on Pittsburgh No. 8 coal using the statistically-determined optimum conditions.

Test No.	Ash Content (% wt)		Ash Rejection (% wt)	Sulfur Content (% wt)		Sulfur Rejection (% wt)
	Feed	Product		Feed	Product	
1	9.87	7.45	32.07	2.960	2.693	18.12
2	9.28	7.78	24.55	2.700	2.620	12.67
3	9.53	8.04	24.07	2.800	2.740	11.93
4	12.16	6.65	51.60	3.630	2.760	32.71

of the parametric tests gave a poor response to CECC processing. Diffuse reflectance analysis of the coal surface verified that these feed samples were oxidized.

Due to this problem, another batch of run-of-mine Pittsburgh No. 8 coal samples were hammer-milled and dry screened to 65 x 325 mesh. These samples were then placed in freezer bags, purged with N_2 gas, sealed, and stored in a freezer. The coal sample used for a test was taken from these bags and wet-screened just prior to testing. This sample preparation procedure was used for all further tests in order to limit the oxidation of the coal samples.

In Test No. 4 (Table XXXIII), this new sample preparation procedure was used. The mineral matter content of this sample was reduced from 12.16% to about 6.65% with an ash rejection of about 51.6%, which is within the range of the predicted mean response. After treatment, the sulfur content was 2.76% and the % sulfur rejection around 32.7%. The amount of sulfur removed is similar to those observed in the parametric tests. However, the mineral matter and sulfur content of the product are still relatively high, which may be due to the high initial ash and sulfur content of this coal sample. A second stage of treatment will presumably improve the cleaning of this sample.

Subtask 4.3 - Mechanistic Studies

Subtask 4.3.1 - Leaching Kinetics

Since the CECC process proved to be capable of removing mineral matter including pyrite by both dissolution and electrochemically induced liberation, the rate of mineral matter dissolution was studied. Batch experiments were carried out to determine the leaching kinetics of mineral matter present in the Middle Wyodak coal. In these experiments, 20 ml aliquots were periodically withdrawn from the coal reactor. The aliquots were then analyzed by atomic absorption spectrometry for Fe, Al, Si, Ca, and Mg content.

Figure 8 shows the concentration of different elements in solution as a function of time. This data was obtained for a Middle Wyodak coal sample treated under the following conditions: 10% solids, 3.3 mM Fe^{3+} addition, 3M H_2SO_4, and 34°C. Significant amounts of Fe, Ca, Al, and Mg ions were observed to be present in solution during the processing of the Middle Wyodak coal. Only minimal amounts of Si were observed to be dissolved by the CECC process. The Ca and Mg found in solution came from the exchangeable cations present in this coal, as discussed in Subtask 4.1. The Fe ions presumably came mostly from the pyrite present in the coal. It should be pointed out that the initial Fe concentration in solution was about 185 ppm, the amount added to the system prior to processing. The amount of Al ions released by the coal probably came from the Al silicates. The amounts of the different mineral matter dissolved, except for the silicates, were found to increase with time. Assuming that the initial concentration of the Ca, Mg, and Al ions was zero, the kinetics of the dissolution of

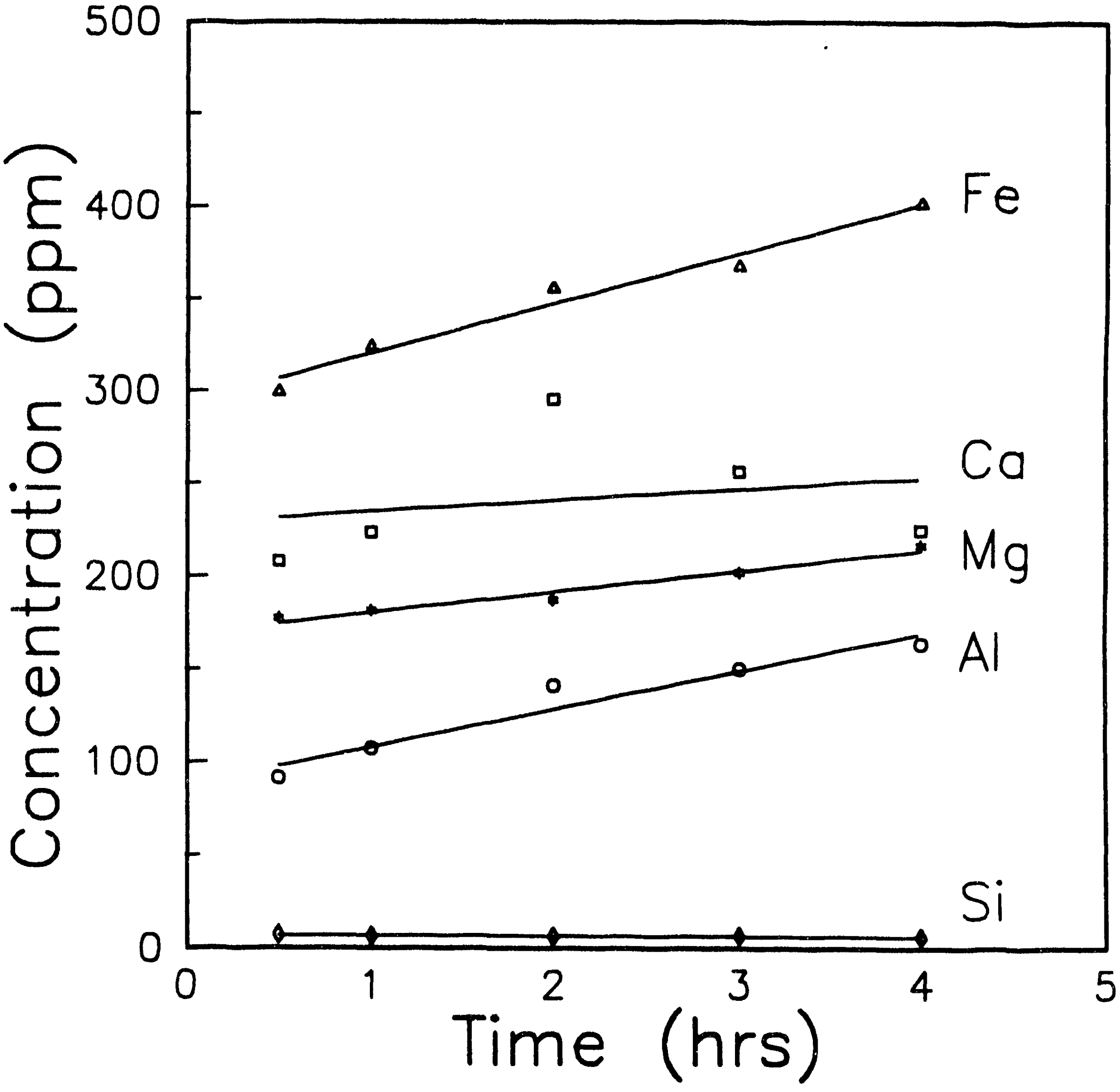

Figure 8. The release of different species from a Middle Wyodak coal as a function of time at 34°C. Feed ash = 6.97%. Product Ash = 4.26%.

these species, including Fe, was relatively fast. The dissolution of the Si-containing minerals did not seem to increase with time at this condition. Based on the relative amounts of the different species at the first sampling period, the mineral matter containing Ca and Mg dissolved fastest, followed by the Fe- and Al- containing minerals.

Since the kinetics of the dissolution of these species was fast, experiments were conducted with samples taken in the first few minutes of the process. These were performed in order to obtain data that might enable us to determine the leaching rate and rate order for the different species. In these experiments, aliquot samples were collected every ten minutes from the reactor. The aliquots were then analyzed by atomic absorption spectrometry for Fe, Al, Si, Ca, and Mg content.

Figure 9 shows the amounts of these elements dissolved from a Middle Wyodak coal sample as a function of time. With the exception of Si, the amounts of the different species that dissolved within the first 10 minutes increased sharply. The change in the amounts released into solution decreased rapidly thereafter and appeared to level off after approximately 30 minutes. The results indicate that the majority of the mineral matter dissolved contained Ca. Significant amounts of Fe-, Mg- and Al-containing minerals were dissolved in this process. However, the amount of Si dissolving over the entire sampling period was almost negligible.

Assuming a first-order reaction, the rate constant k for the dissolution of the different species may be given by the following:

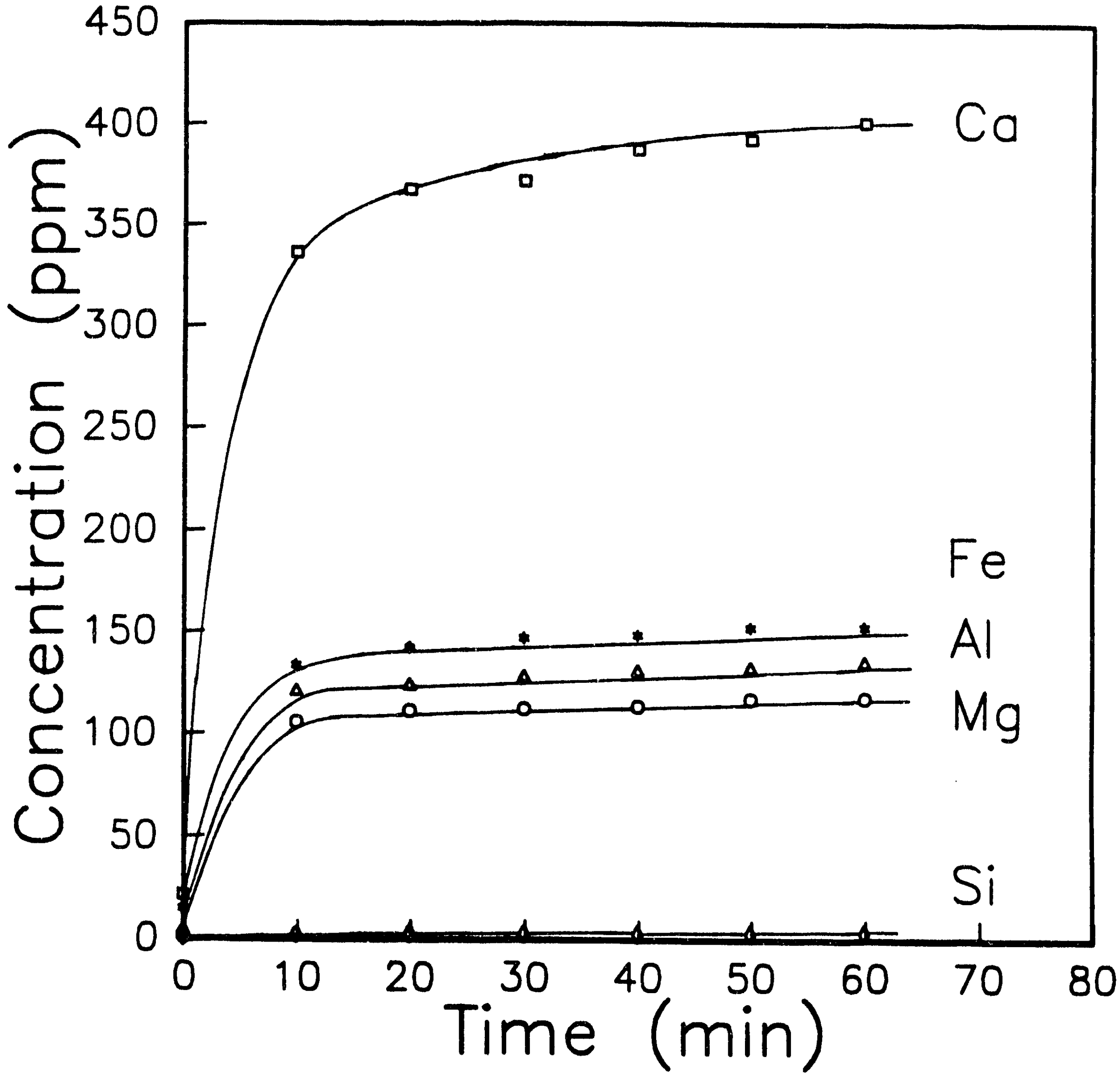

Figure 9. The release of different species from a Middle Wyodak coal as a function of time.

$$-d[A]/dt = k[A] \;,$$

where [A] is the concentration of the species (e.g., Ca, Fe). Using the method of initial rates, the dissolution rate constants were determined. Table XXXIV shows the values obtained from the results given in Figure 9. The dissolution rate constant for Ca is the highest, followed by those for Mg, Fe, Al, and Si. Significant amounts of both Ca and Mg were present in the Middle Wyodak coal as exchangeable cations, which may account for their dissolution rate constants being higher than those for the other elements. The results also show that the leaching of pyrite, and presumably kaolinite, as indicated by the rate constant for Al dissolution, was significant.

The results of the assays for the feed and the product recovered in the last sample (after 1 hour) are given in Table XXXV. For this test, the % ash rejection is lower than the predicted value of 62 - 69% obtained from the optimization studies. This is probably due to oxidation of the feed coal, as suggested by the decrease in the amount of mineral

Table XXXIV. Rate of dissolution of the different elements from Middle Wyodak coal.

Element	k (mol-li^{-1}-sec^{-1})
Ca	3.891×10^{-5}
Mg	1.445×10^{-5}
Fe	1.172×10^{-5}
Al	1.081×10^{-5}
Si	1.052×10^{-6}

Table XXXV. Results of CECC processing of Middle Wyodak coal.

Ash Content (% wt)			Ash Rejection (% wt)		
Feed	Product	Reject	Total	Liberated	Dissolved*
7.37	3.73	10.66	59.51	4.30	95.70

* and/or lost

matter removed through liberation. Results of the parametric tests (Subtask 4.1) showed that liberation accounts for about 20 to 30% of the total amount of mineral matter removed, while only about 4% was observed here.

The amount of mineral matter dissolved was also back-calculated from the results of the dissolution study by assuming that the Al, Ca, Mg, Fe, and Si found in solution came from kaolinite, calcite, dolomite, pyrite and quartz, respectively. The total amount of these minerals dissolved, based on the amount of the dissolved species found at the end of the sampling period, was about 1.744 g. From the ash analysis of the feed and product samples given in Table XXXV, the amount of ash removed was about 1.849 g, indicating that only 5.68% of mineral matter was removed by liberation. This is in agreement with the value obtained from the mass balance analysis based on the assay of the solids.

Increasing the temperature to 58°C was accompanied by an increase in the amount of Fe and Ca dissolved into solution (Figure 10). The dissolution of the Al, Mg and Si did not seem to be significantly affected by the increase in temperature, though. This probably indicates that only pyrite dissolution and the Ca ion exchange were affected by

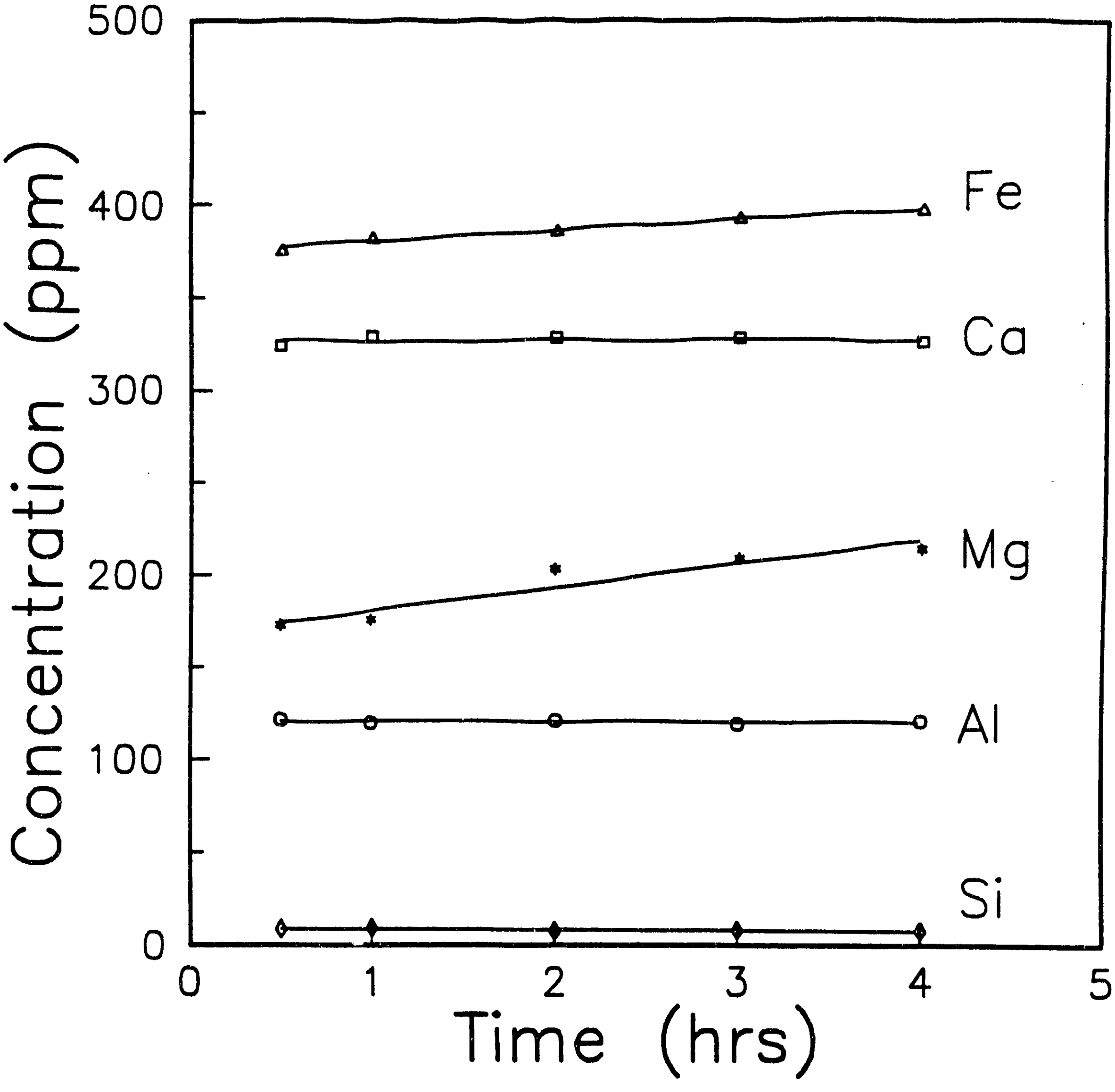

Figure 10. The release of different species from a Middle Wyodak coal as a function of time at 58°C. Feed ash = 7.09%. Product Ash = 3.31%.

the increase in temperature. Though not observed in this experiment, the release of Mg was also expected to increase with temperature.

The change in the concentration of the different species after the first sampling period was almost negligible, except for Mg. This probably suggests that the amount of the species that had dissolved had a reached maximum prior to or during the first sampling period. The solubility limit of these mineral matters is probably attained faster at a higher temperature. This is expected based on our assumption that the rate of the dissolution of these mineral matters should increase with increasing temperatures.

Figure 11 shows the dissolution behavior of Fe, Ca, Al, Mg, and Si at a lower acid concentration. This test was conducted at the same conditions as the previous test, except that the acid concentration was decreased to 1.5 M. It can be seen that the dissolution rates and the total amounts of Fe, Al, and Si dissolved in this experiment are similar to those obtained at a higher acid concentration (Figure 10). However, the amount of Ca dissolved is lower at the lower acidic concentration. Surprisingly, the opposite situation was observed for the dissolution of Mg. This discrepancy may be attributed to the difference in the initial amounts of these exchangeable cations present in the two coal samples.

In general, the results show that dissolution did play a more important role than liberation in the removal of mineral matter from the Middle Wyodak coal. This was also shown in our mass balance experiments reported above in Subtask 4.1. As shown in our earlier discussion and here, most of the mineral matter dissolved was actually exchangeable ions of Ca and Mg, pyrite, and the Al from aluminum silicates. However,

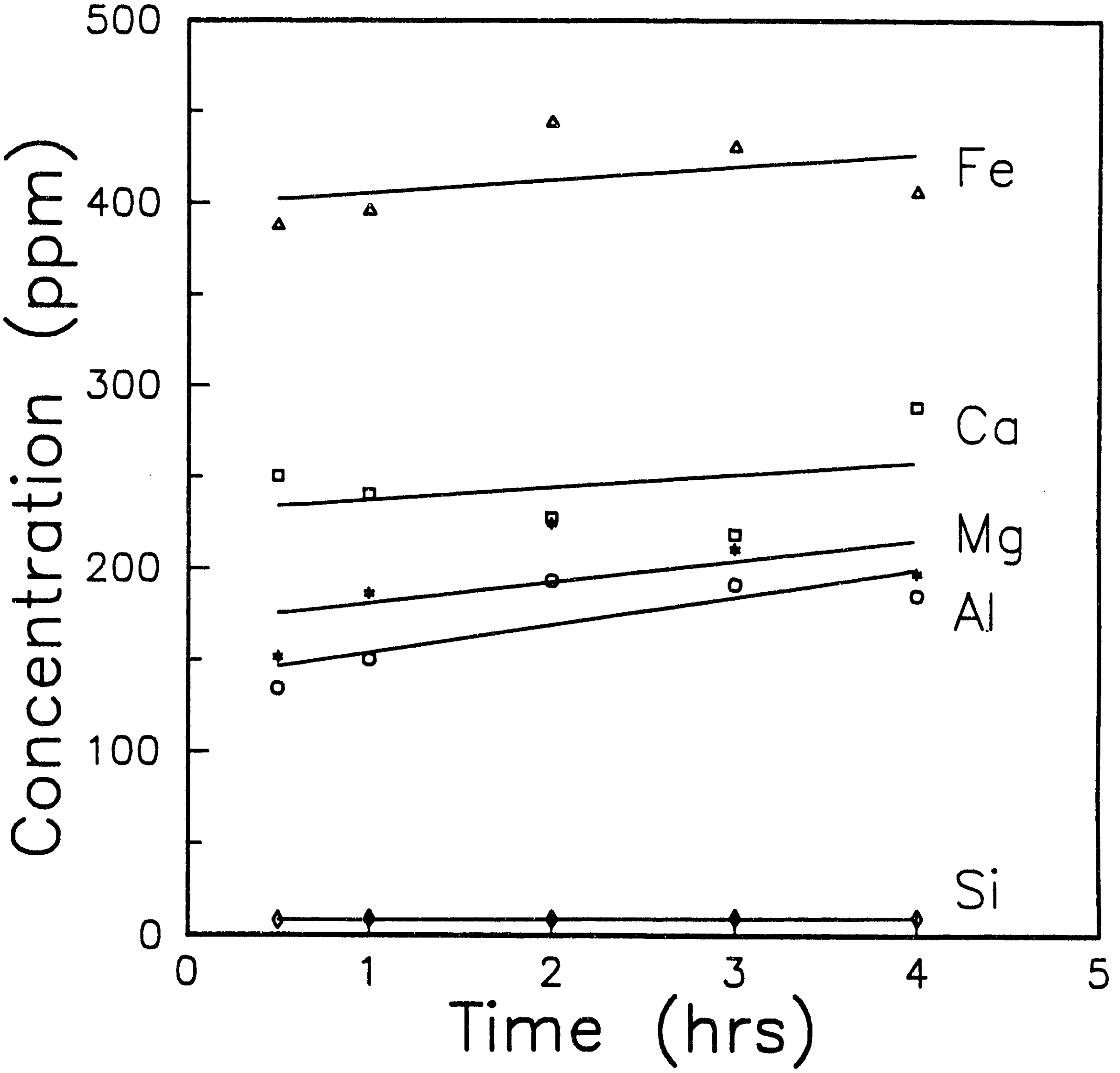

Figure 11. The release of different species from a Middle Wyodak coal as a function of time at 58°C and 1.5 M H_2SO_4. Feed ash = 7.09%. Product Ash = 3.31%.

it has been shown above that some mineral matter removal from this coal sample could be attributed to liberation.

Batch experiments were also carried out to determine the leaching kinetics of mineral matter present in the Pittsburgh No. 8 coal. The experiments were conducted in the same manner as those for the parametric tests in which the sample was presoaked overnight prior to the electrolysis period. 20 ml aliquots were withdrawn periodically from the coal reactor during the electrolysis period and were then analyzed by atomic absorption spectrometry for Fe, Al, Si, Ca, and Mg content.

Figure 12 shows the leaching behavior of these elements for a Pittsburgh No. 8 coal treated at the optimum conditions. It can be seen that there is almost no change in the dissolution of the different species during the electrolysis period, except for Fe and Al. This is due to the release of the majority of the dissolved species during the presoaking period. The dissolution of the mineral matter has presumably reached its maximum prior to the start of the electrolysis period, which was when the first sample was taken.

The amounts of Ca and Mg released into solution were less than those observed for the Middle Wyodak coal, probably because Pittsburgh No. 8 coal contains much lower amounts of these species. These minerals were present in the Pittsburgh No. 8 coal mainly as oxides, not as ion-exchangeable carboxylates. The amounts of Al and Si found in solution were also much lower, although analysis of the low-temperature ash for both samples showed that the Pittsburgh No. 8 coal had higher Al and Si contents than did the Middle Wyodak coal. However, the amount of Fe released into solution was

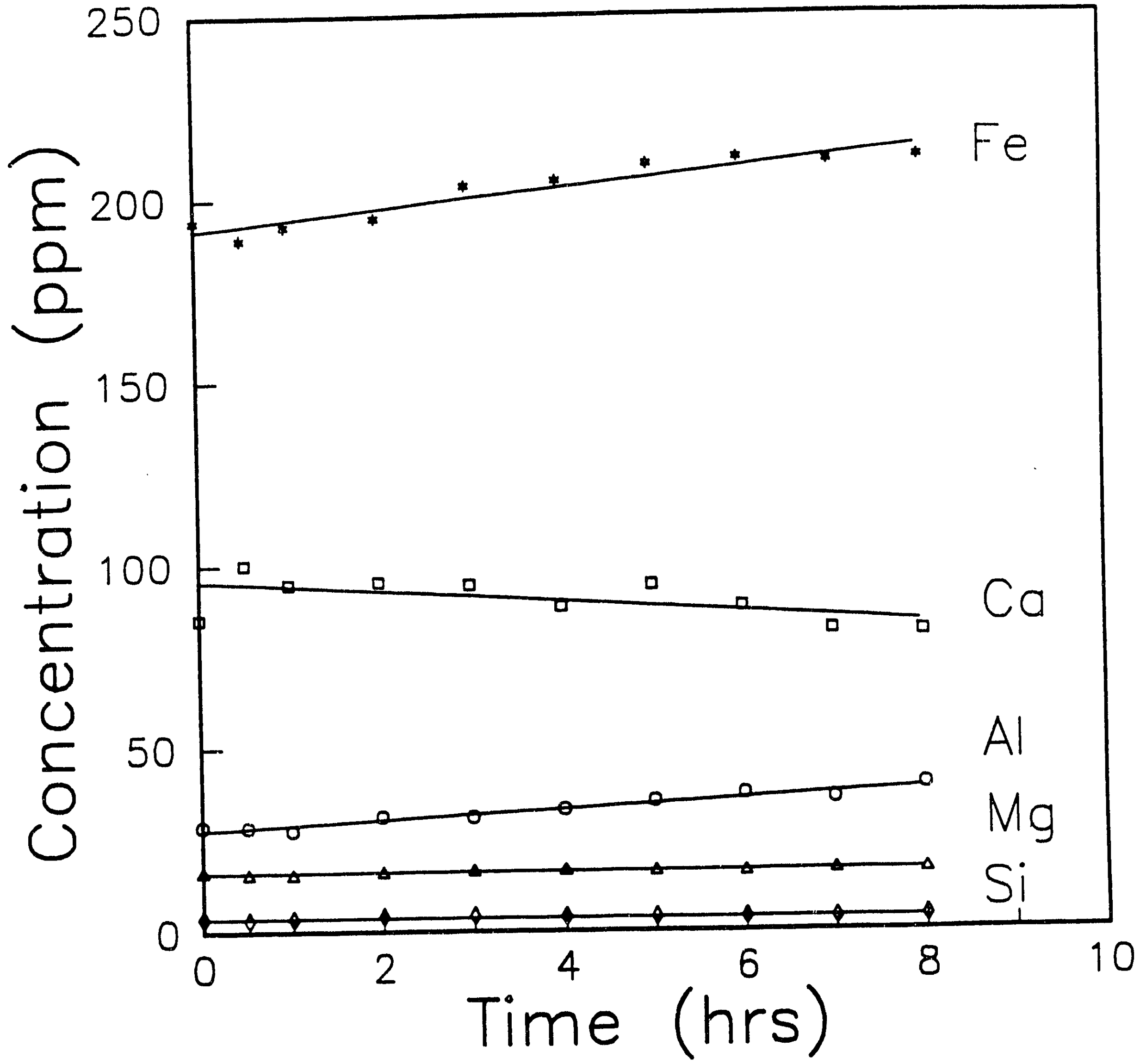

Figure 12. The release of different species from a Pittsburgh No. 8 coal as a function of time.

higher for the Pittsburgh No. 8 coal. This was expected since the Pittsburgh No. 8 coal has a much higher pyritic sulfur content than the Middle Wyodak coal. It should be noted that the initial amount of ferric ions added was only about 0.56 ppm, much lower than that for the Middle Wyodak coal. Thus, the majority of the Fe^{3+} ions found in solution came from the pyrite and other ferruginous minerals present in the Pittsburgh No. 8 coal.

Since the samples of leach solution taken after the coal was presoaked indicated that mineral matter dissolution had almost reached its maximum, tests were repeated for this coal without presoaking. Aliquots were collected within the first few minutes of the processing since presumably the rate of mineral matter dissolution was fast during the early stage of the process.

Assays for the feed and the product recovered in the last sampling (after 8 hrs) are given in Table XXXVI. The mineral matter removal for the Pittsburgh No. 8 coal was lower than that predicted by the optimization studies, which can be attributed to the likelihood that the feed coal was oxidized. The diffuse reflectance FTIR spectroscopy spectrum of this sample showed this in fact to be the case. Repeat tests for this coal were carried out using relatively fresh samples.

Table XXXVI. Results of CECC processing of Pittsburgh No. 8 coal.

Ash Content (% wt)		Sulfur Content (% wt)	
Feed	Product	Feed	Product
8.99	6.48	3.15	2.82

The amount of mineral matter dissolved was back-calculated on the assumption that the mineral matter present in this coal was kaolinite, quartz, calcite and pyrite. It was found that the total amount of these minerals dissolved at the end of the sampling period was about 0.676 g. Based on the ash analysis of the feed and product samples, the amount of ash removed was about 1.745 g. The amount of mineral matter dissolved would then account for 38.7% of the total mineral matter removed by the CECC process.

The rate of pyrite dissolution was also investigated by monitoring the potential of the slurry as a function of time. This was accomplished by inserting a platinum-Ag/AgCl reference electrode pair into the coal reactor. The electrode pair was attached to an electrometer from which the slurry potential was read. The measured potential was directly related to the ratio of ferric to ferrous ion concentrations.

The change in potential with time for the Middle Wyodak coal is shown in Figure 13. A sharp decrease in the potential during the first few minutes of the process indicates a decrease in the ferric to ferrous ion ratio. This decrease can be attributed to an increase in the concentration of ferrous ions brought about by pyrite dissolution in the acidic solution. The dissolution of pyrite by ferric ions is known to produce sulfate as well as elemental sulfur. However, it should be pointed out that ferric ions are also reduced to ferrous ions in the charging of the coal surface to promote osmotic pressure build-up. Thus, the change in the ferric to ferrous ion ratio would also be indicative of the rate of mineral matter liberation by the CECC process.

It should be noted that the ferrous ions were continuously being oxidized back to ferric ions due to the oxidizing potential applied between the working and counter

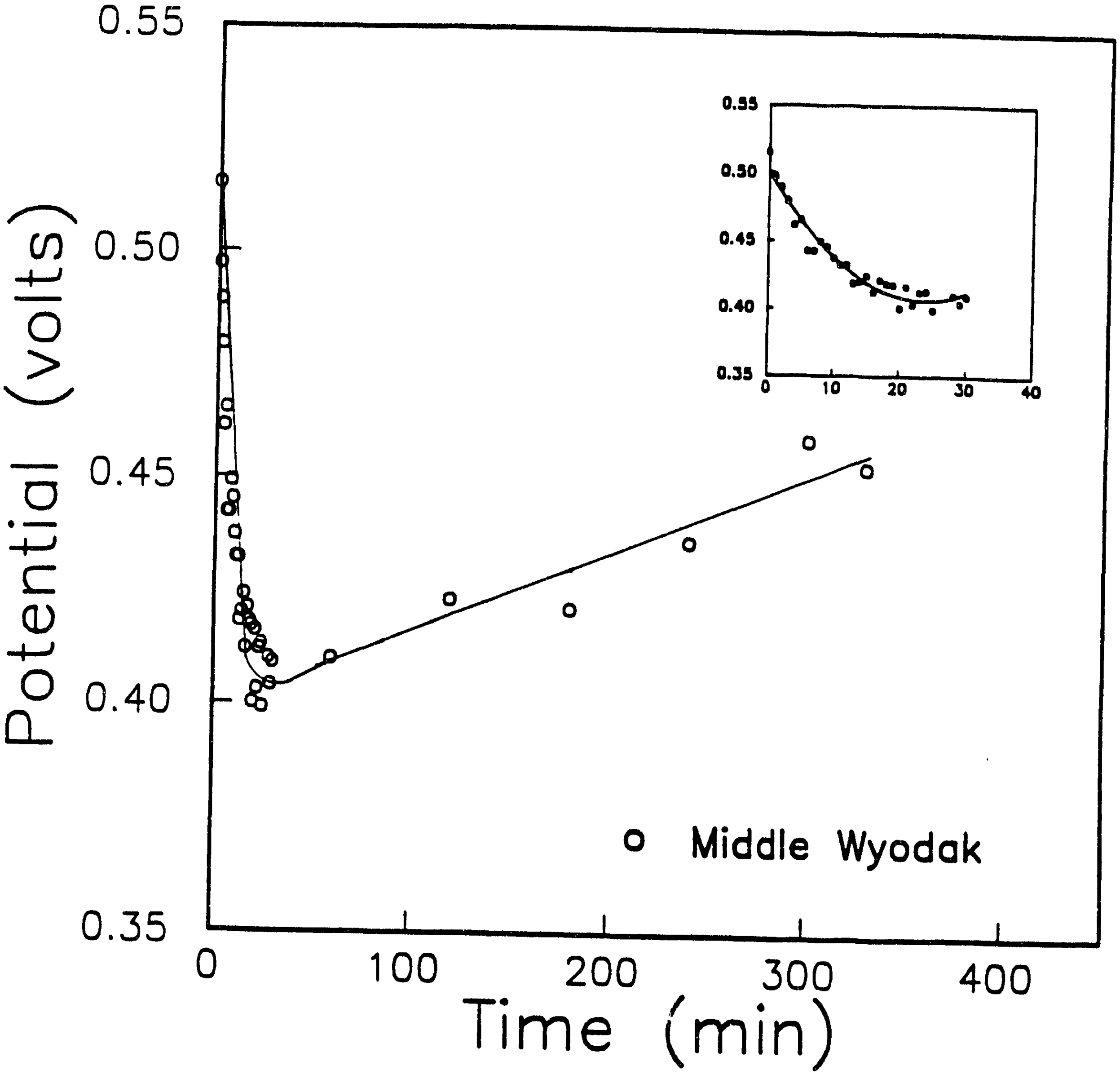

Figure 13. The change in redox potential as a function of time during the CECC processing of a Middle Wyodak coal.

electrodes of the reactor. This might be responsible for the increase in potential (increase in ferric to ferrous ratio) after 1 hour of processing. It should be pointed out that the increase in potential did not mean that the coal surface oxidation had stopped. It indicated, rather, that the rates of the pyrite dissolution and coal oxidation reactions were then less than that of the regeneration of the ferric ions in the electrochemical reactor; thus the potential would have increased.

The insert in Figure 13 illustrates more clearly the results during the first 30 minutes of the process. There is a linear decrease in potential during the first 10 minutes after which the potential appears to level off. The kinetics of pyrite dissolution and mineral matter liberation can only be inferred from this curve. Based on the potential versus time curve, the results indicate that the pyrite dissolution rate, as well as the coal surface oxidation, is probably relatively fast within the first 10 minutes and decreases afterwards. The decrease in the rate is expected since the amount of ferric ions is much lower than that of the ferrous ions at this point. This is indicated by the relatively low potential measured after 10 minutes. Another reason for the decrease in the dissolution rate may be that since the Middle Wyodak coal contained very little pyrite, almost all the pyrite in contact with the solution probably dissolved within this time period.

The results of the potential versus time measurements for a Pittsburgh No. 8 coal processed at the optimum conditions are shown in Figure 14. Again, the potential decreases sharply during the first few minutes of the process, leveling off after 2 hrs. However, the change in potential observed here is less than that observed for the Middle Wyodak coal. The slope of the curve observed for the Middle Wyodak coal is steeper

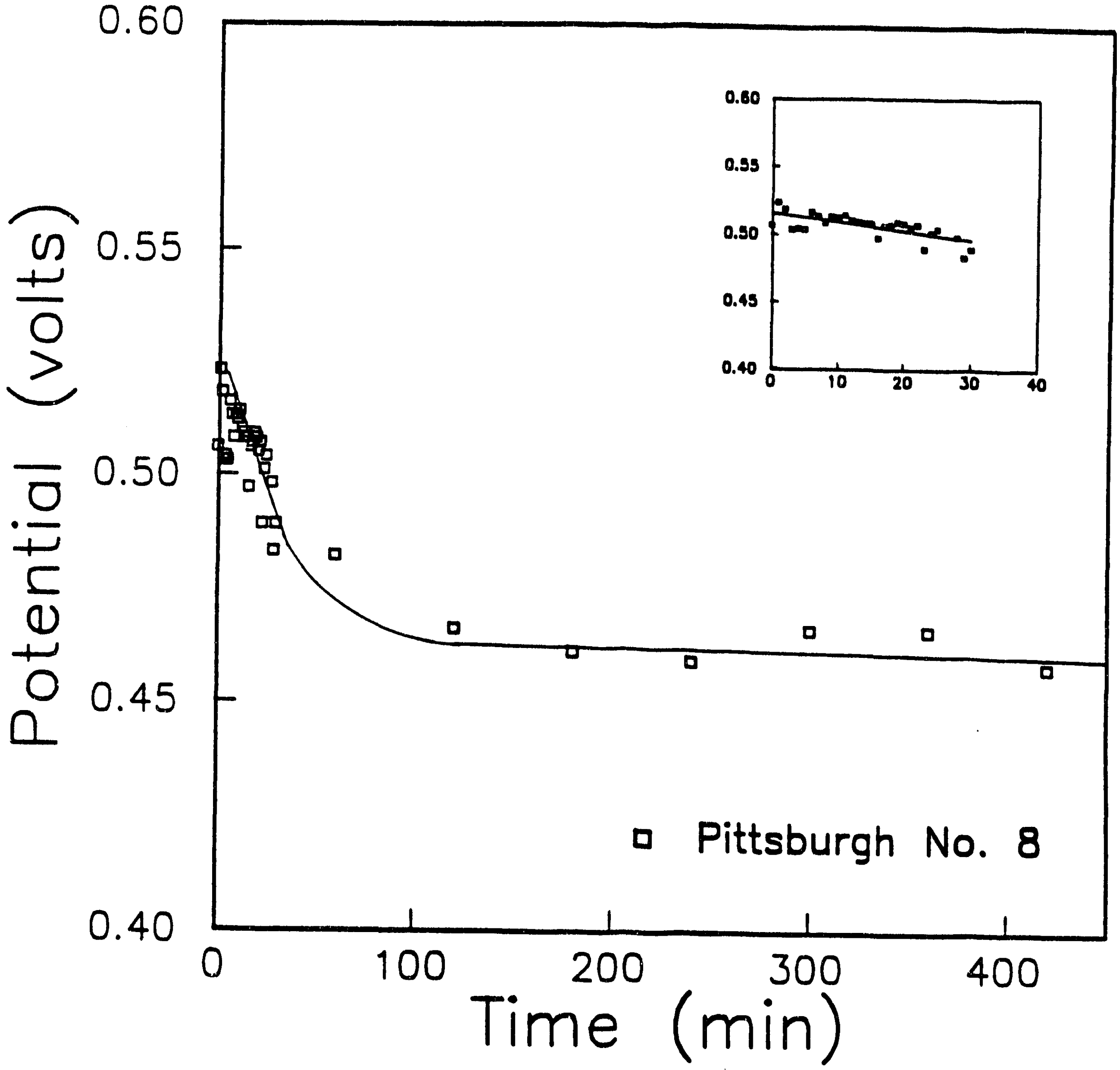

Figure 14. The change in redox potential as a function of time during the CECC processing of a Pittsburgh No. 8 coal.

than that for Pittsburgh No. 8 coal, suggesting that the decrease in the ferric to ferrous ion ratio, which is related to the rate of pyrite dissolution and coal oxidation by the ferric ions, is less for the latter coal. The insert in Figure 14 indicates more clearly that the pyrite leaching and coal oxidation rates for the Pittsburgh No. 8 coal are lower than those for the Middle Wyodak sample. The smaller amount of ferric ions initially added to the reactor for this test may be responsible for this observation. It should be pointed out that the ferric ions are responsible for the oxidation of pyrite and the coal surface, which results in pyrite dissolution and mineral matter liberation.

The leveling off of the potential after 2 hrs indicates a decrease in the pyrite leaching and coal oxidation rates for the Pittsburgh No. 8 coal. Due to this decrease, the regeneration of the ferric ions by the applied potential in the electrochemical reactor probably causes the potential to increase fast enough to offset any decrease in the ferric ion concentration. Also, the pyrite content of the Pittsburgh No. 8 coal was higher so that dissolution of pyrite was expected to occur over a longer time period than expected for the Middle Wyodak coal. In fact, the total amount of Fe found in solution was higher for the Pittsburgh No. 8 coal than for the Middle Wyodak coal.

Subtask 4.3.2 - Ferric Ion Regeneration

In Subtask 4.1, ferric ions were regenerated by electrolysis. However, these ions may be regenerated by other means such as bacteria and air oxidation. In the bacterial test work, *Thiobacillus Ferrooxidans* was used for the regeneration of the Fe^{3+} ions. Parametric tests were conducted to study the effects of the following parameters: pH, temperature, substrate concentration, inoculum concentration and lead time on the CECC process. Similar to the work carried out in Subtask 4.2, the parametric test results were analyzed statistically to determine the conditions for optimum mineral matter removal by the CECC process. The optimum conditions were then used in tests employing an apparatus where the ferric ion regeneration was separate from the coal reactor. In the air oxidation work, the spent solution was aerated to oxidize the ferrous ions to ferric ions and recirculated back to the reactor.

It should be noted that a large number of experiments were required in the parametric tests since there are five variables being studied. Based on the preliminary work, it was found that a long testing time was also required to achieved significant ash and sulfur removal. These conditions made impractical the use of a set-up where the regeneration of ferric ion is separate from the reactor. Therefore, the parametric tests were carried out by batch experiments using Erlenmeyer flasks, so that different tests were conducted simultaneously and completed within the required period of time. The drawback to this is that the coal is in direct contact with the bacteria, which is known to result in the direct removal of pyrite through a bacterial mechanism. However, as the results here showed, significant ash rejection occurred through the osmotic pressure mechanism of the CECC process. The primary focus of these parametric tests is still on the bacterial regeneration of ferric ions, while the direct sulfur removal can be considered to be a beneficial side effect.

Ferric Ion Regeneration by *Thiobacillus Ferrooxidans.* Preliminary experiments were conducted on Middle Wyodak coal to determine the effects on ash and sulfur removal of the following parameters: particle size, treatment time, slurry percent solids, lead time, pH, temperature, and inoculum concentration.

In the first series of experiments, wet-screened 65 x 200 mesh Middle Wyodak coal was used. For each test, 9K media were added to 10 grams of dry coal to make a total of 100 grams of slurry in an Erlenmeyer flask. The pH was adjusted to 2.6, and 5 ml of bacterial inocula, consisting of equal amounts of strain nos. 19859 and 21834, was added with no lead time. The flasks containing the coal slurry were placed in a shaking water bath at a constant temperature of 28°C and the shaker set at 180 rpm. Control tests in the absence of bacterial inocula were run in identical 9K media to determine the effects of auto-oxidation. Samples, taken at 7-day intervals for analyses, were washed with water on a 200 mesh screen and then contacted for 20 minutes with HCl solutions to remove the $Fe(OH)_3$ precipitates. The acid solutions were removed afterwards by filtration using Whatman filter papers. The filtered samples were then oven-dried and stored in a freezer before analysis for ash and sulfur content.

Figure 15 shows that ash rejection generally increases with treatment time. However, probably due to experimental error, the 14-day treatment removed less ash than the 7- and 21-day treatment tests. The improvement in ash rejection consistently observed with microbial treatment is presumably due to ferric ion oxidation. The *Thiobacillus ferrooxidans* bacteria use ferrous ions as an energy source and produce ferric ions as a result of their metabolism. Therefore, these iron oxidizing bacteria may function in the same way as the working electrode in the electrochemical stirred-tank reaction vessel shown in Figure 4. As ferrous ions are produced by coal oxidation, the

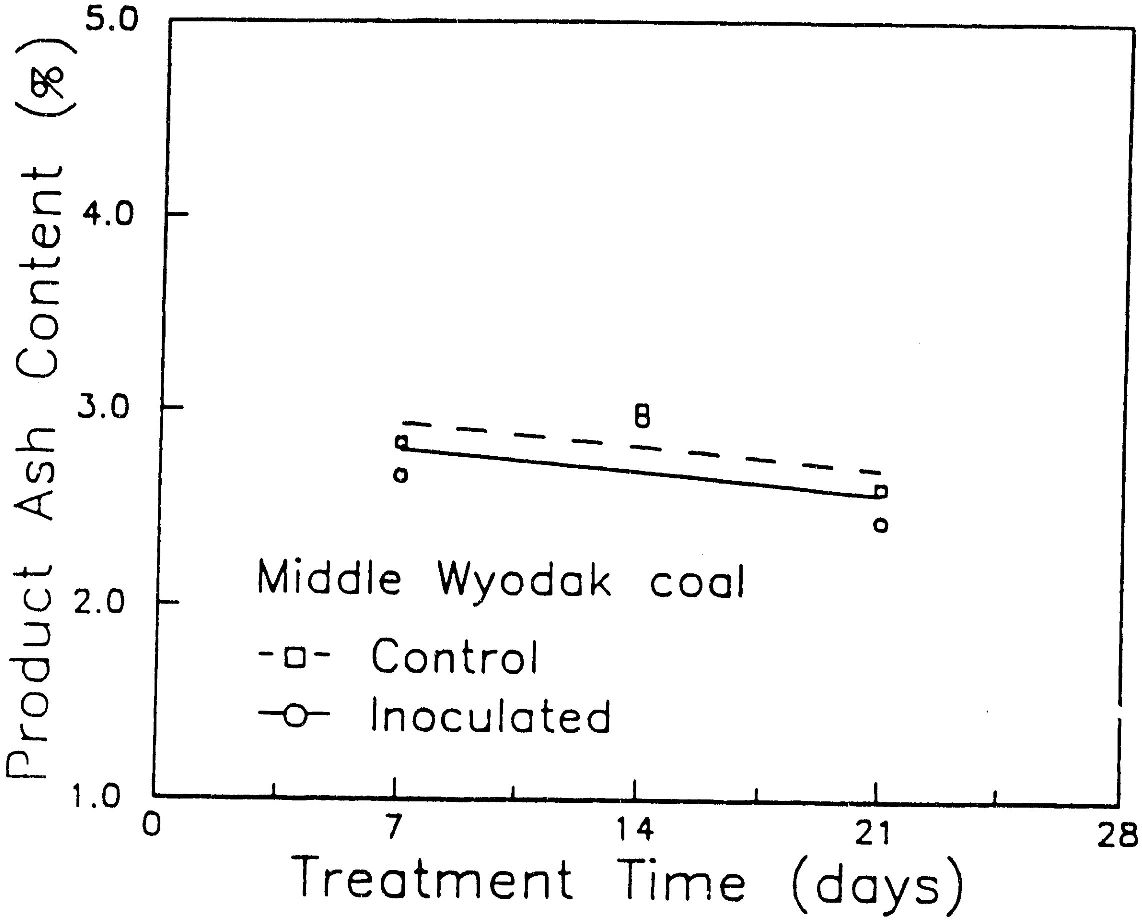

Figure 15. Ash removal as a function of treatment time for Middle Wyodak coal (65 x 200 mesh).

bacteria rapidly oxidize them to the ferric state. This process maintains the high oxidation potential of the solution, which may result in increased ash rejection.

Sulfur rejection also increases with treatment time, as shown in Figure 16. Significant coal desulfurization is known to result from this type of microbial treatment. The mechanisms of coal desulfurization by iron oxidizing bacteria have been studied extensively and can be found in the literature (Torma, 1977; Olsen *et al.*, 1980; Brierly, 1978; Kargi, 1982; Torma and Banhegyi, 1984; Dugan, 1972; Murr, 1980; Silverman *et al.*, 1963).

The effects of pH on ash and sulfur removal efficiencies were determined under experimental conditions similar to those described above except that the pH was adjusted from 2.0 to 7.0 by the addition of either HCl or NaOH. A treatment time of 15 days was used and the solids content was decreased to 4% for each test.

The results, shown in Figure 17, indicated that the sulfur removal efficiency improved with decreasing pH for the inoculated samples. This may be attributed to that fact that *Thiobacillus ferrooxidans* grows best in acidic media and that above pH 3-3.5, the regeneration of ferric ions and the oxidation of pyrite by the acidophilic thiobaccilli would be inhibited. This may decrease the concentration of ferric ions in the solutions and thereby decrease the sulfur rejection. Ash rejection also increased with decreasing pH (Figure 18). The inoculated samples showed improvement in ash removal over the control samples at the pH range of these tests. The increased efficiency of ash rejection in microbial treatment indicates that *Thiobacillus ferrooxidans* may be capable of functioning the same way as the working electrode in the electrochemical reactor used in

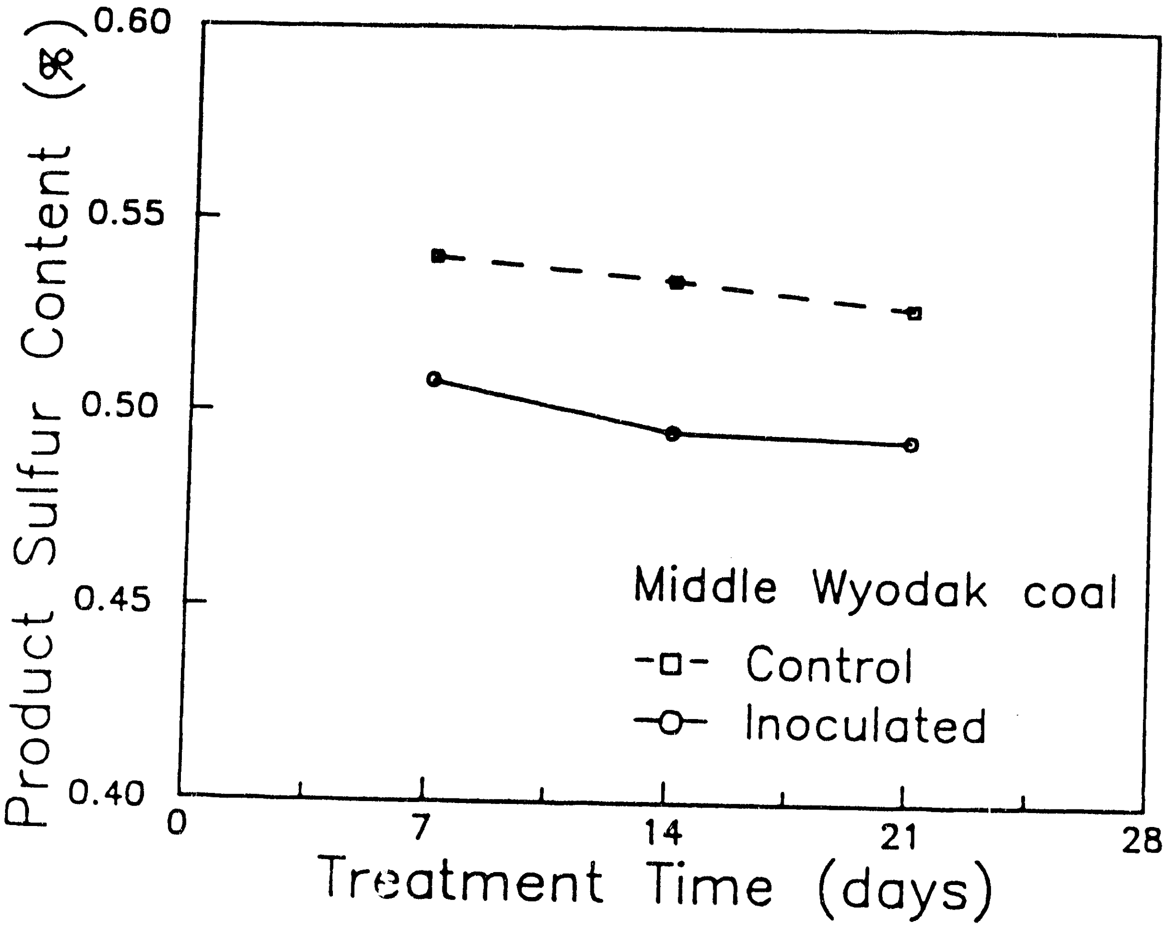

Figure 16. Sulfur removal as a function of treatment time for Middle Wyodak coal (65 x 200 mesh).

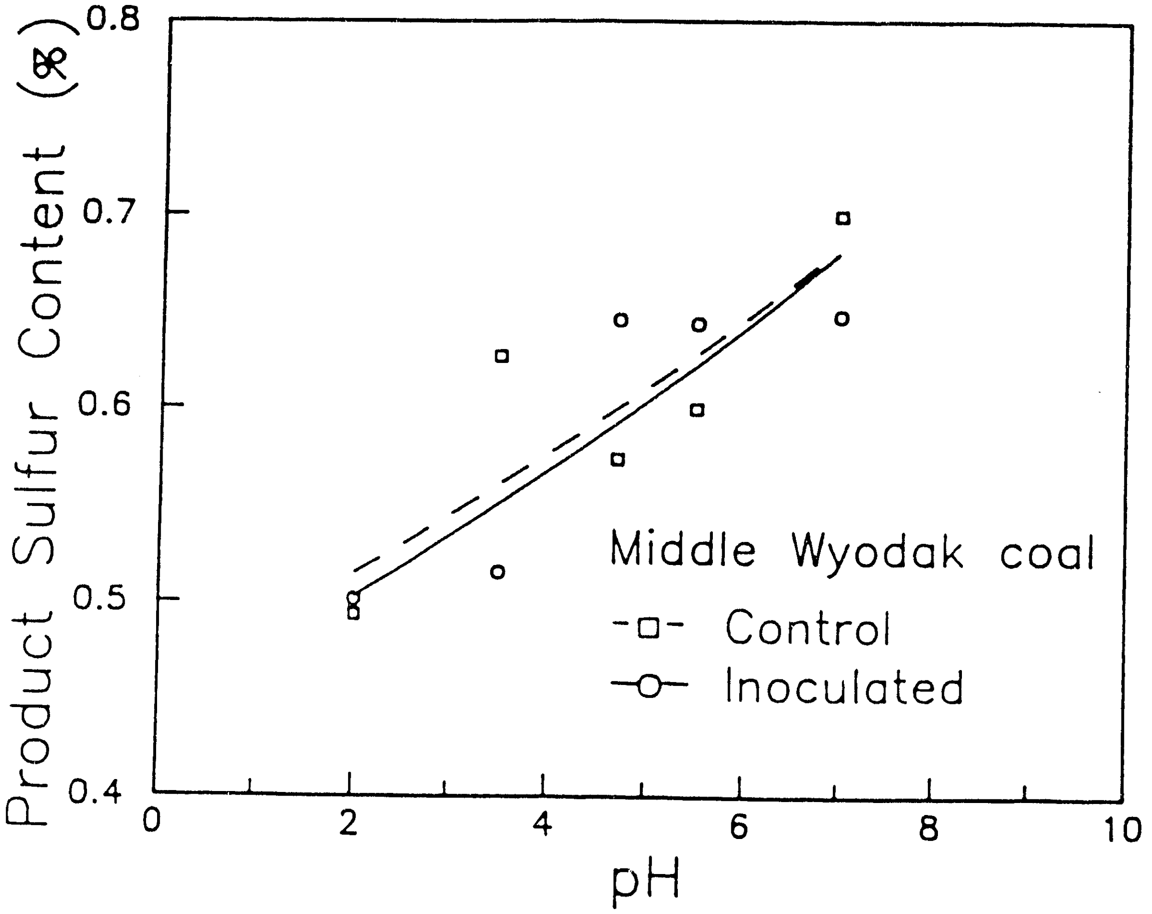

Figure 17. Sulfur removal as a function of pH for Middle Wyodak coal (65 x 200).

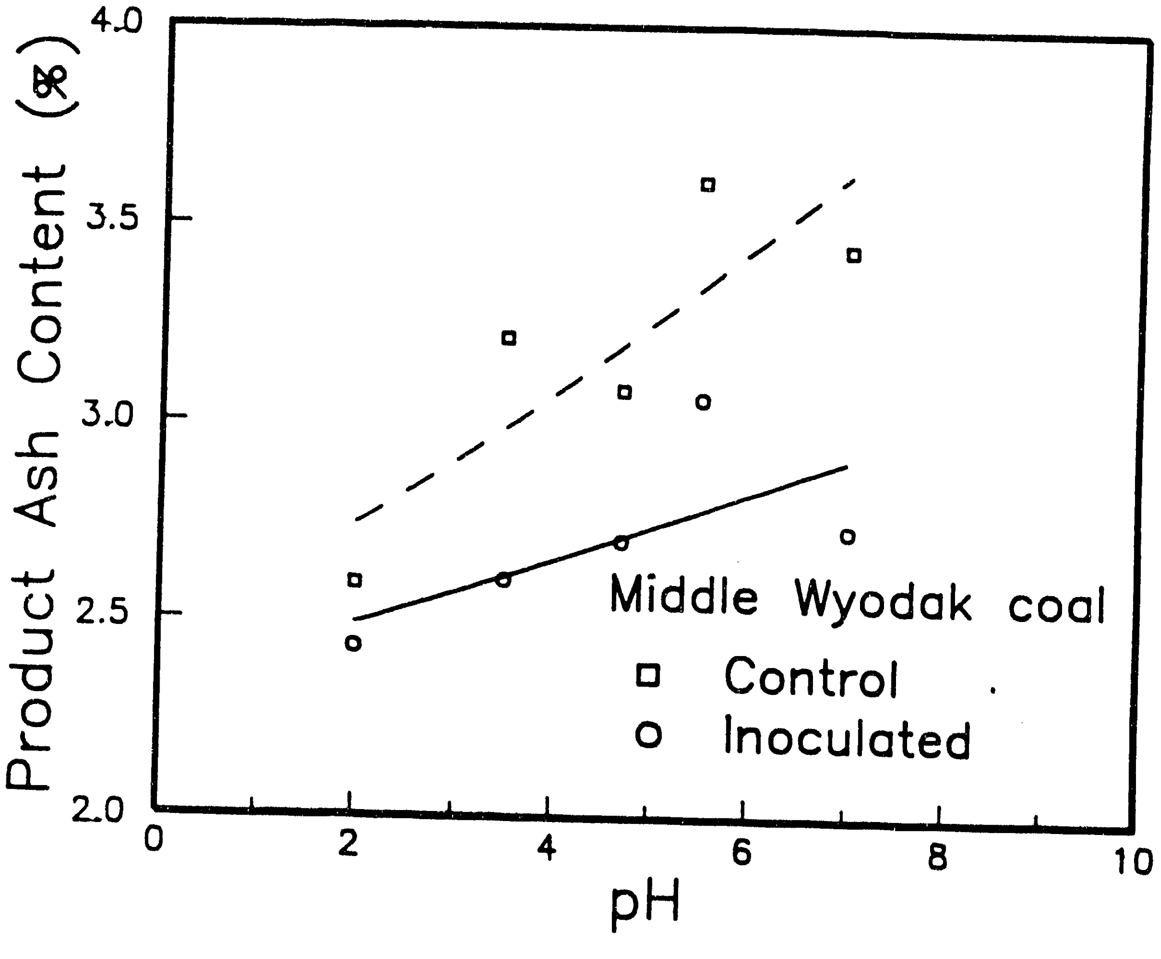

Figure 18. Ash removal as a function of pH for Middle Wyodak coal (65 x 200 mesh).

Subtask 4.1.

For parametric tests using *Thiobacillus ferrooxidans*, a statistically designed experiment was carried out to determine the optimum operating conditions for using the bacteria in ferric ion regeneration. The parameters studied were pH, temperature, substrate concentration, inoculum concentration and lead time. The test program, similar to that used in Subtask 4.1, is given in Table XXXVII, and details of the experiments are similar to those for the preliminary tests described above. The experiments were conducted using wet-screened 65 x 200 mesh feed samples with a treatment time of 14 days.

In these batch experiments, the *Thiobacillus ferrooxidans*, which were in direct contact with the coal, were used to regenerate the ferric ions. For each test, the pH of the electrolytic media was adjusted to the required value by the addition of H_2SO_4 or NaOH, and afterwards the bacterial inoculum. After the desired lead time was attained, the 65 x 200 mesh size coal sample was added to make a coal slurry that was 10% solids (by weight). The flasks containing the inoculated coal slurry were then placed in the shaking water bath and held at the required temperature for the treatment period of 14 days. The coal sample was recovered afterwards, wet-screened to remove the -200 mesh material, and acid-washed to dissolve the iron hydroxide precipitates.

The complete ash and sulfur analysis results for the tests done on the Middle Wyodak coal are given in Table XXXVIII. The ash content was reduced to as low as 2.49%, even lower than that obtained using electrolysis, with an average of about 3.30%. The % ash rejection ranged from 39% to 62%, averaging 51%. The sulfur removal was

Table XXXVII. Experimental design for ferric ion regeneration by bacteria.

Experiment Number	pH	Substrate Conc.	Inoculum Conc. (ml)	Lead time	Temperature (°C)
1	2.875	2.25	2.5	1.25	23.75
2	5.625	2.25	2.5	1.25	23.75
3	2.875	6.75	2.5	1.25	23.75
4	5.625	6.75	2.5	1.25	23.75
5	2.875	2.25	7.5	1.25	23.75
6	5.625	2.25	7.5	1.25	23.75
7	2.875	6.75	7.5	1.25	23.75
8	5.625	6.75	7.5	1.25	23.75
9	2.875	2.25	2.5	3.75	23.75
10	5.625	2.25	2.5	3.75	23.75
11	2.875	6.75	2.5	3.75	23.75
12	5.625	6.75	2.5	3.75	23.75
13	2.875	2.25	7.5	3.75	23.75
14	5.625	2.25	7.5	3.75	23.75
15	2.875	6.75	7.5	3.75	23.75
16	5.625	6.75	7.5	3.75	23.75
17	2.875	2.25	2.5	1.25	41.25
18	5.625	2.25	2.5	1.25	41.25
19	2.875	6.75	2.5	1.25	41.25
20	5.625	6.75	2.5	1.25	41.25
21	2.875	2.25	7.5	1.25	41.25
22	5.625	2.25	7.5	1.25	41.25
23	2.875	6.75	7.5	1.25	41.25

continued on next page

Experiment Number	pH	Substrate Conc.	Inoculum Conc. (ml)	Lead time	Temperature (°C)
24	5.625	6.75	7.5	1.25	41.25
25	2.875	2.25	2.5	3.75	41.25
26	5.625	2.25	2.5	3.75	41.25
27	2.875	6.75	2.5	3.75	41.25
28	5.625	6.75	2.5	3.75	41.25
29	2.875	2.25	7.5	3.75	41.25
30	5.625	2.25	7.5	3.75	41.25
31	2.875	6.75	7.5	3.75	41.25
32	5.625	6.75	7.5	3.75	41.25
33-1	4.25	4.50	5.0	2.50	32.50
33-2	4.25	4.50	5.0	2.50	32.50
33-3	4.25	4.50	5.0	2.50	32.50
34	1.50	4.50	5.0	2.50	32.50
35	7.00	4.50	5.0	2.50	32.50
36	4.25	0	5.0	2.50	32.50
37	4.25	9.00	5.0	2.50	32.50
38	4.25	4.50	0	2.50	32.50
39	4.25	4.50	10.0	2.50	32.50
40	4.25	4.50	5.0	0	32.50
41	4.25	4.50	5.0	5.00	32.50
42	4.25	4.50	5.0	2.50	15.00
43	4.25	4.50	5.0	2.50	50.00

Table XXXVIII. Results of parametric tests conducted on wet-screened Middle Wyodak coal using bacteria for ferric ion regeneration.

	Ash Content (% wt)			Sulfur Content (% wt)		
Test No.	Feed	Product	Ash Rejection (% wt)	Feed	Product	Sulfur Rejection (% wt)
1	6.02	2.92	57.83	0.443	0.429	15.81
2	6.02	2.79	60.08	0.443	0.467	9.20
3	6.02	3.71	46.34	0.443	0.554	-
4	6.02	3.52	49.01	0.443	0.537	-
5	6.02	3.42	51.75	0.443	0.500	4.14
6	6.02	3.34	51.62	0.443	0.489	3.74
7	6.02	3.64	48.89	0.443	0.530	-
8	6.02	3.66	46.50	0.443	0.502	0.28
9	6.02	3.18	51.82	0.443	0.513	-
10	6.02	2.99	56.16	0.443	0.518	-
11	6.02	3.38	50.82	0.443	0.571	-
12	6.02	3.60	46.74	0.443	0.552	-
13	6.02	3.39	50.22	0.443	0.520	-
14	6.02	2.95	55.83	0.443	0.508	-
15	6.02	4.02	39.46	0.443	0.627	-
16	6.02	3.67	44.73	0.443	0.571	-
17	6.02	4.11	40.65	0.443	0.467	8.36
18	6.02	3.47	46.66	0.443	0.467	2.45
19	6.02	3.50	50.23	0.443	0.468	9.57
20	6.02	3.39	47.44	0.443	0.451	4.98
21	6.02	3.34	50.14	0.443	0.467	5.26
22	6.02	3.31	52.93	0.443	0.449	13.24
23	6.02	3.13	52.58	0.443	0.466	4.06

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Test No.	Ash Content (% wt)		Ash Rejection (% wt)	Sulfur Content (% wt)		Sulfur Rejection (%wt)
	Feed	Product		Feed	Product	
24	6.02	3.08	53.34	0.443	0.445	8.39
25	6.02	2.77	57.18	0.443	0.479	-
26	6.02	2.66	59.11	0.443	0.435	9.14
27	6.02	2.49	62.61	0.443	0.453	7.56
28	6.02	3.65	43.57	0.443	0.474	0.42
29	6.02	3.22	50.58	0.443	0.434	9.48
30	6.02	3.54	45.67	0.443	0.471	1.76
31	6.02	3.32	48.82	0.443	0.438	8.25
32	6.02	3.61	43.95	0.443	0.495	-
33-1	6.02	3.11	51.99	0.443	0.470	1.40
33-2	6.02	2.72	58.67	0.443	0.477	1.51
33-3	6.02	2.60	60.49	0.443	0.496	-
34	6.02	3.09	52.09	0.443	0.518	-
35	6.02	3.97	43.89	0.443	0.584	-
36	6.02	3.12	51.14	0.443	0.558	-
37	6.02	3.06	60.73	0.443	0.546	-
38	6.02	4.12	41.03	0.443	0.576	-
39	6.02	2.60	57.41	0.443	0.497	-
40	6.02	3.21	53.50	0.443	0.524	-
41	6.02	3.11	55.23	0.443	0.514	-
42	6.02	3.18	54.78	0.443	0.548	-
43	6.02	3.90	45.84	0.443	0.580	-

negligible. In fact, there were cases where the final sulfur contents were higher than the initial amounts. This was also observed in the batch tests done in Subtask 4.1. This behavior may result from the use of H_2SO_4 to control the pH. The Middle Wyodak coal probably adsorbed some of the sulfate ions during treatment, which caused the increase in final sulfur content.

The effects of all five parameters were found to be statistically significant from the analysis of the data for the Middle Wyodak coal. The response model indicated that mineral matter removal increases with decreasing pH, substrate concentration, and temperature. The inoculum addition and the lead time were found to show opposite effects.

The effects of pH and substrate concentration on the product ash content are shown in Figure 19. This contour plot of the product ash content was obtained from the response surface model fitted for the parametric test data. The values for the other parameters were set constant and correspond to the optimum values determined for these parameters. The product ash content can be minimized at pH conditions between 2.4 and 3.3 with the substrate concentration set around 3 to 4.5 g Fe^{2+}/l. Figure 19 also shows the nonlinearity of the effect of pH on mineral matter removal, and of the decrease in the mineral matter rejection at the extremes of the experimental pH range. The effect of relatively extreme temperature conditions can be seen in Figure 20. The trend is similar to that seen for the effect of pH. Also shown in this response surface is the effect of lead time. It can be seen that optimum mineral matter rejection may be obtained at longer lead times. This is expected since for a more effective removal of mineral matter and

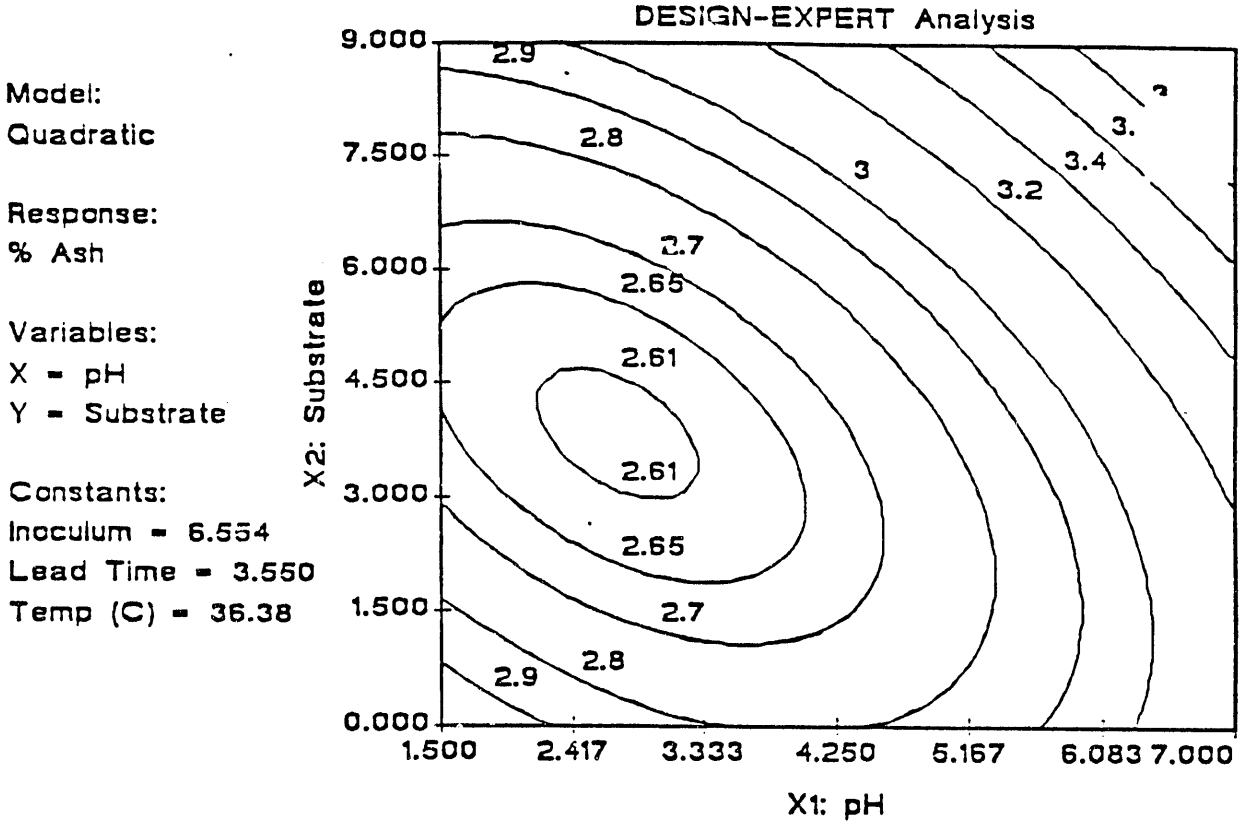

Figure 19. The effect of pH and substrate concentration on the product ash content (% wt) for the Middle Wyodak coal.

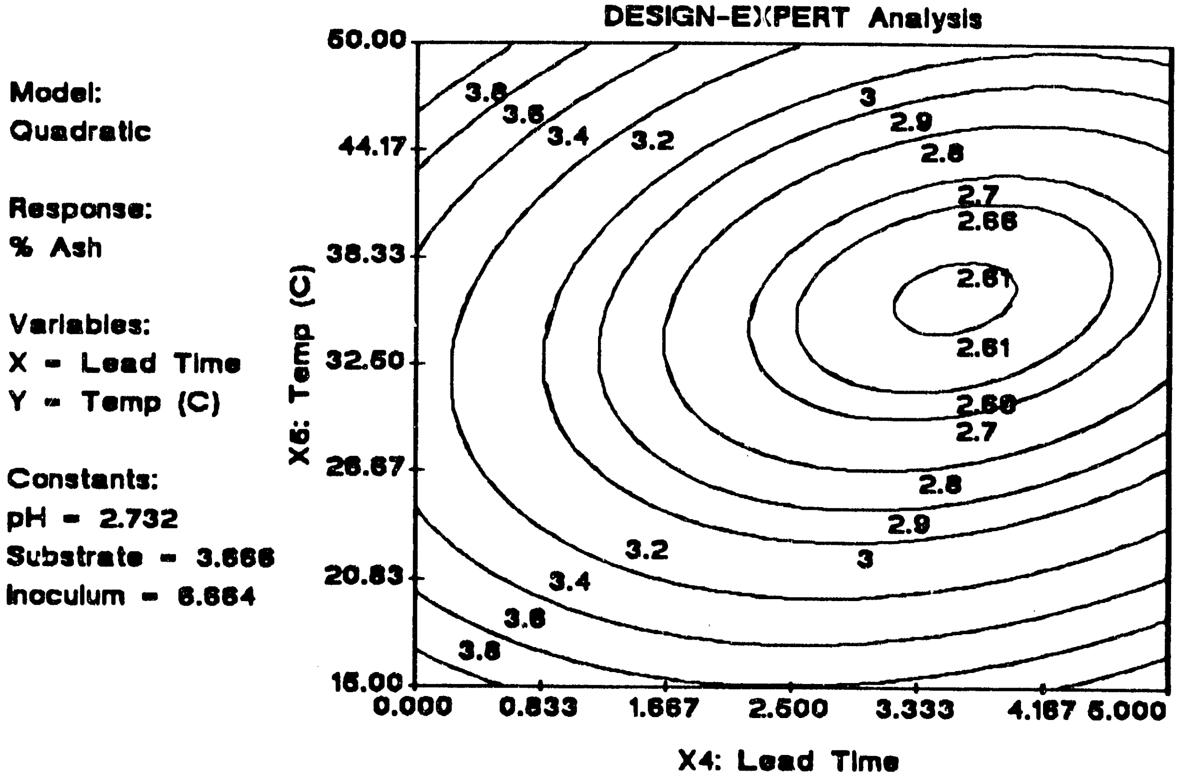

Figure 20. The effect of temperature and lead time on the product ash content (% wt) for the Middle Wyodak coal.

sulfur, the Fe^{2+} must be oxidized to Fe^{3+} by the bacteria prior to the addition of coal. The effects of the other variables and their interactions can be seen in these response surfaces (Appendix 4).

Table XXXIX shows the complete ash and sulfur analyses for the parametric tests conducted on wet-screened Pittsburgh No. 8 coal. The cleanest product was obtained from Test No. 39, which had ash and sulfur contents of 6.08% and 1.83%, and % ash rejections ranging from 17.4% to 52.28%. These values were not as good as those obtained for the Middle Wyodak coal. However, the sulfur removal for this particular coal was significant. The product sulfur content was brought down from 2.97% to as low as 1.72%, the average being close to 2.15%.

The response model obtained from the statistical analysis of the parametric test data indicates that mineral matter removal is favored at decreasing pH and temperature. This was also observed previously for the Middle Wyodak coal. On the other hand, an increase in inoculum addition, substrate concentration, and lead time would result in higher mineral matter rejection. The interaction effect of pH and substrate concentration is shown in Figure 21. This response surface was obtained by setting the other variables at values corresponding to the optimum point determined from the response model. The minimum product ash content can be obtained at around pH 2.9 and a substrate concentration between 5 and 6 g Fe^{+}/l. Similar to that found for the Middle Wyodak coal, mineral matter removal is not favored at the extremes of the pH range for these experiments. The effect of the other variables can be seen in the response surfaces plotted for the different variables in Appendix 5.

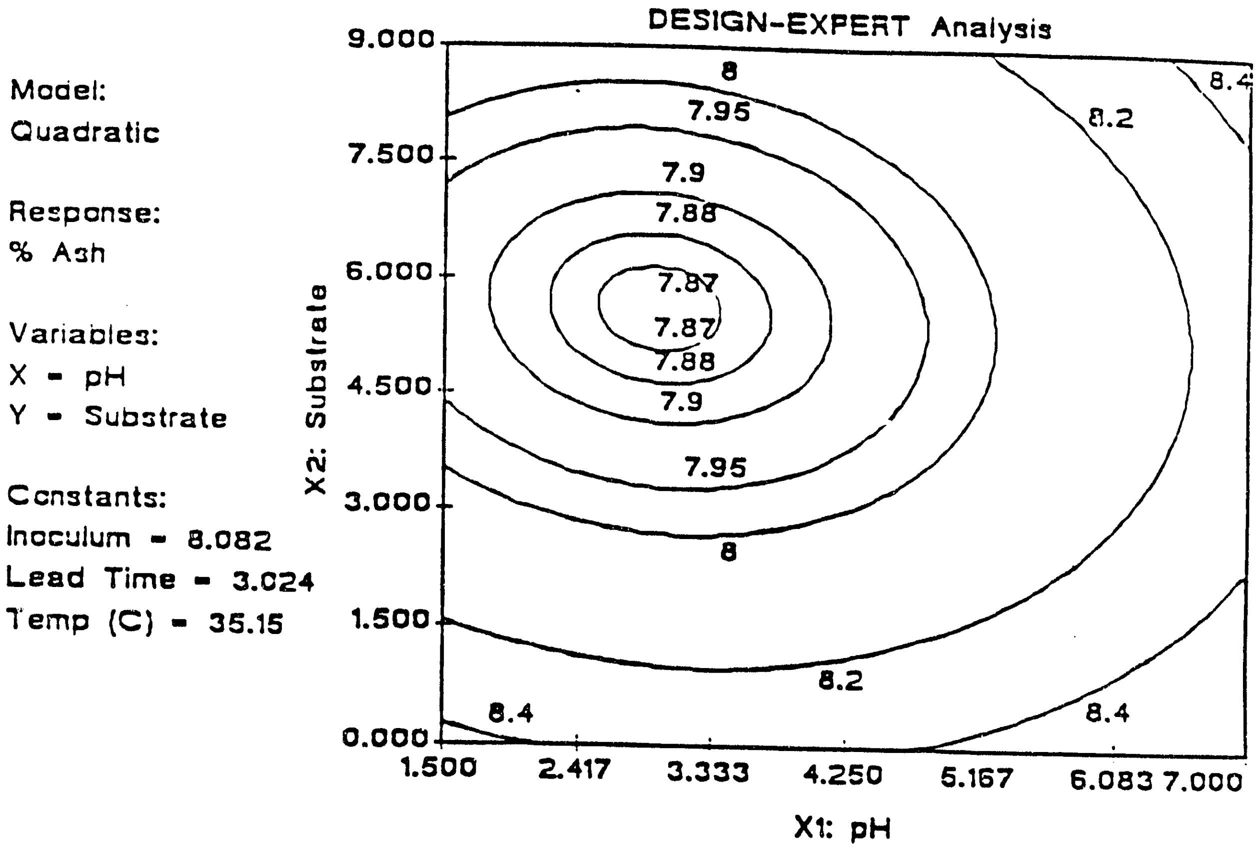

Figure 21. The effect of pH and substrate concentration on the product ash content (% wt) for the Pittsburgh No. 8 coal.

Table XXXIX. Results of parametric tests conducted on wet-screened Pittsburgh No. 8 coal using bacteria for ferric ion regeneration.

	Ash Content (% wt)			Sulfur Content (% wt)		
Test No.	Feed	Product	Ash Rejection (% wt)	Feed	Product	Sulfur Rejection (% wt)
1	9.87	7.92	28.21	2.97	1.900	42.76
2	9.87	8.54	22.47	2.97	2.091	36.92
3	9.87	8.15	26.78	2.97	2.028	39.46
4	9.87	8.34	25.08	2.97	2.183	34.83
5	9.87	8.27	25.37	2.97	2.323	30.34
6	9.87	8.05	27.79	2.97	2.182	34.96
7	9.87	8.45	24.89	2.97	2.274	32.83
8	9.87	8.36	23.54	2.97	2.111	35.84
9	9.87	8.46	24.23	2.97	2.239	35.75
10	9.87	8.28	27.63	2.97	2.212	35.75
11	9.87	8.882	21.48	2.97	2.216	34.45
12	9.87	8.64	24.95	2.97	2.242	35.28
13	9.87	8.80	20.59	2.97	2.363	29.14
14	9.87	8.42	25.72	2.97	2.287	32.95
15	9.87	8.28	26.29	2.97	2.273	32.74
16	9.87	8.48	23.02	2.97	2.313	30.23
17	9.87	8.73	21.93	2.97	2.191	34.88
18	9.87	8.67	19.89	2.97	2.235	24.42
19	9.87	8.48	21.41	2.97	2.454	24.42
20	9.87	8.64	23.90	2.97	2.533	25.86
21	9.87	8.24	30.54	2.97	2.363	33.80
22	9.87	8.10	31.28	2.97	1.916	45.98
23	9.87	8.56	23.22	2.97	2.510	25.18

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x 200 mesh).

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	Ash Content			Sulfur Content (% wt)		
Test No.	Feed	Product	Ash Rejection (% wt)	Feed	Product	Sulfur Rejection (% wt)
24	9.87	8.23	35.07	2.97	2.051	46.23
25	9.87	8.41	27.74	2.97	2.006	42.72
26	9.87	7.87	29.19	2.97	1.874	43.97
27	9.87	7.88	27.61	2.97	2.149	34.43
28	9.87	8.74	22.07	2.97	2.290	32.15
29	9.87	8.17	30.03	2.97	1.865	46.92
30	9.87	8.50	22.95	2.97	2.057	38.04
31	9.87	8.43	21.19	2.97	2.338	27.37
32	9.87	7.89	25.82	2.97	1.864	41.76
33-1	9.87	7.99	30.38	2.97	1.752	49.27
33-2	9.87	7.91	32.47	2.97	1.721	51.15
33-3	9.87	7.96	29.35	2.97	1.781	47.46
34	9.87	7.54	32.67	2.97	1.771	47.46
35	9.87	8.35	19.57	2.97	2.226	27.66
36	9.87	8.31	18.77	2.97	2.717	15.24
37	9.87	7.71	31.36	2.97	1.862	44.91
38	9.87	8.71	17.40	2.97	2.710	14.58
39	9.87	6.08	52.28	2.97	1.834	52.15
40	9.87	8.33	23.70	2.97	2.151	34.40
41	9.87	7.99	27.36	2.97	1.825	44.86
42	9.87	7.66	26.43	2.97	2.066	34.07
43	9.87	8.49	26.21	2.97	2.642	17.00

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The optimum conditions determined for cleaning coal using bacteria for the regeneration of ferric ions are given for Middle Wyodak and Pittsburgh No. 8 coals in Table XL. For these coals, the pH, lead time, and temperature required for optimum removal of mineral matter are similar. The Pittsburgh No. 8 coal, though, requires a higher substrate and inoculum addition, probably because the Pittsburgh No. 8 coal is harder to clean than the Middle Wyodak coal, as suggested by the results in Subtask 4.1. To grow the larger amount of bacteria required for optimum mineral removal from Middle Wyodak coal, a corresponding increase in substrate is needed. Due to the inability of the *Thiobacillus ferrooxidans* to grow and survive at temperatures greater than 50°C, the optimum temperatures suggested here are much lower than those suggested using the electrochemical reactor in Subtask 4.2. The predicted product ash contents for the Middle Wyodak and Pittsburgh No. 8 coal at these optimum conditions are 2.60 and 7.86%.

Table XL. Optimum conditions determined for the CECC treatment of Middle Wyodak and Pittsburgh No. 8 coal using bacteria to regenerate ferric ions.

Operating Parameters	Middle Wyodak	Pittsburgh No. 8
pH	2.73	2.87
Substrate Concentration (g Fe^{2+}/1)	3.85	5.55
Inoculum Addition (ml)	6.55	8.08
Lead Time (days)	3.55	3.02
Temperature (°C)	36.38	35.15
Predicted Product Ash Content	2.60%	7.86%

The mineral matter rejections observed in the bacterial experiments for both coal samples are lower than those obtained using the electrochemical reactor. The decrease in mineral matter rejection may be attributed to slower kinetics and/or less efficient ferric ion regeneration by the bacteria. Another factor to consider is that the starting ferric ion concentration and the Fe^{3+}/Fe^{2+} ratio used in the bacterial experiments are also quite different from those used in the electrochemical reactor. The decreased rejection may also be due to the less acidic conditions used in the bacterial experiments. The pH conditions used in these tests are usually higher than the PZC of most of the mineral matter present in the coal (i.e., quartz). This means that presumably no ionic double layer will be created between these minerals and the coal surface and, therefore, there will be no osmotic pressure build up. The temperatures used in the bacterial tests are also much lower than those used in the electrochemical reactor. It was found in Subtasks 4.1 and 4.2 that higher temperatures favor the removal of mineral matter. Also, faster kinetics of both ferric ion regeneration and mineral matter removal are generally expected at higher temperatures. The increase in sulfur removal observed for the Pittsburgh No. 8 coal samples, though, is probably brought about by the bacterial desulfurization caused by the direct contact of the bacteria with the coal. Other investigators have already explained the mechanism by which sulfur is removed by *Thiobacillus ferrooxidans* (Silverman, 1967; Torma, 1977; Olsen *et al.*, 1980; Brierly, 1978; Kargi, 1982; Torma and Banhegyi, 1984; Dugan, 1972; Murr, 1980; Silverman *et al.*, 1963).

Tests were conducted on the Middle Wyodak and Pittsburgh No. 8 coals at the optimum conditions determined through parametric testing in order to validate the response surface model obtained for these coal samples. The results of the validation tests for the Middle Wyodak and Pittsburgh No. 8 coal samples are given in Tables XLI and XLII, respectively. Three tests were conducted for each coal sample with a treatment time of two weeks. In these tests, the bacteria was in direct contact with the coal. For the Middle Wyodak coal, the mineral matter content was reduced from 6.56% to an average of about 2.86%, higher than the value predicted by the response model.

Table XLI. Results of CECC tests conducted on Middle Wyodak coal using the statistically-determined optimum conditions.

Test No.	Ash Content (% wt)		Ash Rejection (% wt)	Sulfur Content (% wt)		Sulfur Rejection (% wt)
	Feed	Product		Feed	Product	
1	6.56	2.86	59.19	0.510	0.505	7.41
2	6.56	2.82	60.16	0.501	0.476	13.59
3	6.56	2.90	58.44	0.501	0.498	8.30
Avg		2.86	59.26		0.487	9.77

Table XLII. Results of CECC tests conducted on Pittsburgh No. 8 coal using the statistically-determined optimum conditions.

Test No.	Ash Content (% wt)		Ash Rejection (% wt)	Sulfur Content (% wt)		Sulfur Rejection (% wt)
	Feed	Product		Feed	Product	
1	10.45	8.33	24.11	2.890	2.009	34.08
2	10.45	8.39	24.85	2.890	2.249	27.16
3	10.45	8.25	25.47	2.890	2.200	28.14
Avg		8.32	24.81		2.152	29.79

However, the average % ash rejection obtained from the validation tests was about 59.26%, which agrees with the predicted value of 59.57%. The discrepancy is due to the lower ash content of the feed used in the parametric tests. The sulfur rejection is almost negligible, as was observed in the parametric tests. The average sulfur content obtained after treatment at the optimum condition is about 0.487% with the % sulfur rejection ranging from 7.41 to 13.59%. The poor sulfur removal observed for the Middle Wyodak coal was attributed previously to the adsorption of sulfate ions.

The mineral matter content of the Pittsburgh No. 8 coal samples was reduced to as low as 8.25% after treatment with an average product ash content and % ash rejection of about 8.32% and 24.81%. Again, the product ash content was higher than the predicted value, 7.86%. However, the ash content of the feed used in the parametric tests was only 9.87% with a predicted % ash rejection of 24.82%. Therefore, the % ash rejections obtained from the validation tests are still in good agreement with the predicted value. The removal of sulfur from the Pittsburgh No. 8 coal was higher than that observed for the Middle Wyodak coal. The sulfur content was reduced from 2.89% to as low as about 2.01% with the % sulfur rejection ranging from 27.16 to 34.08%. The amount of sulfur removed in these tests was slightly higher than that observed in the parametric tests.

After the optimum conditions were determined and validated, an apparatus was designed and constructed for the separate regeneration of ferric ions using bacteria (Figure 22). The ferrous ions are oxidized to ferric ions by the bacteria in the microbial reactor and recirculated back to the coal reactor. In this set-up, the coal being treated was kept separate from the bacteria by a system of membranes and filters. Since these

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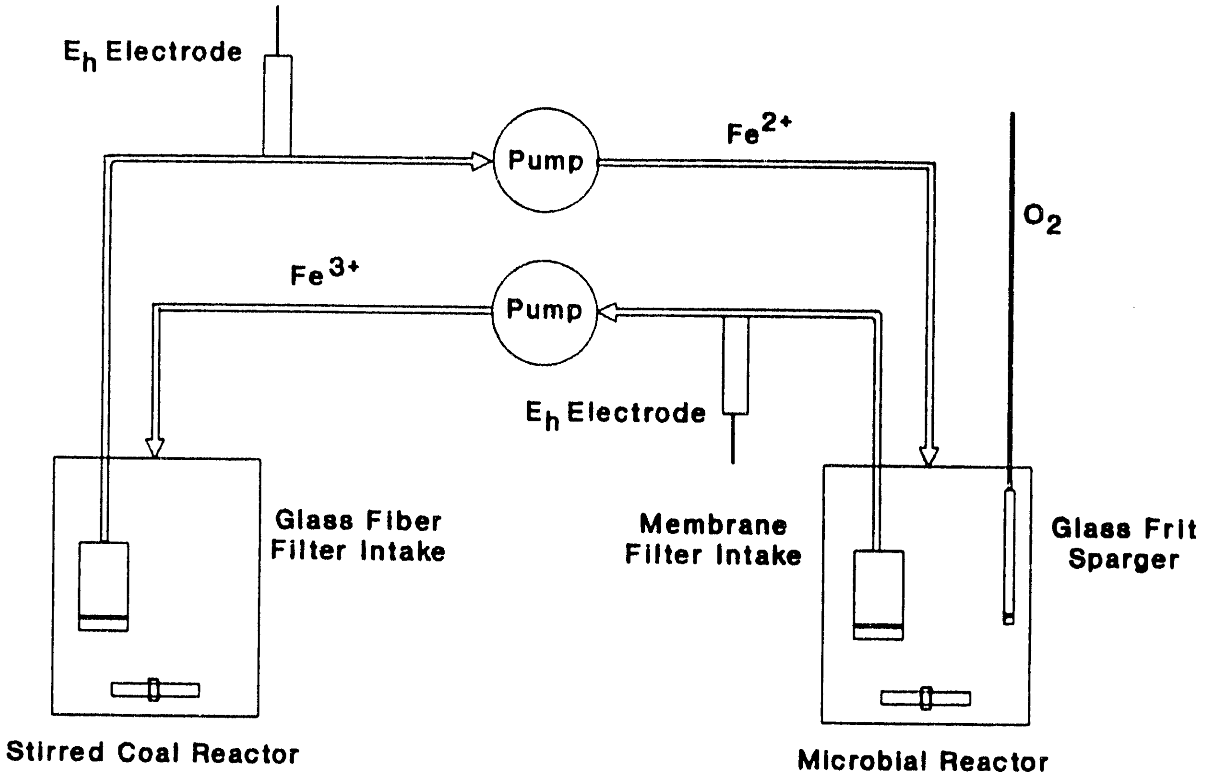

Figure 22. Schematic representation of the experimental apparatus for the separate regeneration of ferric ions by bacteria of by aeration.

tests were carried out at acidic conditions to prevent ferric ion precipitation to $Fe(OH)_3$, the bacteria had to be adapted to these conditions. This was accomplished by slowly lowering the pH of the media while maintaining an active bacteria culture. The potential of the media was monitored in these experiments since it is indicative of the growth and survival of the *Thiobacillus ferrooxidans* culture.

Figure 23 shows the change in potential of the media with time at different pH conditions. At pH 2.7, the potential of the media increased to about 625 mv (versus Ag/AgCl) after 3 days, indicating that the *Thiobacillus* culture survived and was growing. The bacteria were also able to adapt to pH 1.5 after about 4 days, as shown by the increase in potential. However, there were no indications that the microbes were able to survive at pH 1.3 over the entire duration of the experiments. Consequently, the microbes that survived at pH 1.5 were used in the separate ferric ion regeneration experiments.

In preliminary work using the experimental apparatus for the separate regeneration of ferric ions by *Thiobacillus ferrooxidans*, the bacteria were introduced into the microbial reactor, which was conditioned at pH 1.5. There was only a slight increase in the potential of the solution after one week, which indicated poor bacterial growth. This may have been due to insufficient aeration in the reactor. To remedy this problem, air was continuously introduced to the reactor, resulting in a noticeable increase in potential. The bacterial culture started to grow and the microbial reactor was ready for testing after a few days. A test run was conducted with a 65 x 200 mesh Pittsburgh No. 8 coal sample, which was treated for 2 days. The coal reactor was set at 60°C with a percent

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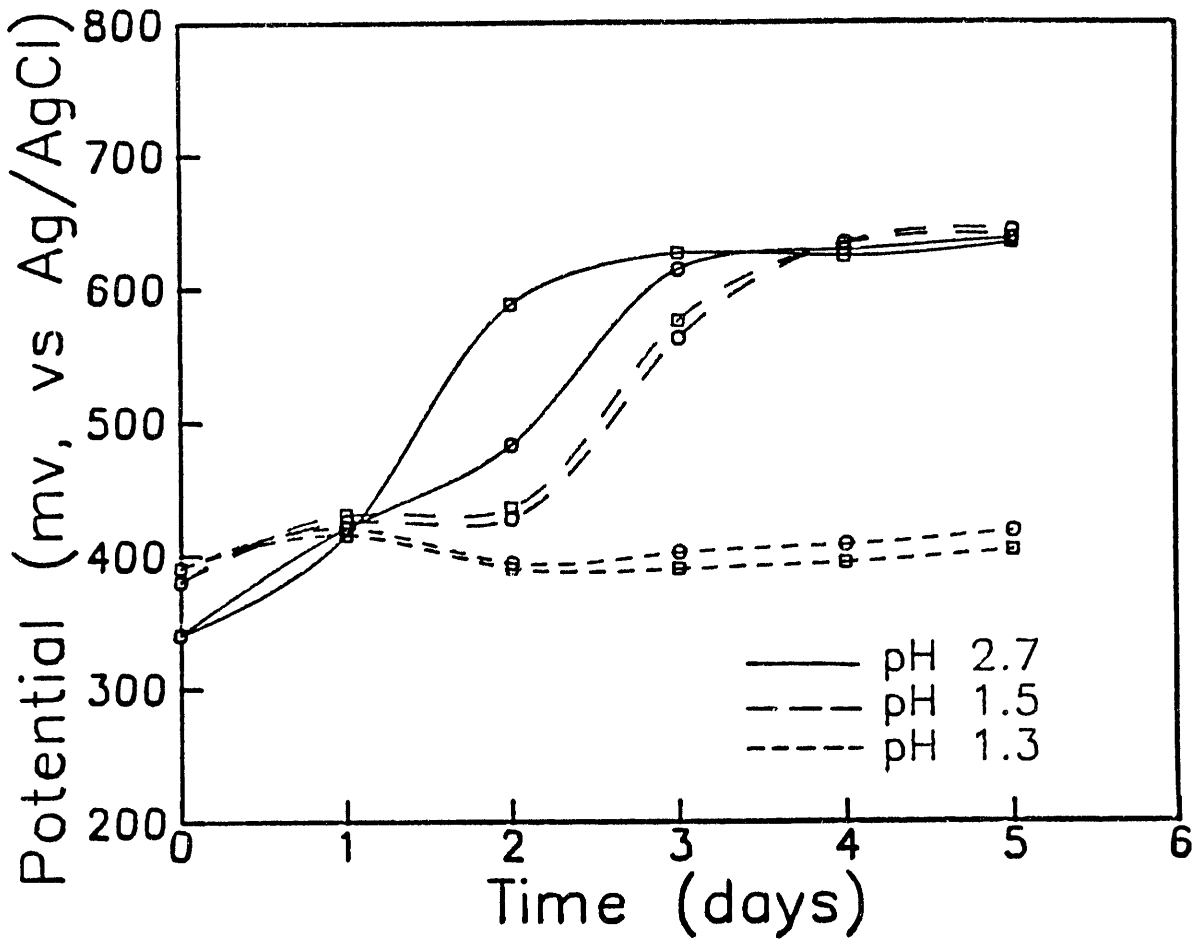

Figure 23. The effect of pH on Thiobacillus Ferrooxidans (Strain #19859, O; Strain #21834, □), as indicated by the potential of the media.

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solids of 10%. The result of this preliminary test is given in Table XLIII. The feed ash was reduced from 10.60% to 8.45% with a coal recovery of 89%. The result observed here is similar to that found for the batch test, which had a treatment time of 14 days. This may be indicative of an increase in the kinetics of the process with the use of the continuous reactor. Also, since there was no direct bacterial contact with the coal in this apparatus, the mechanism involved is presumably not the same as that observed for a bacterial leaching process. It should be noted that the percentage of mineral matter removed in this test is lower than that obtained using electrolysis at slightly similar conditions. The kinetics of ferric ion regeneration by *Thiobacillus ferrooxidans* is presumably slower than by electrolysis.

The apparatus for the separate regeneration of ferric ions was used to test the response of the Middle Wyodak coal to alternative methods of ferric ion regeneration. In this test, a culture of *Thiobacillus ferrooxidans* was used in the ferric ion regenerator cell. This cell was set at the optimum conditions determined from the parametric tests for the bacterial regeneration of ferric ions (Subtask 4.3). On the other hand, the conditions

Table XLIII. Results of CECC treatment on Pittsburgh No. 8 coal using *Thiobacillus ferrooxidans* for ferric ion regeneration.

Reaction Time	Ash Content (% wt)		Ash Rejection (% wt)	Yield (% wt)
	Feed	Product		
48 hrs	10.60	8.45	29.05	89.00

used in the coal reactor were those determined from the optimization tests (Subtask 4.2). The coal sample was processed at a temperature of 80°C with the coal reactor containing 6.86% solids. However, the pH and the ferric ion addition were set to conform to the optimum conditions determined for the bacterial regeneration scheme. This was done since the extremely acidic pH condition and low ferric ion addition determined to be optimum for the electrochemical scheme would not be suitable for bacterial growth. The solution coming from the coal reactor was cooled down by passing through a water-jacketed distillation column prior to re-introduction into the regenerator cell.

Table XLIV shows the results obtained after treating a 65 x 325 mesh Middle Wyodak coal sample for 20 hrs. Using the bacterial regeneration scheme, the mineral matter content was reduced from 6.28% to only about 5.67%. This is much lower than that obtained using the electrochemical reactor in the parametric batch tests. The

Table XLIV. Results of CECC treatment on Middle Wyodak coal using *Thiobacillus ferrooxidans* for ferric ion regeneration.

Test No.	Ash Content (% wt)		Ash Rejection (% wt)	Sulfur Content (% wt)		Sulfur Rejection (% wt)
	Feed	Product		Feed	Product	
1	6.28	5.67	9.71	0.572	0.526	8.04

Feed Size = 65 x 325 mesh
Fe^{2+} addition = 3.85 gm/1
% Solids = 6.86
pH = 1.60
Temperature
Coal reactor = 80 °C
Fe^{3+} regenerator = 35 °C
Treatment Time = 20 hrs

advantage of the electrochemical regeneration scheme may be attributed to the lower pH conditions used in this scheme and more efficient regeneration of ferric ions. The lower pH conditions have been explained above as being responsible for assuring that the ionic double layer is created between the mineral matter and the coal surfaces. Also, the direct electrochemical oxidation of Fe^{2+} to Fe^{3+} is presumably much more efficient than those observed in bacterial processes.

The tests were also performed to test the response of the Pittsburgh No. 8 coal to separate ferric ion regeneration. In these tests, the apparatus for the separate regeneration of ferric ions was used. A culture of *Thiobacillus ferrooxidans* was grown in the ferric ion regenerator cell, which was set at the experimentally-determined optimum conditions (Subtask 4.3). The conditions used in the coal reactor were those determined from the parametric tests (Subtask 4.2). The Pittsburgh No. 8 coal (65 x 325 mesh) was processed at a temperature of 68°C in the coal reactor with a pulp density set at 6%. However, the pH and the ferric ion addition were set to conform to the optimum conditions determined from the bacterial regeneration tests. This was done since the extremely acidic pH and low ferric ion addition determined to be optimum for the electrochemical regeneration scheme are not suitable for bacterial growth. The solution coming from the coal reactor was also cooled prior to reintroduction into the regenerator cell since the bacteria can not survive at temperatures greater than 50°C.

Table XLV shows the results obtained after processing for 20 hours. The % ash rejections (by weight) obtained for Tests 1 and 2 are 16.65% and 21.58%, respectively. These values are much lower than the average value of 38% obtained in the parametric

Table XLV. Results of CECC processing of Pittsburgh No. 8 coal using *Thiobacillus ferrooxidans* for ferric ion regeneration.

Test No.	Ash Content (% wt)		Ash Rejection (% wt)	Sulfur Content (% wt)		Sulfur Rejection (% wt)
	Feed	Product		Feed	Product	
1	8.87	7.66	16.65	3.526	2.798	24.88
2	9.50	7.62	21.58	3.730	2.770	27.40

Feed Size = 65 x 325 mesh
Fe^{2+} addition = 5.55 gm/l
% Solids = 6.00
pH = 1.60
Temperature:
  Coal reactor = 68 °C
  Fe^{3+} regenerator = 35 °C
Treatment Time = 20 hrs

tests (Subtask 4.1) with the electrochemical reactor. On the other hand, the amount of sulfur removed in this set of experiments is slightly higher than the average value of 18.2% obtained in the parametric tests. However, it should be pointed out that the validation test results (Subtask 4.2) obtained using the electrochemical reactor at the optimum conditions showed an ash and sulfur rejection of 51.6% and 32.71%, respectively.

The better performance of the electrochemical regeneration scheme may be attributed to the lower pH conditions and the more efficient regeneration of ferric ions. As has been suggested previously, the lower the pH, the higher the double layer potential and, hence, the mineral matter liberation. Also, the electrochemical technique is apparently more efficient for oxidizing Fe^{2+} to Fe^{3+} than the microbial technique. The relatively large amount of ferrous sulfate added in the bacterial regeneration scheme may be detrimental to the process, as has been shown in the parametric tests (Subtask 4.1). It is well-known that jarosite can be formed under the conditions employed for the microbial process. The precipitation of jarosite on the coal surface will probably interfere with the oxidation of the coal surface, thus preventing further osmotic pressure build-up.

Ferric Ion Regeneration by Air Oxidation. Tests were also conducted in which air oxidation was used to regenerate the ferric ions. The experimental set-up is the same as that used for the bacterial regeneration experiments (Figure 22). The test conditions used for the coal reactor are given with the results in Table XLVI. In the ferric ion regenerator cell, air was bubbled continuously to oxidize any Fe^{2+} to Fe^{3+}, and the

Table XLVI. Results of CECC treatment on Pittsburgh No. 8 coal using air oxidation for ferric ion regeneration.

Test No.	Ash Content (% wt)		Ash Rejection (% wt)	Sulfur Content (% wt)		Sulfur Rejection (% wt)
	Feed	Product		Feed	Product	
1	10.79	7.32	34.41	3.279	2.716	19.98
2	9.97	7.65	28.39	3.263	3.007	14.05
3	10.79	8.43	27.60	3.279	2.783	21.37

Feed Size = 65- x 325-mesh
Ferric ions = 10^{-4} M
% Solids = 6
HCl = 2 M
Temperature = 60°C
Treatment Time = 20 hrs

solution containing the Fe^{3+} was recycled back into the coal reactor. The results show the ash content was reduced to as low as 7.32% after 20 hours of treatment. The average % ash rejection for the three tests was about 30.13%. The % sulfur removal averaged about 18.5%, but the final sulfur content was only brought down to as low as 2.716%. Both mineral matter and sulfur removals obtained in these tests are lower than those using the electrochemical reactor at the same conditions. This may be indicative of the slower kinetics and less efficient ferric ion regeneration by air oxidation.

The results obtained for the processing of the Pittsburgh No. 8 coal using air for ferric ion regeneration are given in Table XLVII. The 65 x 325 mesh coal was treated at the optimum condition determined in Subtask 4.2, which is also given in Table XLVII.

Table XLVII. Results of CECC processing of Pittsburgh No. 8 coal using air for ferric ion regeneration.

Test No.	Ash Content (%wt)		Ash Rejection (%wt)	Sulfur Content (%wt)		Sulfur Rejection (%wt)
	Feed	Product		Feed	Product	
1	10.79	7.32	34.41	3.279	2.716	19.98
2	9.97	7.65	28.39	3.263	3.007	14.05
3	10.79	8.43	27.60	3.279	2.783	21.37

Feed Size = 65- x 325-mesh
Ferric ions = 10-4 M
% Solids = 6
HCl = 2 M
Temperature = 60°C
Treatment Time = 20 hrs

The % ash and % sulfur rejections obtained for these tests are also lower than those observed with the electrochemical regeneration scheme. However, the amount of mineral matter removed using air oxidation is higher than with the bacterial regeneration scheme. The increase in mineral matter removal may be attributed to the lower pH and the presence of more counter ions in the air oxidation scheme. These conditions were brought about by the higher acid concentration used. Also, the amount of ferric ions added is much lower than that used in the bacterial reactor. As discussed previously, these conditions are all important in building up sufficient osmotic pressure.

Despite the fact that the conditions used in this test were similar to those used in the parametric tests, the response of the coal to the air oxidation regeneration scheme was not as good. This is probably due to less efficient regeneration of the ferric ions by air oxidation. The amount of ferrous iron oxidized back to ferric iron was less using air, as indicated by the much lower potentials observed in the regenerator cell. It should be pointed out that a potential of 1.0 V is continuously applied in the electrochemical reactor, while the open-circuit potentials observed in the regenerator cell with the use of air are usually only around 0.3 to 0.5 V.

Based on the results obtained using different methods of ferric ion regeneration, the use of the electrochemical regeneration scheme appears to be the most appropriate for the CECC process. This regeneration scheme, which is also more versatile than the other regeneration schemes, will be used in the continuous unit designed for the CECC process.

Subtask 4.3.3 - Liberation Analysis

The liberation of mineral matter by the CECC process was investigated using the Scanning Electron Microscope-Image Processing System (SEM-IPS) image analysis system. In these measurements, the feed and processed coals were analyzed for amounts of free coal, free mineral matter, free pyrite, and locked composite particles. Samples of 65 x 325 mesh Pittsburgh No. 8 coal were processed under the optimum conditions established for that coal in Subtask 4.2. After the slurry samples were collected from the reactor at different time periods, the solids were recovered and used for the liberation analysis.

Figure 24 shows the percentage of the total mineral matter (-65 mesh) liberated as a function of time. Also shown in this figure is the amount of liberated -325 mesh mineral matter. The amount of liberated mineral matter present initially in the feed was about 12.2%. This amount increased to about 40% after about 4 hrs of processing and then decreased afterwards. This is direct evidence that mineral matter was liberated as a result of the CECC process. The decrease in liberation observed after 4 hours may be attributed to further liberation and size reduction of the liberated mineral matter, but it should be noted that the measurements were limited to particles larger than 4 microns. Therefore, liberated particles smaller than this size limit could not be accounted for. Some dissolution of the liberated mineral matter might also be responsible for this decrease.

The amount of liberated -325 mesh mineral matter is represented by a curve (Figure 24) similar to that for the total liberated mineral matter. However, the

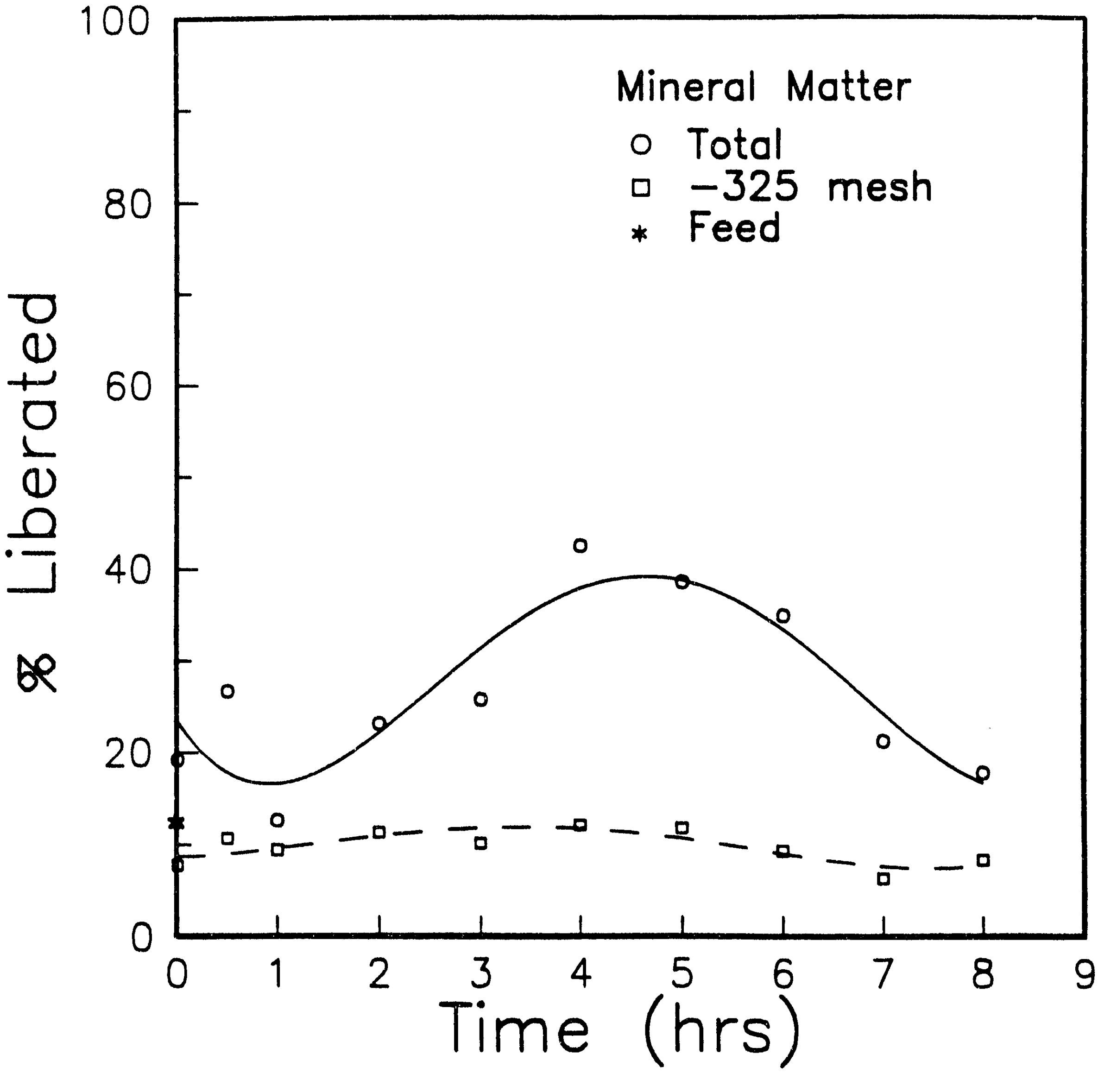

Figure 24. The change in the amount of 65 x 0 mesh xize (total) and -325 mesh size liberated mineral matter as a function of CECC processing time for a Pittsburgh No. 8 coal.

percentage of the mineral matter that is liberated -325 mesh particles is lower over the entire sampling period. Subtracting the amount of -325 mesh liberated mineral matter from the total amount of liberated mineral matter at each sampling period, it can be seen that there was a substantial amount of liberated mineral matter coarser than 325 mesh. This means that some of the liberated mineral matter remained in the coal product after wet-screening at 325 mesh. This fraction is usually greater than 50% of the total liberated mineral matter and is as high as about 70% in some instances. The fact that a large amount of the mineral matter liberated by an electrochemically induced liberation (EIL) mechanism is larger than the lower size limit of the feed sample poses a serious problem in removing the liberated mineral matter. This problem becomes even more serious with samples of a wide size distribution.

The changes in the total amount of pyrite (-65 mesh) liberated with time are shown in Figure 25. The ratio of the liberated pyrite to the total amount of pyrite present is similar to the ratio observed above for the mineral matter. It can be seen from the initial feed value of about 12%, the amount of liberated pyrite increased to about 35% after 4 hours. At longer time periods, the pyrite liberation decreased, which may be attributed to further liberation and size reduction, as well as to pyrite dissolution.

The percentage of the liberated pyrite (-325 mesh) as a function of time is also shown in Figure 25. These results are similar to those observed for the mineral matter liberation shown in Figure 24. There is a slight increase in the first few hours and then a decrease after 4 hours. Again, the fraction of +325 mesh pyrite liberated by the EIL mechanism is significant, which may be one of the main reasons for the observed poor

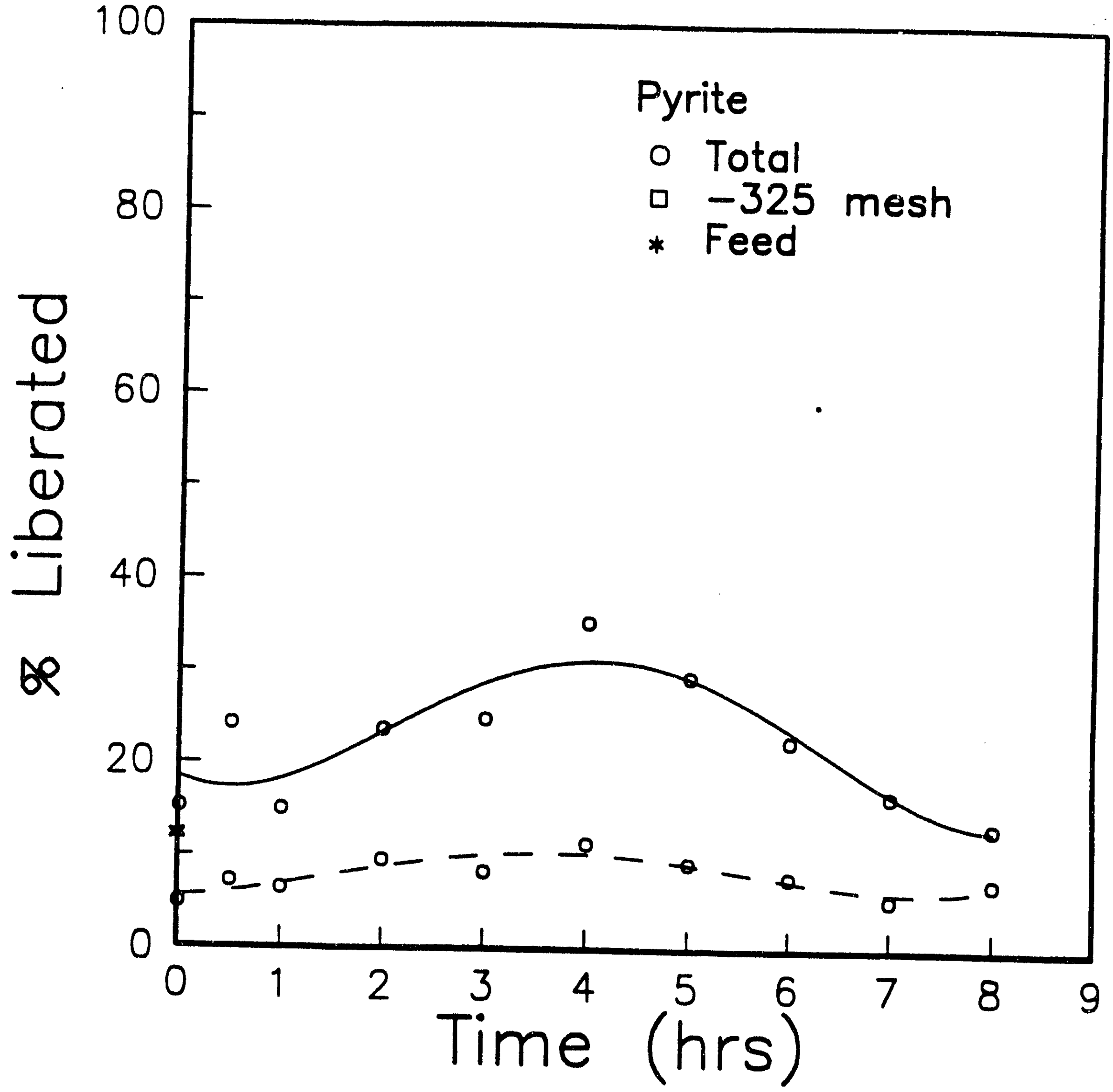

Figure 25. The change in the amount of 65 x 0 mesh size (total) and -325 mesh size liberated pyrite as a function of CECC processing time for a Pittsburgh No. 8 coal.

pyrite rejection. This calls for developing an alternate method of removing liberated mineral matter.

Since the Pittsburgh No. 8 coal was replaced by Elkhorn No. 3 coal in the Continuous Test Work (Task 6), liberation analyses were also conducted on the Elkhorn No. 3 coal. Using the same procedure and optimum conditions found for the Pittsburgh No. 8 coal, the 65 x 150 mesh Elkhorn samples were CECC treated for different periods of time. Slurry samples were collected from the reactor after treatment and the solids were recovered from the slurry, dried, and used for the liberation analysis. The ash analysis results obtained are given in Table XLVIII. As expected, the amount of mineral matter removed by the CECC process increased with treatment time. The % ash rejection increased from 34% to about 51.5% when length of treatment was increased from 1 to 8 hours. However, there was no significant improvement in the rejection of mineral matter between treatment times of 5 and 8 hours, indicating that treatment times

Table XLVIII. Ash analysis results of the CECC treatment of Elkhorn No. 3 coal.

Treatment Time (hrs)	Ash Content (% wt)			Ash Rejection (% wt)			Yield (% wt)
	Feed	Product	Reject	Total	Liberated	Dissolved*	
1	22.08	17.57	45.30	34.43	88.59	11.41	87.40
3	22.08	15.05	37.86	46.25	70.63	29.37	83.85
5	22.08	14.51	38.43	49.20	74.42	25.58	82.30
8	22.08	14.03	38.72	51.53	70.56	29.44	81.28

* and/or lost

longer than 5 hours may not be necessary in the CECC processing of the Elkhorn No. 3 coal.

For the Elkhorn No. 3 coal, the amount of mineral matter removal that may be attributed to liberation decreased with treatment time. The decrease is probably due to the dissolution of the liberated mineral matter, but can also be attributed to the reduction in particle size that occurs when locked particles are liberated. Similar observations were reported above for the Pittsburgh No. 8 coal. Table XLIX shows the total sulfur removed in these tests. The % sulfur rejection (by weight) increases with treatment time. After 8 hours of CECC treatment, a sulfur rejection of about 25% is obtained. However, the sulfur content of the product is not significantly different from that of the feed.

Figure 26 shows the percentage of the total mineral matter that was liberated as a function of time for three different size fractions: 65 x 100, 100 x 150 and -150 mesh. The percentages of free mineral matter present in the feed for each size fraction are given

Table XLIX. Sulfur analysis results of the CECC treatment of Elkhorn No. 3 coal.

Treatment Time (hrs)	Sulfur Content (% wt)			Sulfur Rejection (% wt)
	Feed	Product	Reject	
1	1.72	1.71	2.64	18.08
3	1.72	1.71	2.37	21.60
5	1.72	1.71	2.25	23.15
8	1.72	1.69	2.13	25.05

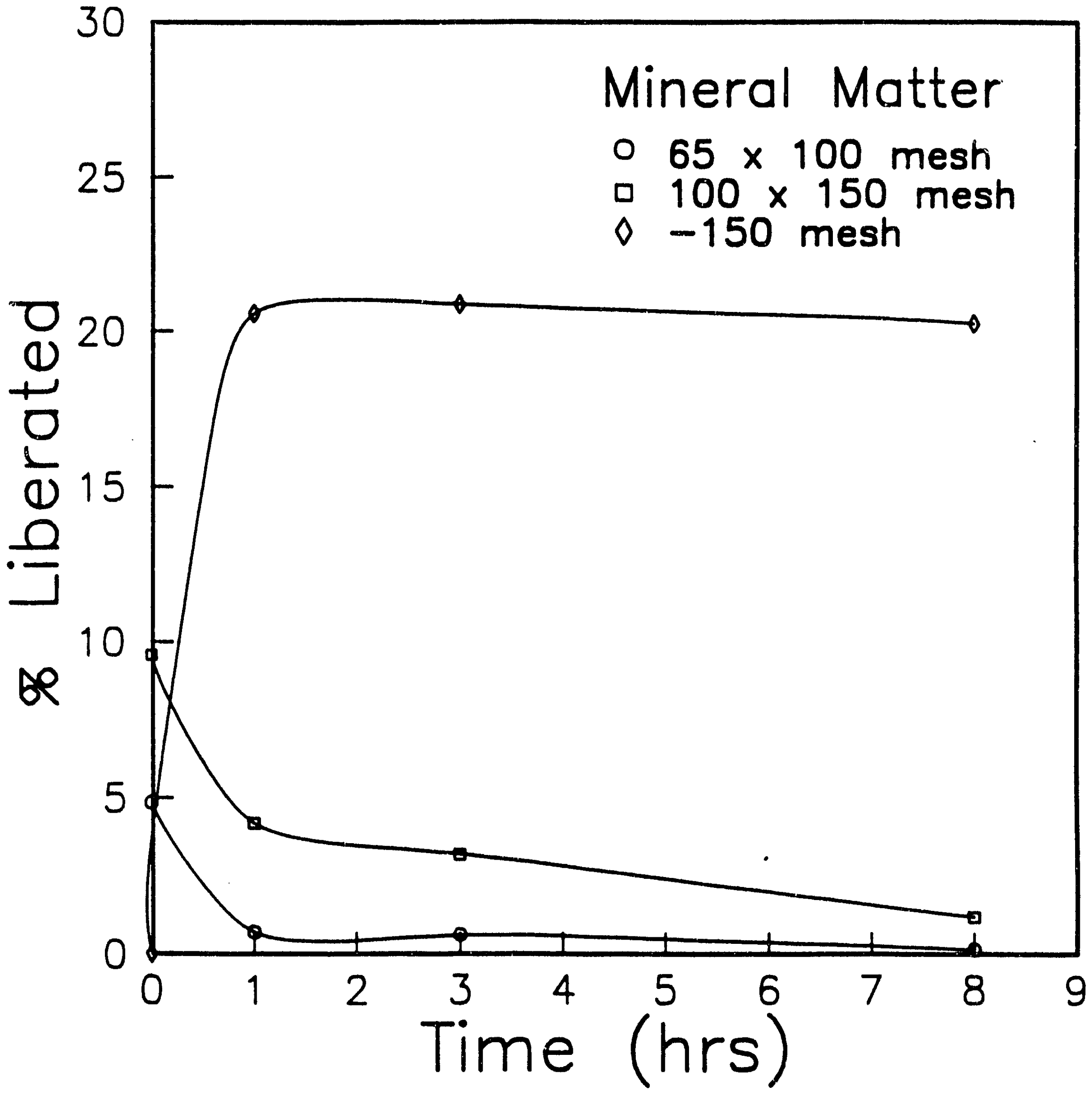

Figure 26. The amount of mineral matter that is liberated as a function of CECC treatment time for Elkhorn No. 3 coal.

by the values at 0 hour. The total percentage of free mineral matter (65 x 150 mesh) in the feed is about 14.4%. The curve for the 65 x 100 mesh fraction shows a sharp decrease in the amount of mineral matter liberated after CECC treatment. After only 1 hour of treatment, the amount of coarse liberated mineral matter is almost negligible. The amount of liberated 100 x 150 mesh mineral matter found in the coal also decreased significantly in the first hour of treatment and decreased continuously with increasing treatment time.

However, the percentage of mineral matter that is liberated -150 mesh particles follows an opposite trend with treatment time. During the first hour of treatment, there is a sharp increase in the amount of liberated mineral matter present in this size fraction. This value is observed to increase slightly after 3 hours and then to decrease slightly with time. It should be noted that the amount of mineral matter rejection attributable to liberation also decreased (Table XLVIII). As discussed earlier, the decrease may be attributed to the size reduction and dissolution of the liberated mineral matter. Also, the size reduction of the liberated mineral matter may have been producing particles that were smaller than the minimum size of 4 microns that the SEM-IPS could detect.

The results also indicated that the liberated mineral matter was reduced to finer sizes after CECC treatment. However, the amount of 100 x 150 mesh liberated particles reporting to next lower size fraction was less than that for the 65 x 100 mesh fraction, presumably because part of the 65 x 100 mesh fraction reported to the 100 x 150 mesh fraction.

Based on a mass balance of the liberated mineral matter, the majority of the liberated mineral matter was shown to be finer than -150 mesh in size. This observation is opposite to that found above for the Pittsburgh No. 8 coal, in which the majority of the liberated mineral matter is coarse. The difference observed here is one of the reason for the better response of the Elkhorn No. 3 coal to the CECC process.

Although not shown here, the analysis of the locked particles indicates that the quantity of +150 mesh locked particles decreased with treatment time, while the quantity of -150 mesh locked particles showed an opposite trend. However, the mass balance for the locked particles did not indicate that the locked particles were merely breaking and going to the -150 mesh locked fraction. Thus, the mineral matter was presumably being liberated from the composite particles and reporting to the -150 mesh liberated fraction. This would account for the increase in the amount of liberated -150 mesh mineral matter.

The total amount of liberated mineral matter present after treatment was greater than that initially present in the feed. This indicates that the removal of mineral matter obtained here was not simply due to the rejection of the free mineral matter in the feed. Rather, the use of the CECC process was responsible for the removal of these particles, as well as for the liberation of some of the locked particles. The mass balance of the results, shown in Table XLVIII, supports this conclusion.

Figure 27 shows the amount of pyrite that was liberated for three different size fractions. The ratio of free pyrite to total pyrite content is higher than that for the mineral matter in this coal sample. The free pyrite accounts for about 38% of the total pyrite content in the feed, with about half of the free pyrite belonging to the 65 x 100

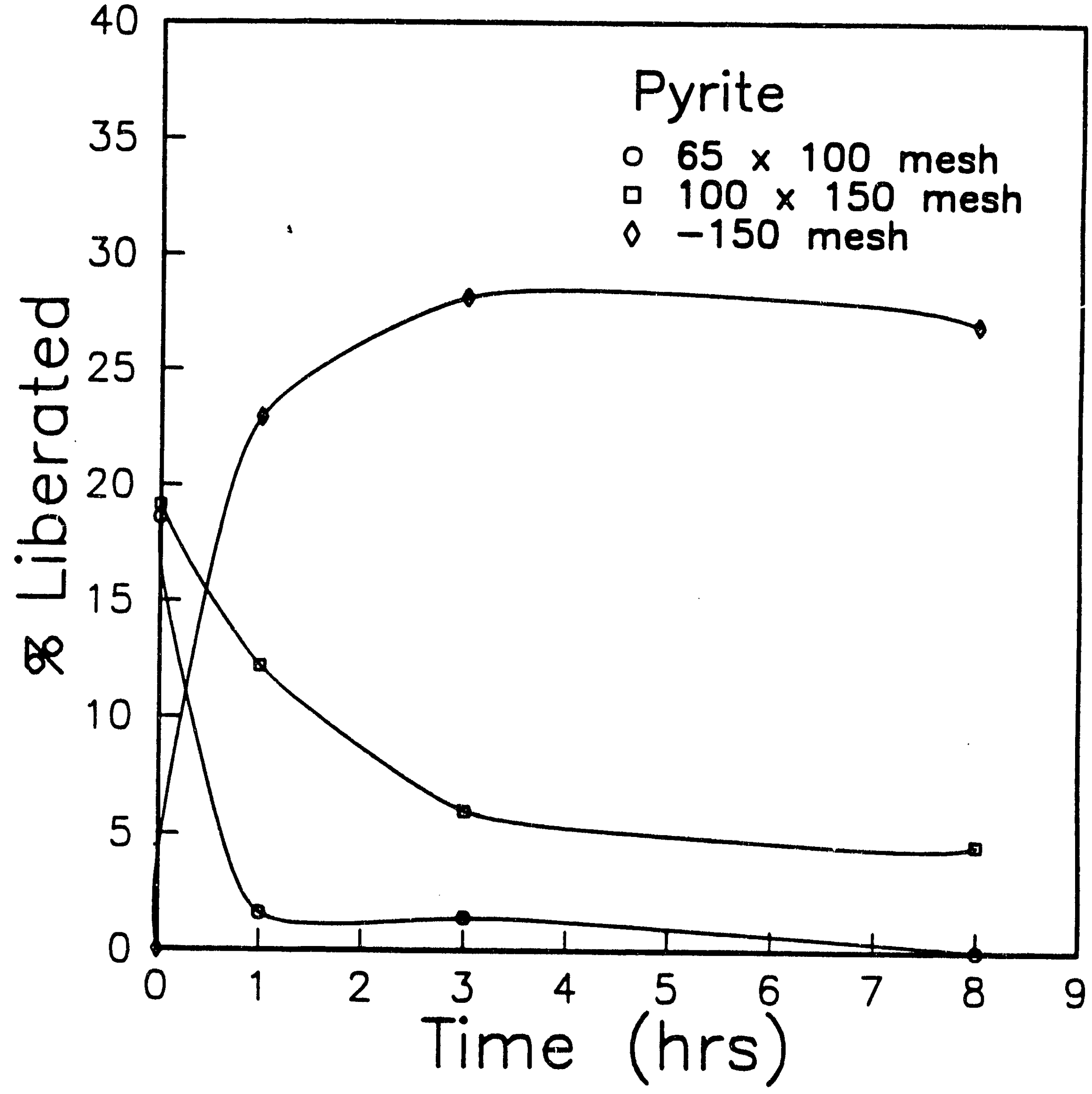

Figure 27. The amount of pyrite that is liberated as a function of CECC treatment time for Elkhorn No. 3 coal.

mesh size fraction. After a 1-hour treatment, the amount of pyrite that was free in the 65 x 100 mesh fraction was reduced significantly. This value continued to decrease, reaching zero after 8 hours. The amount of 100 x 150 mesh size free pyrite particles also decreased with treatment time. However, the decrease was not as large as that observed for the coarser fraction, suggesting that some of the coarse liberated pyrite particles were reduced to this size. It is also possible that some of the pyrite was being dissolved in the acidic solution used in this process.

The amount of -150 mesh pyrite that was liberated increased sharply during the first hour of treatment. This value continued to increase until the 3-hour point and then decreased slightly. This behavior is similar to that found for the mineral matter and may be attributed to the same factors discussed above. However, the total amount of pyrite liberated after treatment was less than that found in the feed. This is presumably because of pyrite dissolution, which is to be expected in the acidic conditions used in this process. The fraction of -150 mesh pyrite liberated by the process was greater than the coarser fraction, which was also observed for the mineral matter. However, the overall sulfur removal for this coal was still not as significant as that for the mineral matter rejection.

Subtask 4.3.4 - Repeat Batch Tests

Two major problems were encountered in this project: i) the ineffectiveness of the liberation of mineral matter by the CECC process on oxidized coal samples, and ii) the ineffectiveness of screening for separating coarse liberated mineral matter from some of the coals tested.

The first problem is not surprising because the CECC process is based on the incipient oxidation of the coal surface. The results obtained in the Parametric Tests for the Pittsburgh No. 8 coal (Subtask 4.1) were reasonably good. The initial validation test using the same Pittsburgh No. 8 coal sample was successful; however, the repeat tests gave poorer ash rejections. This was attributed to the oxidation of the coal sample.

Although this subtask and the subsequent subtasks are not part of the original Work Plan, additional tests were carried out to resolve the problems discussed above. The first problem regarding the detrimental effect of oxidized samples is addressed in this subtask, while the second is investigated in Subtask 4.3.5.

A new batch of Pittsburgh No. 8 coal was obtained from Consolidated Coal Company, which will also be referred to as Consol coal. It should be noted that this sample did not come from the same location as the original sample (Split A-2) used in the Parametric Tests (Subtask 4.1). This new sample was treated using the optimum conditions determined in Subtask 4.2. The results for the different tests are given in Table L. In Test No. 1, a 65 x 200 mesh size feed was treated for 5 hours after presoaking overnight. The amount of mineral matter rejected was less than the predicted optimum % ash rejection of about 54.7% (Subtask 4.2). In Test No. 2, using a dry-screened 65 x 325 mesh size sample, the mineral matter rejection obtained was also poor. Test No. 3 used a wet-screened feed (65 x 325 mesh size) and the results showed a slight improvement. However, the % ash rejections obtained were still lower than those found in the optimization tests. The effect of a longer treatment time was studied in Test No. 4, where the wet-ground 65 x 325 mesh sample was treated for 52 hours after presoaking

Table L. Ash and sulfur analysis results of CECC processing of Pittsburgh No. 8 coal.

a. Ash Analysis

	Ash Content (% wt)			Ash Rejection (% wt)		
Test No.	Feed	Product	Reject	Total	Liberated	Dissolved*
1	8.67	7.41	16.32	22.30	61.20	38.80
2	10.35	9.24	15.88	18.28	54.71	45.29
3	9.57	8.06	18.58	29.02	69.06	30.94
4	8.52	4.66	16.82	55.55	43.98	56.02

* and/or lost

b. Sulfur Analysis

	Sulfur Content (% wt)			Sulfur Rejection (% wt)		
Test No.	Feed	Product	Reject	Total	Liberated	Dissolved*
1	5.33	4.78	8.93	18.47	65.77	34.23
2	5.86	5.72	8.86	10.65	92.55	7.45
3	5.69	5.14	8.24	23.87	62.90	37.10
4	5.06	3.20	6.23	48.61	31.35	68.65

* and/or lost

overnight. The ash content of the coal was reduced from 8.52% to about 4.66% giving a % ash rejection value of 55.55%, slightly higher than the predicted optimum value. However, the treatment time was about 10 times longer. Although these results are disappointing, it should be noted that liberation still played a major role in the removal of mineral matter in these tests.

Sulfur removal values were also slightly lower than those obtained in the previous tests. The use of a longer treatment time again showed a significant increase in the amount of sulfur removed. However, this increase is most attributable to the leaching of the pyrite present in the coal. The mass balance analysis for Test No. 4 indicated that almost 67% of the sulfur removal was attributable to dissolution. On the other hand, the tests conducted at shorter treatment times showed that liberation was playing a major role in sulfur removal.

A test was carried out on a new batch of Pittsburgh No. 8 coal obtained from the Ohio Valley Coal Company. This coal sample, which will be referred to as Ohio Valley coal, had almost the same ash content as our original sample, but its sulfur content was much higher. This test was conducted on a 65 x 325 mesh size sample at the optimum conditions determined previously (Subtask 4.2). The results given in Table LI show that the amount of mineral matter rejected after 5 hours of CECC treatment was lower than those obtained in the Parametric Tests (Subtask 4.1). The ash content of the sample was reduced from 9.3% to about 7.5% with an ash rejection (by %wt) of only around 28.4%. The rejection of sulfur was also not as good as those obtained in Subtask 4.1. These

Table LI. Results of CEEC treatment on Pittsburgh No. 8 coal (Ohio Valley Coal Co.).

Ash Content (% wt)		Ash Rejection (% wt)	Sulfur Content (% wt)		Sulfur Rejection (% wt)
Feed	Product		Feed	Product	
9.31	7.53	28.46	6.10	5.58	19.10

poor results may be because the sample was oxidized prior to the CECC treatment, which was verified in the diffuse reflectance measurements taken on the feed sample. The higher pyritic sulfur content of this sample may also have contributed to the poor results since the higher pyrite content results in an excess amount of ferric ions. As discussed in Subtask 4.1, the presence of excess amounts of ferric ion is detrimental to the CECC process.

Due to the problems associated with the CECC treatment of Pittsburgh No. 8 coal samples, batch tests were conducted on other coal samples. An Elkhorn No. 3 coal sample obtained from the Consolidated Coal Company was selected. This sample was treated under the same optimum conditions used above for the Pittsburgh No. 8 coal. The results of these tests show that the Elkhorn coal responded well to CECC processing (Table LII). When a 65 x 200 mesh size feed was used, the ash content was reduced from 13.1% to about 2.53%. This latter figure corresponds to an ash rejection of about 84%, with almost 80% of the total mineral matter removed attributable to liberation. Less ash was rejected from the 65 x 325 mesh size feed. After 5 hours of processing, an ash rejection of only 68% was obtained. The decrease in mineral matter removal that resulted from the use of a feed with a wider size distribution was also observed above for the Pittsburgh No. 8 coal. This is probably due to the presence of coarse liberated mineral matter that could not be efficiently separated from the clean coal by wet-screening at the lower size limit.

The sulfur removal obtained for the CECC processing of the Elkhorn coal was not as significant. The % sulfur rejections obtained for the tests were about 18.5 and 21%.

Table LII. Ash and sulfur analysis results of CECC processing of Elkhorn coal.

a. Ash Analysis

Size Fraction	Ash Content (% wt)			Ash Rejection (% wt)		
	Feed	Product	Reject	Total	Liberated	Dissolved*
65 x 200	13.10	2.53	52.02	83/93	79.77	20.23
65 x 325	9.51	3.50	38.79	67.79	59.90	40.01

*and/or lost

b. Sulfur Analysis

Size Fraction	Sulfur Content (% wt)			Sulfur Rejection (% wt)		
	Feed	Product	Reject	Total	Liberated	Dissolved*
65 x 200	0.688	0.674	0.676	18.47	75.24	24.76
65 x 325	0.724	0.654	0.678	20.95	55.52	44.48

*and/or lost

The poor sulfur removal for this low-sulfur coal was expected since most of the sulfur in this coal sample is organic sulfur, which is not amenable to removal by the CECC process.

Subtask 4.3.5 - Effect of Feed Size Distribution

The next series of tests were carried out to determine whether the relatively wide size range used for the batch tests was responsible for the poor results obtained for the Pittsburgh No. 8 coal. In processing a sample with a wide size range, i.e., 65 x 325 mesh, some of the liberated mineral matter may still be larger than the lower size limit;

thus such material still reports to the clean coal product. This was observed in the liberation analysis study (Subtask 4.3.3) discussed above for the Pittsburgh No. 8 coal. Using samples with a narrower size distribution partially remedied this problem.

A test was carried out for a 65 x 325 mesh Pittsburgh No. 8 coal (Split A-2) using the optimum conditions determined in Subtask 4.2. After processing, the coal was wet-screened into different size fractions and then assayed. From the results given in Table LIII, it can be seen that the 65 x 100 mesh fraction had the lowest ash and sulfur content. As the particle size increased, both the ash and sulfur contents increased. This may indicate that some mineral matter was liberated only to the smaller size fraction and did not report to the reject. The ash content of the composite (65 x 325 mesh) product was higher than that for the top size fraction. The total % ash rejection, however, was lower than that observed previously for this coal in the Parametric Tests (Subtask 4.1). This may be because the surface of the feed sample was oxidized.

Table LIII. Results of CECC processing of Pittsburgh No. 8 coal.

	Size Fraction	Weight (%)	Ash Content (%)	Sulfur Content (%)
Feed	65 x 325		10.05	3.83
Product	65 x 100	30.07	5.97	2.59
	100 x 200	49.1	7.98	3.69
	200 x 325	20.2	8.58	3.92
	Composite		7.48	3.39
Reject	-325		15.62	6.29

Table LIV. Ash and sulfur analysis results of CECC processing of Pittsburgh No. 8 coal.

a. Ash Analysis

Size Fraction	Ash Content (% wt)			Ash Rejection (% wt)		
	Feed	Product	Reject	Total	Liberated	Dissolved*
65 x 100	8.40	6.64	18.61	29.29	55.53	45.45
100 x 200	8.03	7.29	21.48	20.98	67.23	32.27
200 x 325	10.24	7.80	13.10	32.86	54.54	45.45

*and/or lost

b. Sulfur Analysis

Size Fraction	Sulfur Content (% wt)			Sulfur Rejection (% wt)		
	Feed	Product	Reject	Total	Liberated	Dissolved*
65 x 100	3.40	2.98	7.85	25.23	60.50	39.50
100 x 200	3.26	3.12	8.35	16.70	80.87	19.13
200 x 325	3.75	3.37	4.92	20.79	46.30	53.70

*and/or lost

Table LIV shows the results obtained using samples of different feed size with narrow size distributions. These tests were conducted on Pittsburgh No. 8 coal at the optimum processing conditions. The tests conducted on a 65 x 100 mesh size sample gave lower product ash and sulfur contents than those on smaller size fractions. The product ash and sulfur contents were observed to increase with an increase in the feed mean size. The results obtained here for the three different tests also showed lower ash and sulfur contents than those obtained for a 65 x 325 mesh size feed (Table LIII). These results support the suggestion that the liberated mineral matter may have still been larger than the lower feed size limit. Using flotation to separate the liberated mineral matter for the finer samples (i.e., 200 x 325 mesh) would probably be better than using screens.

Since the previous sample (Split A-2) was already oxidized, tests were conducted on the new batch of Pittsburgh No. 8 coal (Consol coal). This coal had a lower ash and sulfur content than the previous sample. Tests were conducted on this coal using

Table LV. Ash and sulfur analysis results of CECC processing of Consol coal.

a. Ash Analysis

Size Fraction	Ash Content (% wt)			Ash Rejection (% wt)		
	Feed	Product	Reject	Total	Liberated	Dissolved*
65 x 100	5.73	5.00	12.51	16.50	34.18	65.82
100 x 200	6.51	5.79	6.79	29.57	57.58	42.22
200 x 325	5.41	4.67	6.11	36.12	56.91	43.09

*and/or lost

b. Sulfur Analysis

Size Fraction	Sulfur Content (% wt)			Sulfur Rejection (% wt)		
	Feed	Product	Reject	Total	Liberated	Dissolved*
65 x 100	1.45	1.43	-	5.63	-	-
100 x 200	1.32	1.32	1.69	20.81	94.82	5.18
200 x 325	1.57	1.50	1.96	29.29	77.58	22.42

*and/or lost

different size fractions. The results given in Table LV show that this coal also did not respond well to CECC processing for all of the size fractions tested. The coal recoveries for the different tests were also much lower than those obtained previously. The diffuse reflectance spectrum of this coal sample showed significant surface oxidation.

Subtask 4.3.6 - Effect of EDTA Addition

The poor response of the Pittsburgh No. 8 coal samples from Consolidated Coal Company and the Ohio Valley Coal Company may also be attributed to their high pyritic sulfur content. These samples had a sulfur content greater than 4%, while the original samples used in the parametric tests usually had less than 3%. The dissolution of the pyrite may result in the presence of an excess amount of Fe ions in solution, a condition that was previously found (Subtask 4.1) to be detrimental to the CECC process. This was attributed to the formation of jarosite, which prevented the electrocatalytically induced liberation (EIL) of mineral matter by the CECC process. Since ethylenediaminetetraacetic acid (EDTA) is known to complex Fe ions, its effect on the performance of the CECC process was studied in the next set of experiments.

In these tests, 65 x 325 mesh size coal samples were soaked overnight in a 3 M sulfuric acid solution containing 10^{-3} M EDTA at 40°C. The coal samples were then recovered and introduced into a fresh acid solution containing 10^{-5} M ferric sulfate. This procedure was followed to ensure the removal of any excess Fe or other interfering ions present in the solution. The samples were then treated in conditions similar to those used previously.

Table LVI shows the results obtained for the CECC treatment of Pittsburgh No. 8 coal (Ohio Valley coal) in the presence of EDTA. Test Nos. 1 and 2 gave % ash rejection values of about 37 and 46%. The amounts of mineral matter rejection obtained for both tests are higher than those obtained in the absence of EDTA (Table LI). Also improved with the use of EDTA were the amounts of sulfur removed. These results support our speculation that the presence of excess amounts of Fe ions due to the high pyritic sulfur content of the coal may interfere with the electrocatalytically induced liberation of mineral matter. It should be noted that mass balance analysis of the results

Table LVI. Effect of the addition of EDTA on the ash and sulfur removal by the CECC treatment for Pittsburgh No. 8 coal (Ohio Valley Coal Co.).

a. Effect of Addition of EDTA on Ash Removal

	Ash Content (% wt)			Ash Rejection (% wt)		
Test No.	Feed	Product	Reject	Total	Liberated	Dissolved*
1	7.13	5.48	20.33	37.23	82.75	17.25
2	9.29	6.50	22.27	46.20	80.42	19.58

* and/or lost

b. Effect of Addition of EDTA on Sulfur Removal

	Sulfur Content (% wt)			Sulfur Rejection (% wt)		
Test No.	Feed	Product	Reject	Total	Liberated	Dissolved*
1	2.93	2.53	5.81	29.48	65.77	34.23
2	3.38	2.79	6.07	36.53	92.55	7.45

* and/or lost

showed that liberation plays an important role in the removal of mineral matter and sulfur from this coal.

The effect of the presence of EDTA on the CECC treatment of a Pittsburgh No. 8 coal sample (Consol coal) is given in Table LVII. These results show no significant improvement in the response of this coal with the addition of EDTA. This may be because this coal has a much higher pyritic sulfur content, probably requiring a higher amount of EDTA to completely complex all the excess Fe ions.

Table LVII. Effect of the addition of EDTA on the ash and sulfur removal by the CECC treatment for Pittsburgh No. 8 coal (Consolidated Coal Co., new sample).

a. Effect of addition of EDTA on ash removal

Ash Content (% wt)			Ash Rejection (% wt)		
Feed	Product	Reject	Total	Liberated	Dissolved*
7.13	5.48	20.33	37.23	82.75	17.25

* and/or lost

b. Effect of addition of EDTA on sulfur removal

Sulfur Content (% wt)			Sulfur Rejection (% wt)		
Feed	Product	Reject	Total	Liberated	Dissolved*
2.93	2.53	5.81	29.48	65.77	34.23

*and/or lost

Subtask 4.3.7 - Alternative Method of Separating Liberated Mineral Matter from Coal

In Subtask 4.3.3, it was found that a significant amount of the mineral matter being liberated by the CECC treatment of Pittsburgh No. 8 coal is coarse. This finding suggested that screening would not be an effective method for separating such mineral matter from the treated coal. Considerably improved results were obtained in tests conducted using samples with narrow size distributions (Subtask 4.3.5). However, development of other methods for separating the liberated mineral matter from the clean coal that behaves like this particular Pittsburgh No. 8 coal is necessary. Therefore, conventional flotation was used instead of screening in the next series of tests to determine whether flotation would be able to solve this problem.

The 65 x 325 mesh coal samples were treated at the optimum CECC conditions and then wet-screened at 325 mesh to remove the fines. In one group of tests, the +325 mesh fraction was then floated for 1 minute in a 1-liter Denver flotation cell using 1 lb/ton of MIBC. For comparison, other tests were conducted on the same sample using flotation without CECC treatment.

Table LVIII shows the results of these tests on Pittsburgh No. 8 coal samples (Ohio Valley coal). In Test No. 1 for a sample treated using only flotation, an ash rejection of about 26% with coal recovery (by % wt) of about 91% was obtained. In treatments by the CECC process followed by flotation to separate the liberated mineral matter, the mineral matter rejection improved slightly, to about 32.7%, with a coal recovery of around 89%. The sulfur removal, however, did not improve significantly. Similarly, in Test No. 2, a slight improvement in the removal of mineral matter was

Table LVIII. Ash and sulfur analysis results of the flotation with and without CECC treatment of Pittsburgh No. 8 coal (Ohio Valley Coal Co.).

a. Ash analysis

Test No.		Ash Content (%wt)			Ash Rejection (%wt)			Yield (%wt)
	Process	Feed	Product	Reject	Total	Liberated	Dissolved*	
1	Flotation	12.30	9.95	-	26.34	-	-	91.06
	CECC & Flotation	12.30	9.32	38.97	32.75	98.89	1.11	88.76
2	Flotation	10.33	8.51	30.61	25.18	-	-	90.82
	CECC & Flotation	10.33	8.07	42.52	30.65	97.43	2.57	88.77

* and/or lost

b. Sulfur Analysis

Test No.		Sulfur Content (% wt)			Sulfur Rejection (% wt)		
	Process	Feed	Product	Reject	Total	Liberated	Dissolved*
1	Flotation	6.28	6.03	-	12.56	-	-
	CECC & Flotation	6.28	6.06	9.50	14.35	99.66	0.34
2	Flotation	4.58	4.48	4.26	11.16	-	-
	CECC & Flotation	4.58	4.45	6.81	10.08	92.36	7.64

* and/or lost

obtained with the CECC process/flotation method. When flotation was used to separate liberated mineral matter from coal after CECC treatment, slightly more ash was rejected than when screening was used (Table LVIII). The mass balance analysis of the results indicates that liberation was mainly responsible for the removal of mineral matter from this coal. The amount of mineral matter removed by dissolution appears to be almost negligible for this sample.

The results of the tests conducted on the other Pittsburgh No. 8 coal sample (Consol coal) are given in Table LIX. When conventional flotation was used alone, the amount of mineral matter rejected was only about 5% with a coal recovery (by % wt) of about 93%. The mineral matter removal was improved significantly when flotation followed the CECC treatment. In such cases, the ash rejection obtained was about 20% with a recovery of almost 87%. A similar trend was also observed for the sulfur removal from this sample. However, the results obtained here show no significant improvement over those obtained by screening.

Table LX shows the results obtained using the original Pittsburgh No. 8 coal sample (Split A-2) used in the Parametric Tests (Subtask 4.1). The flotation results obtained for this coal sample were better than those using the new batch of Consolidated Coal Company sample (Table LVII). While the ash rejection obtained using conventional flotation only was about 29% with a coal recovery of 91%, around 61% ash rejection was obtained with a recovery of 86% when the CECC process used followed by flotation to separate coarse liberated mineral matter from coal. This is significantly higher than that obtained with conventional flotation only. While the use of screening resulted in a

Table LIX. Ash and sulfur analysis results of the flotation with and without CECC treatment of Pittsburgh No. 8 coal (Consolidated Coal Company, new sample).

a. Ash analysis

Process	Ash Content (% wt)			Ash Rejection (% wt)			Yield (% wt)
	Feed	Product	Reject	Total	Liberated	Dissolved*	
Flotation	9.02	8.69	-	4.96	-	-	93.34
CECC & Flotation	9.02	8.32	40.56	19.76	94.70	5.30	86.99

b. Sulfur Analysis

Process	Sulfur Content (% wt)			Sulfur Rejection (% wt)		
	Feed	Product	Reject	Total	Liberated	Dissolved*
Flotation	6.65	6.65	-	2.84	-	-
CECC & Flotation	6.65	6.16	-	19.42	-	-

* and/or lost

range of % ash rejection values from 13 to 56% (Subtask 4.1), the use of flotation after the CECC treatment gave a higher % ash rejection. The ash rejection obtained when flotation and the CECC treatment are combined even exceeds the predicted ash rejection value of 54.7% that was determined at the optimum condition (Subtask 4.2). The sulfur removal was also improved with the use of flotation to separate the liberated mineral matter from the CECC product. These results indicate that flotation would be a good alternative method for separating coarse mineral matter liberated by the CECC process for this sample. It should be pointed out that the results obtained would be expected to

Table LX. Ash and sulfur analysis results of the flotation with and without CECC treatment of Pittsburgh No. 8 coal (Consolidated Coal Company, original sample).

a. Ash Analysis

Process	Ash Content (% wt)			Ash Rejection (% wt)			Yield (% wt)
	Feed	Product	Reject	Total	Liberated	Dissolved*	
Flotation	10.68	7.91	81.02	29.21	-	-	91.28
CECC & Flotation	10.68	5.11	32.96	60.60	81.07	18.92	85.98

b. Sulfur Analysis

Process	Sulfur Content (% wt)			Sulfur Rejection (% wt)		
	Feed	Product	Reject	Total	Liberated	Dissolved*
Flotation	2.66	2.60	-	6.57	-	-
CECC & Flotation	2.66	2.43	3.92	24.57	61.37	38.62

* and/or lost

improve with the use of a relatively unoxidized sample.

The use of conventional flotation to separate liberated mineral matter from the treated coal was previously found to be more effective than screening for Pittsburgh No. 8 coal. The 65 x 325 mesh size Elkhorn No. 3 coal samples were treated under the following conditions: 6% solids, 3 M H_2SO_4, 10^{-5} M Fe^{3+} ions, and a temperature of 40°C. In each test, a flotation time of 1 minute was used with 1 lb/ton MIBC added as frother. For Test No. 1, the sample was conventionally floated in a 1-liter Denver flotation cell without any CECC pretreatment, while in Test No. 2 the sample underwent

CECC treatment after which the clean coal was recovered by wet-screening at 325 mesh. In Test No. 3, the +325 mesh CECC-treated fraction from Test No. 2 was floated to get the final CECC product. The coal sample was floated directly after CECC treatment without wet-screening in Test No. 4.

Table LXI shows the results obtained using different methods for removing the liberated mineral matter from the CECC-treated Elkhorn No. 3 coal samples. Shown for comparison is the result for the test using flotation without CECC treatment (Test No. 1). The ash content was reduced in the conventional flotation test from 18.46% to about 15.4%, which corresponds to a % ash rejection of 20.8%. For Test No. 2, in which wet-screening followed CECC treatment, the % ash rejection was improved to about 29.3% without a significant decrease in coal recovery. From the mass balance of the ash contents, liberation accounted for about 92.7% of the total mineral matter removed.

Test No. 3, which used flotation instead of wet-screening after CECC treatment, showed a reduction of the ash content to around 10.9% with a coal recovery of about 86.3%. The % ash rejection was calculated to be 49.1%, which is significantly better than the values obtained in Test Nos. 1 and 2. The amount of mineral matter removed that could be attributed to liberation also increased. These results would indicate that a significant amount of coarse liberated mineral matter was being produced in the CECC processing of this sample.

The last test in this series was conducted using flotation without screening to remove the -325 mesh particles produced during the CECC treatment (Test No. 4). The results for this test show that the amount of mineral matter rejected also increased

Table LXI. Ash and sulfur analysis results for Elkhorn No. 3 coal.

a. Ash Analysis

Test No.	Process	Ash Content (%wt)			Ash Rejection (% wt)			Yield % wt
		Feed	Product	Reject	Total	Liberated	Dissolved*	
1	Flotation	18.46	15.40	87.57	20.79	-	-	94.96
2	CECC	18.46	14.00	63.44	29.33	92.68	7.32	93.16
3	CECC & Flotation**	18.46	10.88	53.29	49.14	95.63	4.63	86.30
4	CECC & Flotation***	18.46	9.05	45.57	59.53	79.32	20.68	82.55

b. Sulfur Analysis

Test No.	Process	Sulfur Content (% wt)			Sulfur Rejection (% wt)		
		Feed	Product	Reject	Total	Liberated	Dissolved*
1	Flotation	1.91	1.79	-	12.75	-	-
2	CECC	1.91	1.65	3.10	21.93	56.80	43.20
3	CECC & Flotation**	1.91	1.70	1.05	25.48	63.23	36.77
4	CECC & Flotation***	1.91	1.72	1.62	28.32	55.32	44.77

* and/or lost

** wet-screened (325 mesh) prior to flotation

*** no wet-screening

significantly. The ash content was reduced to about 9% with a slight decrease in coal recovery. This last test resulted in a % ash rejection of almost 60%, higher than in the other tests with CECC treatment. However, the amount of mineral matter removed that could be attributed to liberation decreased to about 79.3%. The increase in mineral matter removal may be due to an increase in the dissolution of the mineral matter, as indicated by the mass balance. Additionally, it was found that the product size distribution of Test No. 4 was coarser than that of Test No. 3, which may also account for the difference in their product ash contents.

It should be noted, however, that the amount of mineral matter removed in these tests is significantly lower than the amounts obtained in Subtask 4.3.4. Using diffuse reflectance FTIR spectroscopy, the feed samples used here were found to be already slightly oxidized. Since the CECC process was found to be ineffective in treating oxidized feed samples, as explained earlier, this would suggest why the results obtained in these tests are relatively poor. Another factor to consider is that although both samples were from the same batch, the ash and sulfur contents of the sample used here were higher than those used in Subtask 4.3.4. Possibly due to the higher pyrite content of the sample used here, an excessive amount of Fe^{3+} ions might have been present in these tests. As discussed earlier, an increase in pyritic sulfur content may result in an increase in the amount of Fe^{3+} ions coming from pyrite dissolution. If the amount excessive, then there would be insufficient counter ions present and/or jarosite formation would occur, which is detrimental to the CECC process.

The amount of sulfur rejected by the different tests is also shown in Table LXI. The use of flotation to recover the clean coal after CECC treatment resulted in slightly better sulfur removal. Also, the CECC treatment gave significantly better sulfur rejection than did flotation. This may be attributed to the additional sulfur rejection brought about by pyrite dissolution in the CECC process.

TASK 5 - DESIGN AND CONSTRUCTION OF THE CECC CONTINUOUS UNIT

Subtask 5.1 - CECC Unit Design

A continuous CECC unit was designed to process 1 to 3 lbs/hr of Middle Wyodak and Pittsburgh No. 8 coal. The bench-scale unit incorporated the stirred reactor in which ferric ions are regenerated electrochemically. This regeneration scheme was chosen based on the test results obtained using alternative methods of ferric ion regeneration. The flowsheets developed for the processing of 65 x 325 mesh Middle Wyodak and Pittsburgh No. 8 coals are given in Figures 28 and 29. The flowsheet and operating conditions designed for the Pittsburgh No. 8 coal were adopted for the processing of the Elkhorn No. 3 coal, which replaced the Pittsburgh No. 8 coal in the Continuous Test Work.

The flowsheets (Figures 28 and 29) also show mass and flow balances to give a better perspective of the process. These values were estimated from the data of the batch experiments (Subtask 4.1). In the design, the feed coal is introduced by a screw-type feeder into the slurry mixing tank where it is mixed with the acid solution containing the requisite amount of ferric ions. This mixture is then pumped to a 5-bank stirred reactor, which was designed to give a reactor retention time of about 12.6 hours for a unit handling 1 lb/hr. The ferric ions are regenerated in the reactors by a DC power supply that is applying a potential of 1 V between two graphite electrodes. The reactor temperature is controlled using a Teflon-coated bayonet heaters equipped with microprocessor PDPI (Proportional-Derivative-Proportional-Integral) temperature controller. The reactor is designed as 5 smaller banks instead of a single large one in

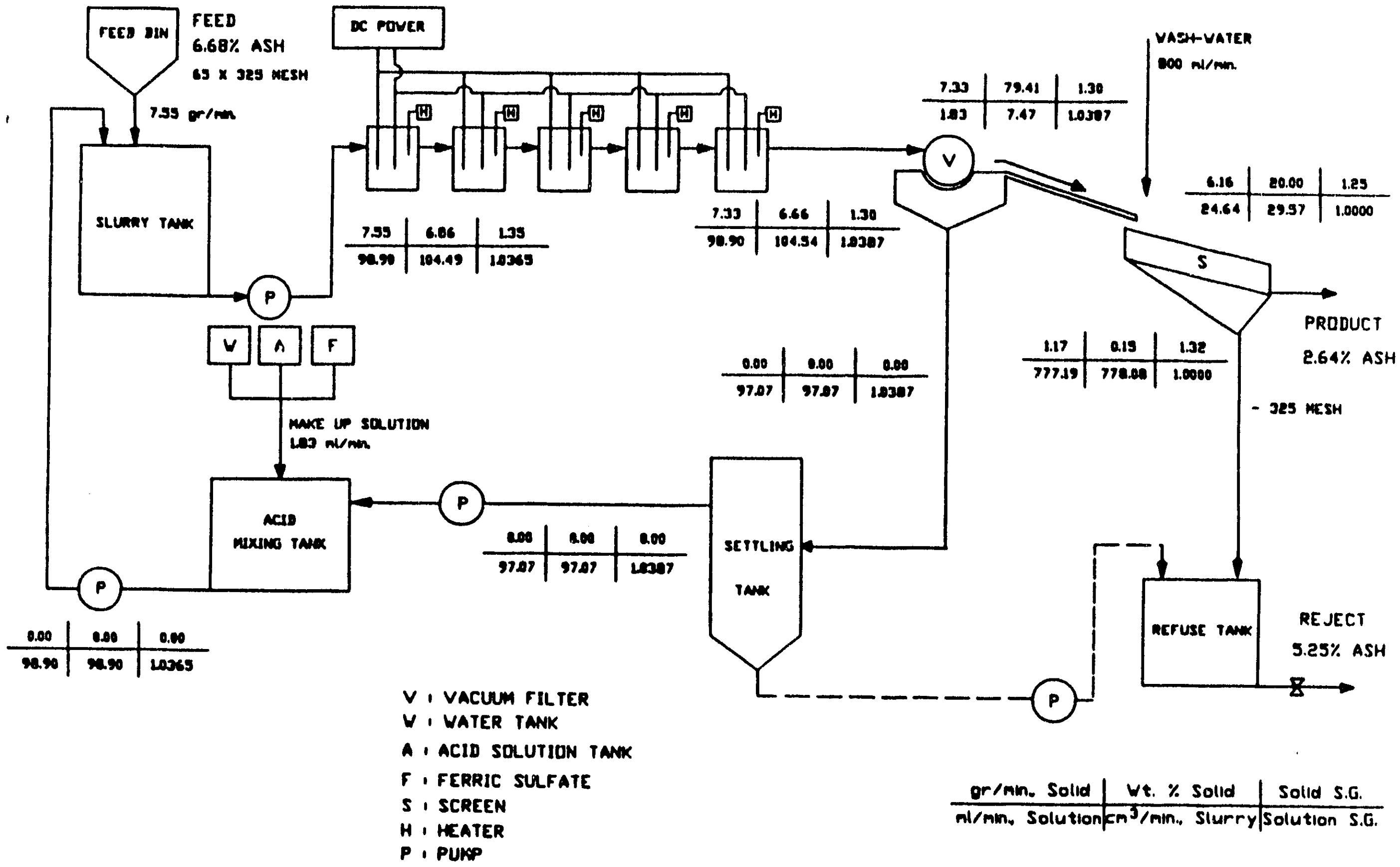

Figure 28. Proposed flowsheet for the CECC processing of the Middle Wyodak coal.

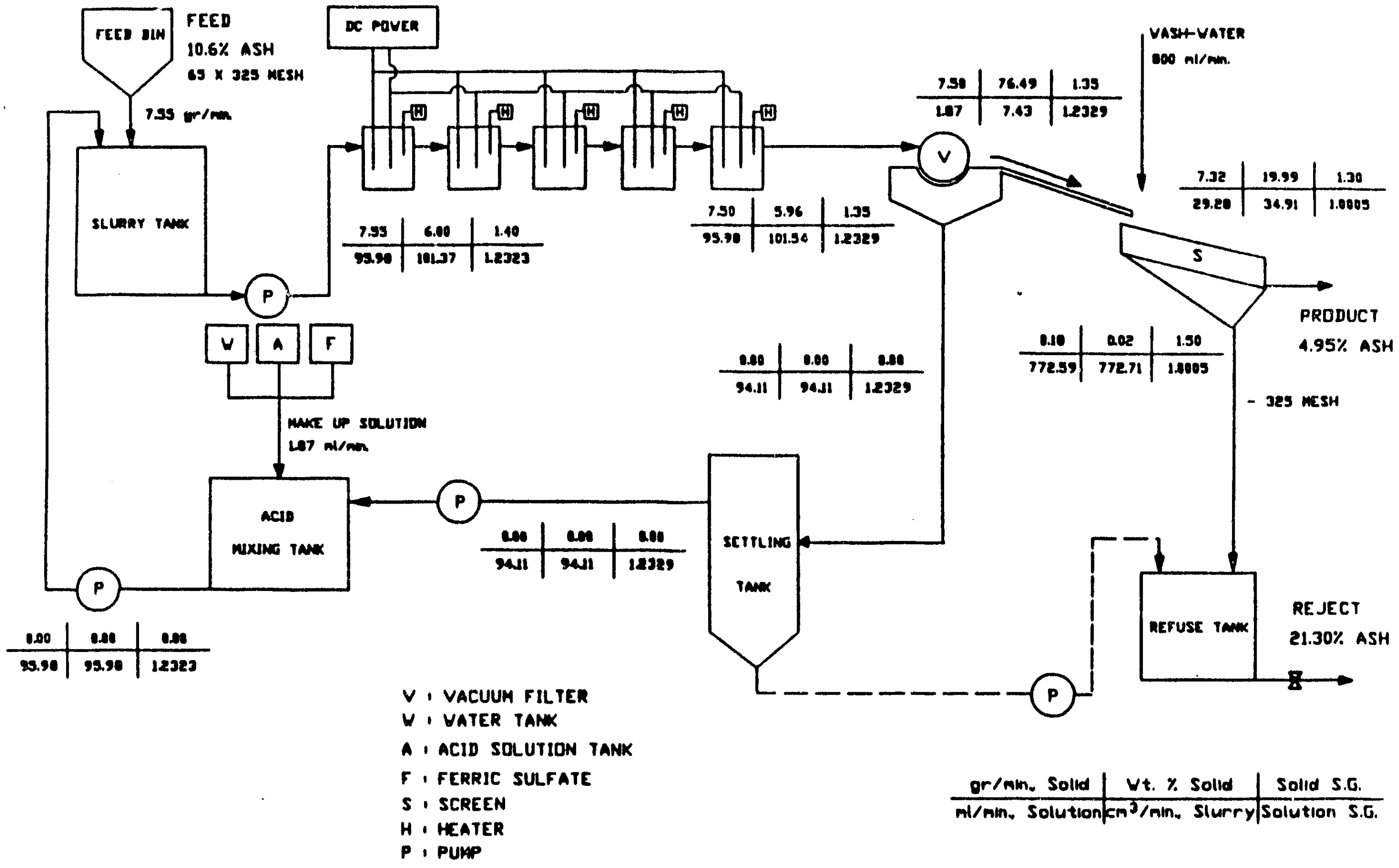

Figure 29. Proposed flowsheet for the CECC processing of Pittsburgh No. 8 coal.

order to maintain better control of the retention time for the coal samples. Also, this design offers superior flexibility since it can be adapted to different retention times and can accommodate other ferric ion regeneration schemes better than could a single reactor. When alternative regeneration schemes such as air (or oxygen-enriched air) or bacterial oxidation are used, the design can be easily adapted for a counter-current flow. As such, it is the more efficient flow design for these types of ferric ion regeneration scheme.

After being processed in the reactor, the slurry passes through a drum vacuum filter, in which the acid solution is separated from the solids. The solids are wet-screened using a Sweco vibratory screen to separate the products (+325 mesh) from the refuse. The screen underflow, composed mostly of liberated mineral matter and the wash water, is recovered in a refuse tank for acid-neutralization.

The acid solution recovered from the filtration stage is stored in a settling tank to allow any fine solid that has passed through the filter to settle down to the bottom of the tank. The fine solids are occasionally pumped out to the refuse tank for acid-neutralization and disposal. The clear acid solution is pumped to an acid mixing tank, where the acid concentration is brought back to the required value. Due to the absence of any practical instrument for the on-line measurement of acid concentration at this high level, the determination of the acid content, as well as that of the ferric ion concentration is designed to be done manually on a daily basis. Based on this measurement, make-up solution are added to the acid mixing tank when needed to bring the solution to the required acid and ferric ion concentration before recirculation. The overall retention time for the entire 1 lb/hr unit is estimated to be 20 hours.

For finer particles (-325 mesh), flowsheets similar to those given in Figures 28 and 29 were designed. Instead of a screen, microbubble column flotation would be used (not shown here) to preclean the coal before CECC processing and to separate the products from the refuse afterwards. For microbubble flotation, the filter cake would be redispersed to reject the mineral matter liberated by the CECC process while the pH is adjusted in a coal washing tank.

The use of a sequenced continuous process (SCP) was also considered. However, the design described above, which is based on a simple continuous process, is better suited to the CECC process. Also contributing to the decision to use a simple continuous process is that the SCP would require numerous automatic controls and would be much more complex.

Subtask 5.2 - CECC Unit Construction

In constructing the CECC continuous unit, an enclosure equipped with a blower that vents to atmosphere was erected to contain any acid fumes generated by the bench-scale unit processing. Reactor and vacuum filter stands were also constructed, and the equipment was installed as it was received. The reactors consisting of 5-gallon polyethylene tanks and the other acid containers were installed, including the solution and slurry pumps and lines connecting them. The graphite electrodes were installed in the reactors and hooked up to the DC power supply. The heaters, which were controlled by it own individual temperature controller and the temperature probes were also installed in the reactors. Figure 30 shows the reactors installed for the continuous bench-scale unit.

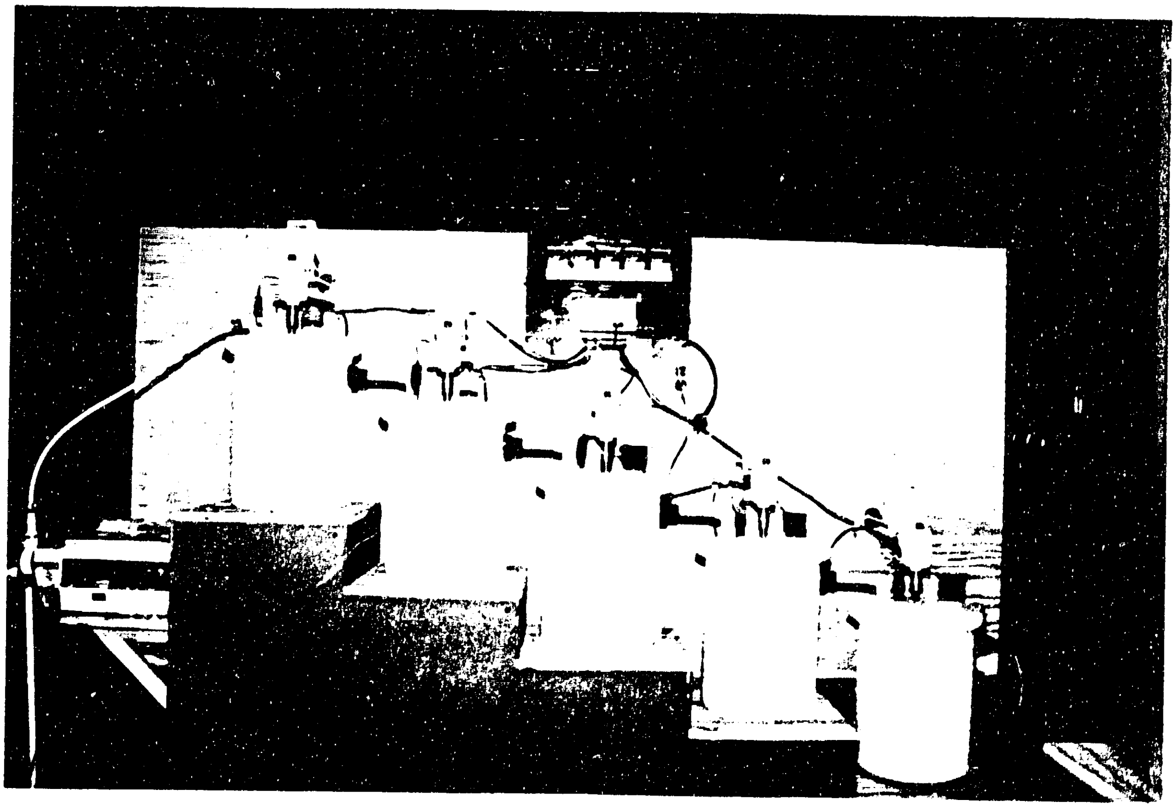

Figure 30. CECC reactors for the continuous bench-scale unit.

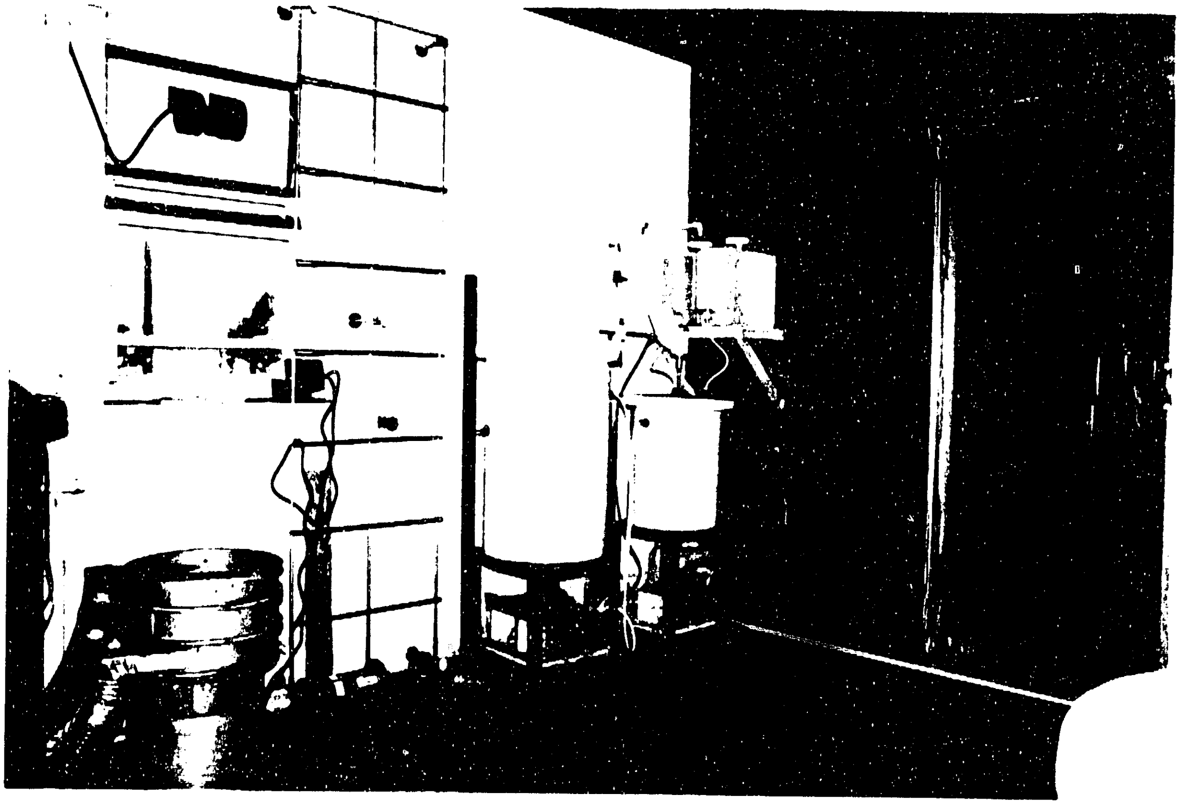

Figure 31. Settling and acid mixing tanks for the continuous bench-scale unit.

The settling and acid mixing tanks are shown in Figure 31, which also depicts an 18-inch Sweco Circular screen for separating the liberated mineral matter from the clean coal. Tests were conducted for leakage of the reactors and lines.

Subtask 5.3 - CECC Unit Modification

After construction of the unit, start-up was carried out using the optimum conditions determined for the Middle Wyodak coal, but in the absence of acid. During the start-up, the flow rate to the reactor was found to be less than the filtration rate of the vacuum filter. Consequently, there was not enough slurry being fed into the filter for efficient filtration. This problem was solved by doubling the flow rate of all components of the system. Thus, the entire unit was modified to process coal at the rate of 2 lbs/hr, instead of the original design of 1 lb/hr. Due to this modification, the overall retention time of the unit was decreased to about 10 hours. Aside from the problem with the slow flow rate, there were no major problems found in the unit during the start-up procedures.

The CECC continuous bench-scale unit was also modified to satisfy the strict requirements of the Health and Safety Department of the university regarding the possibility of accidental acid discharge to the sewer system. The recirculation system on the slurry mixing tank, which had leaked during the shakedown testing, was replaced by a new stirred tank system. Level controllers were installed on all the tanks that did not have them previously to ensure that no tank would overflow. Heavy duty polyethylene and PVC trays were placed under all the tanks to contain any drips or leaks. Also, acid-resistant adsorbent dikes were placed around the base of each tank and around the floor drains to prevent spills from leaking into the sewer system. All fittings, tubing, and pumps were inspected and any loose fittings or tube connections were tightened.

TASK 6 - CONTINUOUS UNIT OPERATION

Subtask 6.1 - Shakedown Testing

After the satisfactory start-up of the continuous unit, shakedown testing was started using Middle Wyodak coal samples. The coal used here, instead of the original sample, was a recently acquired Middle Wyodak coal from the Kerr-McGee Coal Corporation. This substitution was made because the original sample (split-B) obtained from Task 2 was found to be already oxidized. As discussed previously, the removal of mineral matter by the CECC process is ineffective on oxidized samples.

Shakedown testing was conducted under the following operating conditions: 6% solids, 2.28×10^{-4} M Fe^{3+} ion added, 2.32 M H_2SO_4, and a temperature of 80°C. These conditions were found to be optimum for the Middle Wyodak coal in Subtask 4.2. The 65 x 325 mesh coal samples were fed at a rate of 2 lbs/hour with a total retention time of about 10 hours.

Table LXII shows the results obtained for the Middle Wyodak coal. For Day 1, the ash content of the first batch of samples was reduced from 5.37% to about 2.02%. On Day 2, the ash content of the wet-screened product was reduced to about 1.58%, the reject having an ash content of about 5.51%. After the unit was run for 5 days, the ash content of the product was 1.16%. The product ash contents obtained here were much lower than those obtained in the parametric tests. This may be because this coal sample was less oxidized than the original sample used in the parametric tests.

The % sulfur rejections obtained in all the tests were negligible. In fact, the sulfur content appeared to have increased due to the adsorption of the sulfate ions by the

Table LXII. Results of CECC shakedown testing on Middle Wyodak coal.

	Ash Content (% wt)		Sulfur Content (% wt)	
Sampling Period	Feed	Product	Feed	Product
Day 1	5.37	2.20	0.375	0.650
Day 2	5.37	1.58	0.375	0.672
Day 3	5.37	1.16	0.375	0.616

coal. Given that Middle Wyodak coal is a low sulfur coal, this was not surprising.

Subtask 6.2 - Continuous Test Work

The continuous unit was run at a rate of 2 lb/hr with a corresponding retention time of about 6.3 hrs in the reactor and about 10 hours overall. Table LXIII shows the conditions used for the continuous testing of the Middle Wyodak and Elkhorn No. 3 coal samples. These conditions were determined to be optimum for processing the samples of these coals in Task 4. To minimize oxidation-related problems, a fresh batch of run-of-mine Elkhorn No. 3 coal from the Consolidated Coal Company was used.

The Elkhorn No. 3 coal replaced the Pittsburgh No.8 coal in the Continuous Test Work due to the problems found in the CECC treatment of the latter sample (Task 4). The Pittsburgh No.8 coal sample obtained in Task 1 was found to be oxidized and efforts to obtain this sample from the same seam where it was obtained was unsuccessful since the mine has been closed. As discussed in Subtasks 4.4 - 4.6, Pittsburgh No. 8 coal samples obtained from other locations did not respond well to CECC treatment due to

Table LXIII. Conditions used for the continuous testing of Middle Wyodak coal and Elkhorn No. 3 coal.

Operating Parameters	Middle Wyodak	Elkhorn No. 3
% Solids	6.86	6.0
Fe^{3+} Addition (M)	$10^{-3.54}$	10^{-5}
H_2SO_4 Concentration (M)	2.32	3.0
Reactor Temperature (°C)	80	60
Predicted % Ash Rejection	65.5	54.7

other problems such as large amount of the liberated mineral matter being coarse (i.e., not amenable to wet-screening after treatment) and presence of high amounts of ferruginous minerals, which leads to very high ferric ion content. However, tests conducted on the Elkhorn No. 3 coal at optimum conditions found for the Pittsburgh No. 8 sample indicated good mineral matter removal by the CECC process. With approval from DOE, this sample was then selected to replace the Pittsburgh No. 8 sample in the continuous test work. Based on the batch tests, the optimum conditions found for the Pittsburgh No. 8 coal were also adopted in the continuous testing of the Elkhorn No. 3 coal.

The continuous tests were conducted on dry-screened 65 x 325 mesh Middle Wyodak and Elkhorn No. 3 coal samples. The feed samples were dry-screened because the screw feeder in the continuous unit could not handle moist samples. The option of wet-screening the feed and drying the samples afterwards was not considered because oxidation of the feed would result, which is detrimental to the CECC process. For the continuous test work on the fine by-zero coal, dry-screened -325 mesh samples were used. After the CECC treatment, the clean fine by-zero coal was separated from the liberated mineral matter by microbubble column flotation, instead of wet-screening. The continuous tests on the fine coal were limited to the Elkhorn No. 3 coal sample since subbituminous Middle Wyodak coal does not respond well to flotation.

Table LXIV shows the results obtained for the continuous testing of the 65 x 325 mesh Middle Wyodak coal, which had feed ash and sulfur contents of 6.96% and 0.52%. On the first day, the ash content of the Middle Wyodak coal after treatment was 3.38%. On the second day, the average ash content of the product obtained was reduced to 2.48%. The reaching of steady state level by the various parameters, particularly the reactor temperature and pulp density, may have been responsible for this improvement.

The average ash content of the product obtained on Day 3 was 1.88%, while that of the reject was 5.2%. The ash rejection by % weight was calculated in this work according to the Equation 1, which was given in Subtask 4.1. The ash rejection calculated for Day 3 was 80.4% with a yield of 81.3% (by weight). Samples taken during Day 3 indicated that no significant changes occurred in the process once the system had attained steady state. The results obtained for Day 4 show that the product had an ash content of 1.84%. This corresponds to an ash rejection of 80.5% at a yield of 81.4%, which was a slight improvement from that obtained on Day 3. Based on the ash analysis of the product and reject samples taken during Days 3 and 4, there were no significant fluctuations occurring in the process, except for during the period between 4:00 and 5:00 PM on Day 4.

Table LXIV. Results of the continuous testing on Middle Wyodak coal (65 x 325 mesh)

Sampling Period	Ash Content (% wt)		Ash Rejection (% wt)	Sulfur Content (% wt)		Yield (% wt)
	Product	Reject		Product	Reject	
Day 1	4.38	5.49	-	0.85	1.11	-
Day 2	2.48	5.52	-	0.65	1.06	-
Day 3 (avg)	1.88	5.20	80.28	0.75	1.48	81.30
10:30 AM	1.95	5.53	79.94	0.73	1.57	83.10
2:30 PM	1.86	5.00	80.67	0.76	1.52	80.36
5:30 PM	1.83	5.07	80.52	0.75	1.35	80.43
Day 4 (avg)	1.84	5.63	80.54	0.76	1.20	81.35
11:00 AM	1.76	5.58	81.68	0.76	1.41	80.46
2:00 PM	1.61	5.28	83.30	0.85	1.20	80.24
4:00 PM	1.73	5.63	81.88	0.72	1.00	80.80
5:00 PM	2.17	5.49	77.16	0.75	0.97	81.07
7:00 PM	1.96	6.16	78.66	0.76	1.43	84.19
Day 5	2.18	5.58	77.32	0.64	0.99	80.47

Feed: 6.96% ash
0.52% sulfur

The effect of a lower reactor temperature on the CECC process is shown by the results for Day 5, when the reactor temperature was set at 60°C. The ash content of the product increased to 2.18%, which gave a lower ash rejection of 77.3% at a yield of 80.4%. The negative effect of a lower temperature on the CECC processing of the Middle Wyodak coal had also been observed in the parametric batch tests (Task 4).

The yield in the continuous testing of Middle Wyodak coal was lower than that obtained in the parametric batch tests (Task 4). Also, the ash contents of the reject were relatively low, as shown in Table LXIV. These problems may be attributed to the fact that the feed for the continuous testing was prepared by dry-screening. As a result, the feed coal contained considerable amounts of fine coal that passed through the 325 mesh screen and reported to the reject. Wet-screening would have eliminated this problem, but would have been difficult to feed the wet coal at the slow feed rate (2 lb/hr).

The sulfur contents of the products obtained over the entire testing period were considerably higher than the feed sulfur contents. This was observed in Task 4, where the increase in sulfur content was attributed to the adsorption of sulfate ions on the oxygen functional groups of this low-rank coal. However, further washing of the product prior to filtering and drying decreased the sulfur content of the product (see Task 4). An alternative remedy may be to use hydrochloric acid instead of sulfuric acid, but this might increase the chlorine content of the product coal.

In general, the results obtained for Middle Wyodak coal with the continuous unit were better than those obtained in the parametric batch tests (Subtask 4.1) or those predicted by the optimization and validation tests (Subtask 4.2). This may be because the coal used for the continuous testing was processed as soon as it was received, which minimized oxidation. As discussed previously, oxidation prior to treatment is detrimental to the CECC process since the process is based on the incipient oxidation of the coal. It should also be noted that the ash rejection obtained in the continuous testing was lower than that obtained in the shakedown testing (Subtask 6.1). This may be attributed to the slight oxidation of the coal that occurred while the continuous unit was being modified after the shakedown testing.

In preparation for continuous testing, the fresh batch of run-of-mine Elkhorn No. 3 coal (+1 inch) was crushed, ground, and dry-screened to obtain the 65 x 325 mesh size fraction. The 325 x 0 mesh fraction was stored in the freezer and used for the continuous test work on the fine by-zero fraction.

Table LXV shows the results obtained for the continuous testing of the 65 x 325 mesh sample of Elkhorn No. 3 coal. The feed coal had ash and sulfur contents of 9.43% and 1.57%. Samples were not taken during the first two days of operation since the continuous unit did not attain steady state until after about 36 hours because some of the lines were clogged. On Day 3, the average ash contents of the product and reject were 2.00% and 10.31%. The ash rejection, as given by Equation 1, was 85.23% with a yield of about 70.71%. As discussed above for the Middle Wyodak coal, the yield was lower than that obtained in the parametric batch testing (Subtask 4.1), probably due to the fact that the coal used here was dry-screened while that used in the batch testing was wet-screened.

For Day 4, the ash content was reduced to an average of 2.1% with an ash rejection of 83.7%. The ash rejection was slightly lower than that for Day 3, but the yield obtained was higher. The results of the samples taken every 2 hours for Day 4 are also given in Table LXV. The ash content after CECC treatment varied from 1.79% to about 2.29%. However, there were no significant changes in the amount of ash rejected over time. This would indicate that there are no significant fluctuations in the operating

Table LXV. Results of the continuous testing on Elkhorn No. 3 coal (65 x 325 mesh).

a. Ash Rejection

Sampling Period	Ash Content (% wt)			Ash Rejection (% wt)			Yield (% wt)
	Feed	Product	Reject	Total	Liberated	Dissolved	
Day 1	9.43	-	-	-	-	-	-
Day 2	9.43	-	-	-	-	-	-
Day 3	9.43	2.00	10.31	85.23	62.99	37.01	71.62
Day 4	9.43	2.10	8.58	83.68	71.62	28.28	73.77
8:00 AM	9.43	1.79	8.11	86.13	74.60	25.40	74.17
10:00 AM	9.43	2.29	9.01	82.37	69.95	30.05	73.70
12:00 AM	9.43	2.24	8.39	82.99	69.64	30.36	71.69
2:00 PM	9.43	2.01	8.83	84.20	71.24	28.76	72.14
4:00 PM	9.43	2.17	8.58	82.71	72.66	27.37	75.14
Day 5	9.43	2.27	10.04	82.97	66.26	33.74	72.90

b. Sulfur Rejection

Sampling Period	Sulfur Content (% wt)			Sulfur Rejection (% wt)
	Feed	Product	Reject	
Day 1	-	-	-	-
Day 2	-	-	-	-
Day 3	1.57	0.95	1.85	57.95
Day 4 (avg)	1.57	1.21	3.05	43.87
8:00 AM	1.57	0.90	2.44	57.34
10:00 AM	1.57	1.45	4.07	31.93
12:00 PM	1.57	1.17	3.06	46.58
2:00 PM	1.57	1.28	2.60	39.55
4:00 PM	1.57	1.26	3.11	39.69
Day 5	1.57	1.33	3.12	38.24

conditions of the unit.

When the reactor temperature was lowered to about 50°C for Day 5, there was a slight decrease in the amount of mineral matter removed. The average product ash content was 2.27%, while the ash rejection was calculated to be around 83% with a yield of 72.9%. The ash rejection and yield were slightly lower than those obtained at a higher temperature, but the decrease was not significant enough to indicate any temperature dependence.

The mass balance showed that liberation accounted for a majority of the mineral matter rejected by the CECC process. The amount of mineral matter removed due to liberation varied from about 63% to 74%. These values were much higher than those for the Middle Wyodak coal, which contained a significant amount of acid-soluble carbonates.

Table LXV shows that sulfur removal by the CECC process is significant for the Elkhorn No. 3 coal. The sulfur content was reduced to as low as 0.9% by the CECC process. The sulfur rejection (by %weight), which was calculated using an equation similar to Equation [1], varied from 32% to 58%. The fact that the sulfur content of the reject was higher than that of the product suggests that liberation plays a major role in sulfur rejection. The amount of sulfur removed by the CECC process from the Elkhorn No. 3 coal was significantly higher than that for the low sulfur Middle Wyodak coal sample. This is because a higher rank coal such as Elkhorn No. 3 does not have significant oxygen functional groups on which sulfate ions can adsorb.

Continuous CECC tests were also conducted on -325 mesh coal samples, with the product being treated by microbubble column flotation to separate the clean coal from the liberated mineral matter. The use of flotation was necessary because the wet-screening technique cannot be used for the by-zero coal. Since the Middle Wyodak coal is not amenable to flotation, the continuous test work on the -325 mesh samples were limited to the Elkhorn No. 3 coal.

In these tests, the continuous unit was run under using the same conditions used for the 65 x 325 mesh samples. The CECC-treated samples were collected, rinsed with water, and filtered to remove any acid solution present in the moist sample. The clean coal was then subjected to flotation using a 3-inch diameter by 6-ft long column equipped with a microbubble generator. For all the tests, the sample was fed as 5% solids (by weight) slurry with frother additions of 0.5 lb/ton of Dowfroth 250.

Table LXVI shows the continuous test results on -325 mesh Elkhorn No. 3 coal samples. Also shown for comparison are the flotation test results obtained with the coal that was not treated by the CECC process. There was no collector added in this set of flotation tests. For the untreated sample that was floated at a feed rate of 150 ml/min (Test No. 1), the ash content was reduced from 5.46% to 2.91%. There were no significant changes in the removal of mineral matter when the feed rate was increased to 300 ml/min (Test No. 2). However, the sulfur rejection was lower with that obtained at a higher feed rate. Using a flotation feed rate of 1000 ml/min (Test No. 3), the %ash and sulfur rejection increased to about 86.7 and 79.4%. However, the yield (% wt) obtained for this test was only 29.5%.

Table LXVI. Results of the continuous testing on Elkhorn No. 3 coal (-325 mesh).

a. Ash Rejection

Test No.	Process	Ash Content (% wt)			Ash Rejection (% wt)			Yield (% wt)
		Feed	Product	Reject	Total	Liberated	Dissolved	
1*	Flotation	5.46	2.91	35.27	48.60	-	-	95.53
2**	Flotation	5.46	2.95	43.22	49.09	-	-	95.13
3***	Flotation	3.59	1.49	3.17	80.73	-	-	29.55
4*	CECC & Flotation	6.93	2.44	10.90	76.86	70.17	29.88	65.72
5**	CECC & Flotation	6.93	2.63	9.43	74.56	60.18	39.82	67.01

b. Sulfur Rejection

Test No.	Process	Sulfur Content (% wt)			Sulfur Rejection (% wt)		
		Feed	Product	Reject	Total	Liberated	Dissolved
1*	Flotation	1.53	1.08	2.08	32.57	-	-
2**	Flotation	1.53	1.24	2.52	22.90	-	-
3***	Flotation	1.63	0.969	1.07	79.43	-	-
4*	CECC & Flotation	2.43	1.25	1.47	66.20	31.33	68.67
5**	CECC & Flotation	2.43	1.35	1.55	62.77	33.51	66.49

* Flotation feed rate = 150 ml/min

** Flotation feed rate = 300 ml/min

*** Flotation feed rate = 1000 ml/min

For the CECC-treated samples (Test Nos. 4 and 5), the ash rejections were much higher than those for the untreated samples. The amount of mineral matter rejected by the CECC process was as high as 76.9%, while the sample floated directly gave an ash rejection of only 49%. This was expected since the CECC process liberates the mineral matter. However, the yield was lower for the CECC-treated sample than for the untreated sample. The lower yield may be attributed to the decrease in the sample's floatability brought about by the oxidation of the coal during the CECC process.

The amounts of sulfur removed from the CECC-treated samples were higher than those for the untreated samples (Table LXVI). For the CECC-treated sample, the average sulfur rejection in the two tests was about 64.5%, which was more than double that for the untreated samples. This was due to the liberation and dissolution of pyrite in the CECC process.

The mass balance indicated that liberation plays a major role in the removal of mineral matter by the CECC process. As much as 70% of the mineral matter removed was due to liberation. On the other hand, the average amount of sulfur rejection due to liberation was only about 32%. This is opposite what was observed for the 65 x 325 mesh sample. However, total sulfur removal in the CECC treatment of the -325 mesh sample was improved probably because pyrite liberation and dissolution increased with the decrease in particle size.

To increase the flotation yield for the CECC-treated samples, another set of tests was carried out on -325 mesh coal samples using 1 to 3 lb/ton of kerosene as a collector during the flotation stage. For these tests, the flotation feed rate was set at 300 ml/min, except for Test No. 4 which used a flotation feed rate of 50 ml/min. The rest of the test conditions were similar to those employed for tests conducted without collector addition. Table LXVII shows the results obtained for untreated and CECC-treated Elkhorn No. 3 coal samples. Using 1 lb/ton of kerosene (Test No. 1), the ash content of the untreated sample was reduced from 5.27% to 2.75%, representing an ash rejection of 51.4%. For the CECC-treated sample that was floated using 1 lb/ton of kerosene (Test No. 2), the ash content was reduced from 6.66% to 2.35%. In this case, the ash rejection was determined to be 72.4% with a yield of about 78.25%. At a higher kerosene addition of 3 lbs/ton (Test No. 3), the yield increased to 86.2% with only a slight decrease in the ash and sulfur rejection. It can be seen that the addition of kerosene in the flotation stage can help to significantly improve the recovery without causing any noticeable decrease in ash and sulfur rejection. According to the mass balance analysis, the amount of mineral matter rejection due to liberation was about 83.7%, which was higher than that obtained without collector addition (Table LXVI). In order to increase the yield, another test was conducted where the flotation feed rate was decreased to 50 ml/min (Test No. 4) with the kerosene addition maintained at 3 lbs/ton. The result show a yield of almost of 96%, but the %ash and sulfur rejection decreased to 66.1 and 30.72%. The amount of mineral matter and sulfur removal due to liberation also decreased in this test. It should be pointed out that the decrease in mineral matter liberation is not due to a decrease in the performance of the CECC process since the CECC-treated samples for the flotation tests where obtained from the same batch. The decrease in the amount of mineral matter liberation is due to changes in the flotation conditions employed in these tests.

Table LXVII. Results of the continuous testing on Elkhorn No. 3 coal (-325 mesh).

a. Ash Rejection

Test No.	Process	Ash Content (% wt)			Ash Rejection (% wt)			Yield (% wt)
		Feed	Product	Reject	Total	Liberated	Dissolved	
1*	Flotation	5.27	2.75	28.17	51.41	-	-	93.12
2*	CECC & Flotation	6.66	2.35	18.56	72.39	83.74	16.26	78.25
3**	CECC & Flotation	6.66	2.43	25.24	68.54	76.24	23.76	86.21
4***	CECC & Flotation	3.59	1.27	29.60	66.10	52.23	42.23	95.81

b. Sulfur Rejection

Test No.	Process	Sulfur Content (% wt)			Sulfur Rejection (% wt)		
		Feed	Product	Reject	Total	Liberated	Dissolved
1*	Flotation	1.91	1.44	3.58	29.79	-	-
2*	CECC & Flotation	2.22	1.26	1.96	55.59	34.55	65.45
3**	CECC & Flotation	2.22	1.29	2.02	29.90	25.14	74.86
4***	CECC & Flotation	1.30	0.94	2.03	30.72	21.28	78.72

* Collector addition = 1 lb/ton kerosene
** Collector addition = 3 lb/ton kerosene
*** Collector addition = 3 lb/ton kerosene, Flotation Feed Rate = 50 ml/min

Figure 32 shows the combustible recovery versus ash rejection curves for the tests conducted on the -325 mesh Elkhorn No. 3 coal. The curve for the CECC-treated samples was shifted to the right of that for the untreated samples suggesting that the combination of CECC process and flotation gives better ash rejection than flotation only. A similar trend is shown in the combustible recovery versus sulfur rejection curves

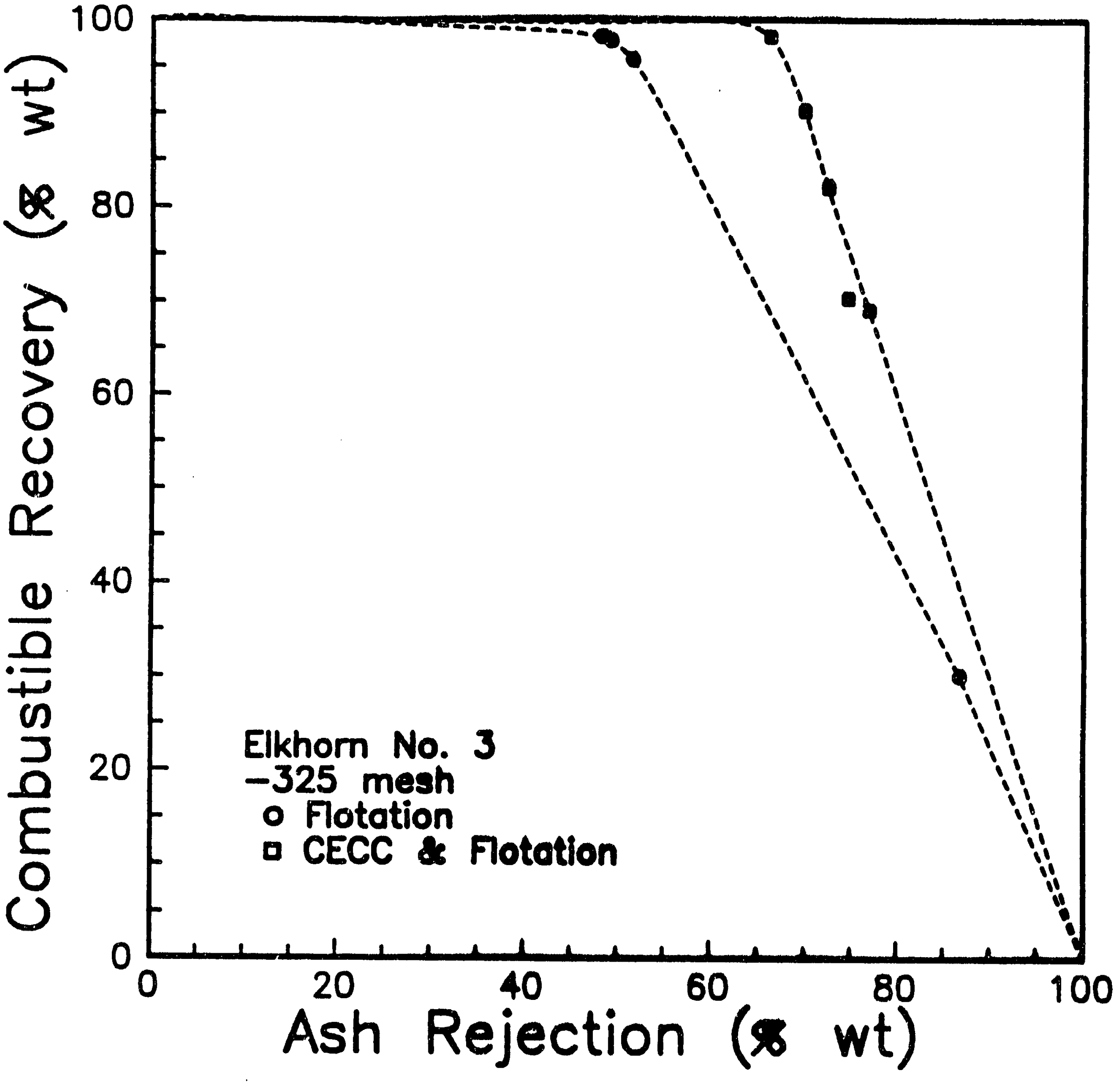

Figure 32. Combustible recovery versus ash rejection curves for the continuous testing of -325 mesh Elkhorn No. 3 coal.

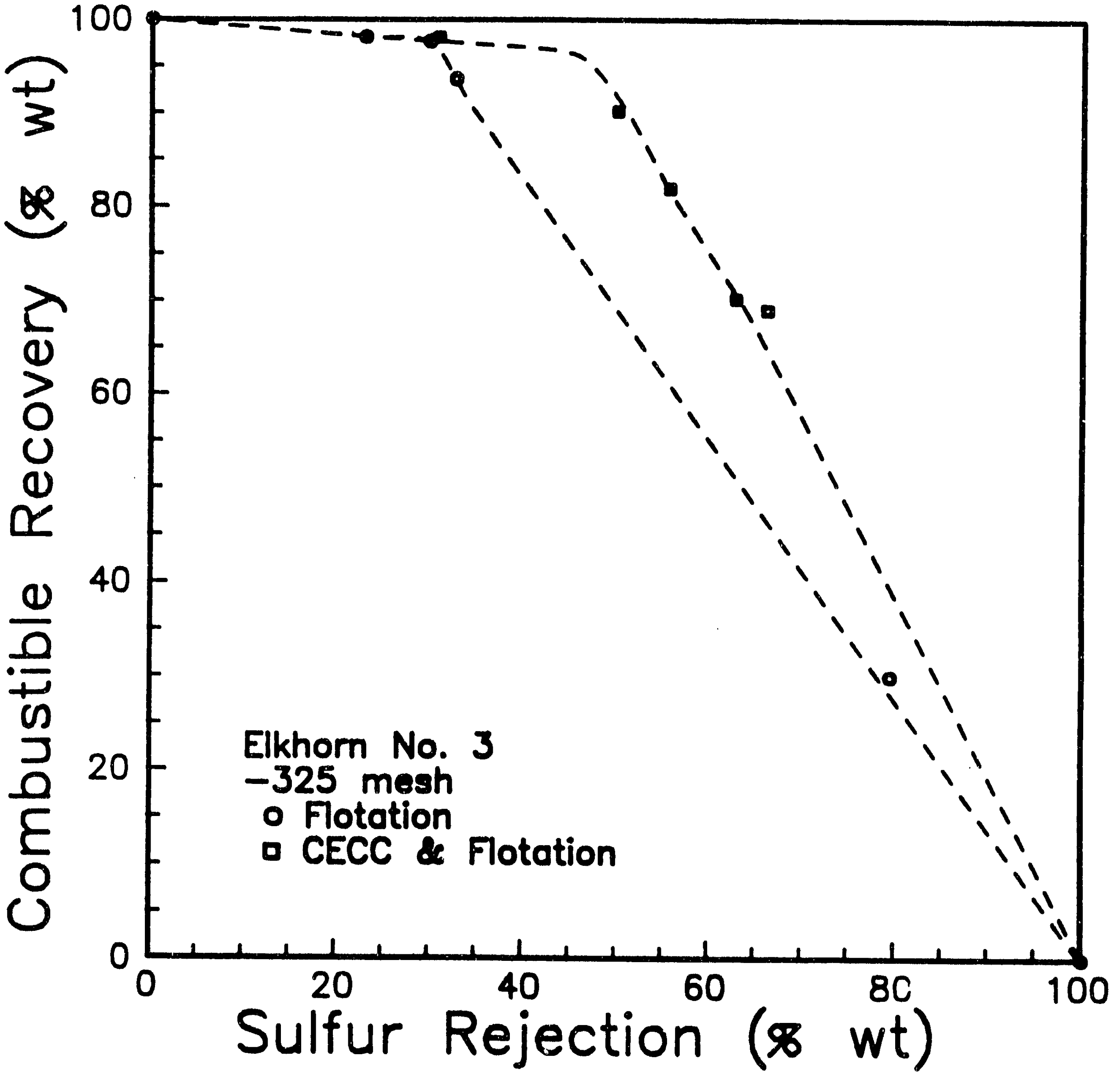

Figure 33. Combustible recovery versus sulfur rejection curves for the continuous testing of -325 mesh Elkhorn No. 3 coal.

(Figure 33). This suggests that sulfur rejection improves with the use of the CECC process.

The mineral matter rejection obtained with the -325 mesh sample was not as good as that obtained with the 65 x 325 mesh sample, although mineral matter rejection should increase with decreasing particle size. The poorer results obtained with the -325 mesh sample may be attributed to the difficulty in separating the liberated mineral matter from the clean coal.

The results obtained here for the Elkhorn No. 3 coal samples were significantly better than those obtained in the parametric batch tests (Subtask 4.1) or those predicted in the optimization and validation tests (Subtask 4.2). This finding may be attributed to the likelihood that the samples used for the continuous testing were less oxidized. The Elkhorn No. 3 coal sample used in the continuous testing was fresh run-of-mine sample (+1 inch) that was shipped directly to our laboratory and processed as soon as it was received, which minimized oxidation. As discussed above, the use of oxidized feed samples is detrimental to the CECC process.

SUMMARY AND CONCLUSIONS

The majority of the work was conducted on the Middle Wyodak and Pittsburgh No. 8 coals, with the Elkhorn No. 3 coal replacing the Pittsburgh coal in the continuous test work (Subtask 6.2). Some batch tests were also conducted on Upper Freeport, Widow Kennedy and Illinois No. 6 coals.

Coal samples were obtained, prepared and stored in Task 2. The Middle Wyodak, Upper Freeport, Pittsburgh No. 8 and Elkhorn No. 3 coal were characterized (Task 3) for a variety of physical and chemical properties. The characterization work included proximate, ultimate BET surface, and pore size analyses. FTIR spectroscopy, X-ray diffraction, scanning electron microscopy, and image analyses were also used to characterize the coal samples.

A parametric test program (Subtask 4.1) was used to study the effect of temperature, ferric ion addition, acid concentration and percent solids on the CECC process. The operating ranges of the process and the interrelationships of these variables were determined from these tests. Temperature and acid concentration were found to have significant effects on the CECC processing of the Middle Wyodak coal, while ferric ion addition and percent solids did not appear to have any significant impact on the CECC process. For the Pittsburgh No. 8 coal, the effect of percent solids and ferric ion addition on the mineral matter removal were significant, while the effect of temperature was not as significant. A strong interaction between the ferric ion addition and acid concentration was found in these tests. The rejection of mineral matter was favored at low ferric ion addition and high acid concentration. The low ferric ion addition required was attributed to the additional ferric ions coming from the dissolution of pyrite and other ferruginous minerals, while the high acid concentration requirement was due to the need for a corresponding high amount of counter ions. The amount of counter ions required is dependent on the ferric ion concentration in the system.

The mass balance analyses of the parametric test data showed that dissolution, instead of liberation, played a major role in mineral matter rejection for the CECC processing of Middle Wyodak coal, while the opposite was found for the Pittsburgh No. 8, Elkhorn No. 3, Upper Freeport and Widow Kennedy coal samples. Liberation accounted for as much as 80% of the total mineral matter removed from the Elkhorn coal.

The significant amount of mineral matter removal via dissolution in the Middle Wyodak coal was attributed to the presence of large amounts of acid-soluble carbonates and carboxylates of Ca and Mg. On the other hand, the bituminous coal samples did not contain significant amounts of acid-soluble minerals, which accounted for the low amounts of mineral matter removed via dissolution.

A statistical analysis technique, called response surface method, was used in determining the effects of the different parameters and optimizing the process variables. The response models were obtained from the analysis of the parametric test data for the Middle Wyodak and Pittsburgh No. 8 coal. The amount of ferric ions needed for the optimum CECC processing of the Pittsburgh No. 8 coal was much lower than the amount needed for the Middle Wyodak coal. This was due to the higher pyrite and other ferruginous mineral content of the Pittsburgh coal. Also, the percent solids and temperature requirements were lower for the Pittsburgh No. 8 coal. However, the optimum acid requirements were higher for this coal due to the higher total ferric ion concentration in the CECC processing system for the Pittsburgh coal. At the statistically determined optimum conditions, the predicted % ash rejection values for the Middle Wyodak and Pittsburgh coal were 65.5 and 54.7%. Tests conducted at these optimum conditions validated the response model and these optimum conditions.

Precleaning the Middle Wyodak coal by conventional froth flotation resulted in a CECC product that had a lower ash content than those obtained without precleaning. For the Pittsburgh No. 8 coal, precleaning by conventional froth flotation did not seem to be beneficial to the CECC processing of this coal. This was due to the oxidation of the coal in the precleaning stage, which had a negative effect on the CECC process.

The leaching kinetics studies for the Middle Wyodak coal showed that the dissolution of Ca, Mg, Fe and Al was significant. The dissolution rate constants for Ca and Mg were much higher that those for the other species. On the other hand, the dissolution of the Si species, as expected, was negligible. For the Pittsburgh No. 8 coal, the dissolutions of the different minerals, except for the Fe- containing mineral matter, were slow and the total amount dissolved were not as significant. These results were in excellent agreement with the conclusions made in the mass balance analyses.

The use of alternative methods of regenerating ferric ions, such as by bacterial and air oxidation, was investigated. Parametric batch tests were conducted to determine the effects of the following variables on the CECC process via bacterial regeneration: pH, temperature, substrate concentration, inoculum concentration and lead time. The effects of all five parameters were found to be statistically significant with the pH and substrate concentration observed to be more critical in the process. However, the amounts of ash and sulfur rejection obtained via a bacterial regeneration scheme were much lower than those obtained via the electrochemical regeneration scheme. The use of air oxidation showed better ash rejection than bacterial oxidation, but the performance of the aeration scheme was still poorer than that of the electrochemical regeneration method. Based on these findings, the continuous unit was designed around an electrochemical reactor.

The liberation analyses for the Pittsburgh No. 8 and Elkhorn No. 3 coals, which were conducted through the use of image analysis, showed that the amount of mineral matter and pyrite liberated by the CECC process increases with processing time. However, anywhere from 50 to 70% of the mineral matter and pyrite liberated in the CECC treatment of the Pittsburgh No. 8 coal was relatively coarse. This was presumably responsible for the some of the poor results obtained with this coal sample. Due to this situation, the use of screening was not effective in separating the liberated mineral matter and pyrite from the clean coal. On the other hand, the mineral matter and pyrite liberated by the CECC process from the Elkhorn coal were relatively fine; thus, screening was still an effective method of recovering the clean coal. This difference in the size of the mineral matter liberated may be responsible for the better results obtained with the Elkhorn coal.

Two major problems encountered in the CECC process were: i) the poor performance of the CECC process in cleaning oxidized coal, and ii) ineffeciency of screening for separating the coarse liberated mineral matter from some of the coals tested. The rejection of mineral matter via an electrocatalytically induced liberation process is seriously affected by the degree of oxidation of the feed because the liberation process is based on the incipient oxidation of the coal. This was the main reason for the poor results obtained in subsequent tests where the coal samples had oxidized. In this study, the higher the degree of surface oxidation of the feed sample, the lower the ash and sulfur rejection. The second problem was brought about by the coarseness of the liberated mineral matter in some coal samples. The solution to this problem was to use alternative methods of recovering the clean coal. Using flotation to recover the clean coal, instead of wet-screening, improved the mineral matter rejection. Another solution to the problem of coarse liberated mineral matter was the use of coal with a narrow size distribution, for which actual tests showed increases in ash rejection.

Based on the data obtained from the batch tests (Task 4), a bench-scale continuous unit capable of processing 1-3 lbs/hr of coal was designed. The reactor design was a 5-bank unit and used the electrochemical regeneration scheme to oxidize the ferrous ion to ferric ions. The CECC circuit included a screw feeder, conditioning tanks, drum filter, vibrating screen for the +325 mesh coal and a microbubble column flotation unit for the -325 mesh coal. Anything that was going to be in contact with the acid solution in this circuit was constructed of acid resistant materials including teflon coated heaters and stirrers.

Continuous tests operated at a capacity of 2 lbs/hr were conducted on 65 x 325 mesh Middle Wyodak and Elkhorn No. 3 coal. The Elkhorn coal was used due to the problems associated with the oxidation of the original Pittsburgh No. 8 coal sample, unavailability of fresh sample, and inefficiency of screening for removing the coarse mineral matter liberated from this sample. Fresh run-of-mine samples were obtained for these tests since the samples (split B-2) obtained in Task 2 were already oxidized. Shakedown testing on the CECC continuous unit gave products with an ash content of as low as 1.16% for the Middle Wyodak coal. The continuous unit, which was run under the optimum conditions established for these coals, gave average ash rejection values of about 80 and 84% for the Middle Wyodak and Elkhorn No. 3 coal. The sulfur rejection for the low-sulfur Middle Wyodak coal was negligible while that for the Elkhorn coal averaged about 47%. Liberation accounted for as much as 74% of the total mineral matter rejection from the Elkhorn coal in these tests.

The results of continuous tests on -325 mesh Elkhorn No. 3 coal, where flotation was used after CECC treatment to recover the clean coal, showed an ash rejection of as high as 77%. In these tests, the combustible recovery vs. ash rejection and the combustible recovery vs. sulfur rejection curves for the CECC treated samples were shifted to the right of that for the samples that were cleaned by flotation only. This suggests that the combination of CECC process and flotation gives better results than flotation only.

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APPENDIX 1: Adsorption and Desorption Pore Distributions.

BJH Adsorption Pore Distribution for Middle Wyodak Coal

Pore Diameter Range (A)	Average Diameter (A)	Incremental Pore Volume (cc/g)	Cumulative Pore Volume (cc/g)
2757.2 - 1505.9	1788.7	0.002535	0.002535
1505.9 - 1274.6	1370.7	0.000753	0.003288
1274.6 - 1096.0	1171.5	0.000712	0.004000
1096.0 - 954.6	1015.3	0.000740	0.004739
954.6 - 799.1	862.7	0.000817	0.005556
799.1 - 622.7	688.5	0.001226	0.006782
622.7 - 510.8	555.3	0.000959	0.007741
510.8 - 410.0	448.9	0.001005	0.008746
410.0 - 327.7	359.3	0.000944	0.009690
327.7 - 268.2	291.7	0.000758	0.010448
268.2 - 212.3	233.3	0.000861	0.011309
212.3 - 163.7	181.3	0.000803	0.012111
163.7 - 130.7	143.2	0.000561	0.012672
130.7 - 104.6	114.5	0.000466	0.013139
104.6 - 83.4	91.4	0.000325	0.013464
83.4 - 61.3	68.7	0.000275	0.013739
61.3 - 46.5	51.6	0.000114	0.013853
46.5 - 35.8	39.5	0.000039	0.013891
35.8 - 28.8	31.4	0.000022	0.013914
28.8 - 25.8	27.1	0.000020	0.013933
25.8 - 23.1	24.3	0.000025	0.013959
23.1 - 21.0	21.9	0.000047	0.014006
21.0 - 20.6	20.8	0.000009	0.014015
20.6 - 19.6	20.0	0.000036	0.014051
19.6 - 19.1	19.3	0.000021	0.014072
19.1 - 17.6	18.3	0.000055	0.014127

BJH Desorption Pore Distribution for Middle Wyodak Coal

Pore Diameter Range (A)	Average Diameter (A)	Incremental Pore Volume (cc/g)	Cumulative Pore Volume (cc/g)
1807.1 - 1485.7	1614.7	0.000463	0.000463
1485.7 - 1206.7	1317.0	0.000667	0.001130
1206.7 - 985.3	1073.3	0.000883	0.002012
985.3 - 678.2	775.3	0.001879	0.003892
678.2 - 579.0	620.5	0.000757	0.004648
579.0 - 451.6	499.1	0.001189	0.005837
451.6 - 342.2	381.4	0.001084	0.006921
342.2 - 272.9	299.4	0.001007	0.007928
272.9 - 217.5	238.6	0.000859	0.008787
217.5 - 161.5	180.8	0.001029	0.009817
161.5 - 126.3	139.3	0.000806	0.010622
126.3 - 101.3	110.9	0.000699	0.011322
101.3 - 79.8	87.9	0.000777	0.012099
79.8 - 58.1	65.3	0.000975	0.013074
58.1 - 43.2	48.3	0.000555	0.013629
43.2 - 32.7	36.4	0.000218	0.013846

BJH Adsorption Pore Distribution for Upper Freeport Coal

Pore Diameter Range (A)	Average Diameter (A)	Incremental Pore Volume (cc/g)	Cumulative Pore Volume (cc/g)
2886.0 - 1455.9	1740.5	0.001337	0.001337
1455.9 - 1210.6	1310.3	0.000364	0.001702
1210.6 - 1086.8	1141.8	0.000311	0.002012
1086.8 - 927.1	993.9	0.000363	0.002375
927.1 - 776.6	838.2	0.000434	0.002809
776.6 - 627.9	686.1	0.000465	0.003274
672.9 - 514.3	559.4	0.000459	0.003734
514.3 - 403.3	444.8	0.000494	0.004227
403.3 - 323.5	354.2	0.000431	0.004658
323.5 - 262.8	286.5	0.000371	0.005030
262.8 - 211.3	231.1	0.000337	0.005367
211.3 - 165.0	182.0	0.000330	0.005697
165.0 - 130.0	143.0	0.000284	0.005981
130.0 - 105.2	114.7	0.000198	0.006179
105.2 - 81.3	89.9	0.000204	0.006383
81.3 - 61.3	68.2	0.000159	0.006542
61.3 - 45.6	50.9	0.000132	0.006674
45.6 - 36.5	39.9	0.000066	0.006740
36.5 - 28.8	31.6	0.000064	0.006803
28.8 - 25.8	27.1	0.000026	0.006830
25.8 - 23.1	24.2	0.000031	0.006861
23.1 - 21.1	22.0	0.000025	0.006886
21.1 - 20.5	20.8	0.000018	0.006904
20.5 - 19.6	20.0	0.000021	0.006925
19.6 - 17.6	18.3	0.000038	0.006975

BJH Desorption Pore Distribution for Upper Freeport Coal

Pore Diameter Range (A)	Average Diameter (A)	Incremental Pore Volume (cc/g)	Cumulative Pore Volume (cc/g)
1773.9 - 1474.8	1596.4	0.000252	0.000252
1474.8 - 1203.3	1311.1	0.000376	0.000627
1203.3 - 837.4	954.9	0.000853	0.001480
837.4 - 710.2	763.0	0.000417	0.001898
710.2 - 591.0	639.3	0.000506	0.002403
591.0 - 407.8	465.3	0.000929	0.003332
407.8 - 335.3	364.1	0.000456	0.003789
335.3 - 264.6	291.1	0.000517	0.004306
264.6 - 221.6	239.0	0.000344	0.004650
221.6 - 161.3	181.4	0.000541	0.005191
161.3 - 127.7	140.3	0.000330	0.005521
127.7 - 102.9	112.3	0.000257	0.005778
102.9 - 82.6	90.3	0.000213	0.005991
82.6 - 58.9	66.4	0.000259	0.006250
58.9 - 44.8	49.7	0.000148	0.006398
44.8 - 35.4	38.8	0.000218	0.006616
35.4 - 28.8	31.3	0.000023	0.006638
28.8 - 22.9	25.0	0.000021	0.006659
22.9 - 17.7	19.5	0.000054	0.006713

APPENDIX 2: CECC Process Results Obtained with Dry-Screened Middle Wyodak Coal.

Test No.	Size Fraction	Weight (g)	Weight (%)	Cum. Wt. (%)	Ash (%)	Cum. Ash (%)	S (%)	Cum. S (%)
1	65x200	16.40	51.78	51.78	2.88	2.88	0.587	0.587
	200x325	5.51	17.40	69.18	4.35	3.25	0.533	0.573
	-325	8.12	25.64	94.82	6.60	4.16	0.616	0.585
	composite	30.03	94.82					
	Feed	31.67	100.00		7.56		0.478	
2	65x200	30.87	49.20	49.20	3.04	3.04	0.595	0.595
	200x325	10.12	16.13	65.33	4.44	3.39	0.556	0.585
	-325	18.52	29.51	94.84	6.80	4.45	0.762	0.640
	composite	59.51	94.84					
	Feed	62.75	100.00		7.73		0.472	
3	65x200	16.57	47.46	47.46	3.03	3.03	0.599	0.599
	200x325	5.64	16.16	63.62	4.43	3.39	0.556	0.588
	-325	10.39	29.76	93.38	6.76	4.46	0.818	0.661
	composite	32.60	93.38					
	Feed	34.91	100.00		7.81		0.471	
4	65x200	34.86	53.76	53.76	3.43	3.43	0.612	0.612
	200x325	8.58	13.23	66.99	4.09	3.56	0.543	0.598
	-325	18.71	28.86	95.85	6.57	4.47	0.686	0.624
	composite	62.15	95.85					
	Feed	64.84	100.00		7.74		0.479	
5	65x200	16.53	47.91	47.91	2.93	2.93	0.596	0.596
	200x325	5.48	15.88	63.79	4.38	3.29	0.567	0.589
	-325	10.35	30.00	93.79	6.53	4.33	0.630	0.602
	composite	32.36	93.79					
	Feed	34.50	100.00		7.72		0.464	
6	65x200	30.24	47.52	47.52	3.10	3.10	0.584	0.584
	200x325	10.52	16.53	64.05	4.47	3.45	0.564	0.579
	-325	21.13	33.20	97.25	6.47	4.48	1.030	0.733
	composite	61.89	97.25					
	Feed	63.64	100.00		7.70		0.480	
7	65x200	15.99	44.57	44.57	3.23	3.23	0.550	0.550
	200x325	5.68	15.83	60.40	4.70	3.62	0.550	0.550
	-325	13.13	36.59	96.99	6.73	4.79	1.810	1.025
	composite	34.80	96.99					
	Feed	35.88	100.00		7.61		0.456	
8	65x200	31.64	47.78	47.78	3.24	3.24	0.576	0.576
	200x325	10.41	15.72	63.50	4.54	3.56	0.542	0.567
	-325	23.64	35.70	99.20	6.56	4.64	0.782	0.644
	composite	65.69	99.20					
	Feed	66.22	100.00		7.67		0.482	

Test No.	Size Fraction	Weight (g)	Weight (%)	Cum. Wt. (%)	Ash (%)	Cum. Ash (%)	S (%)	Cum. S (%)
9	65x200	16.08	43.97	43.97	2.98	2.98	0.607	0.607
	200x325	4.97	13.59	57.56	4.22	3.27	0.558	0.595
	-325	11.81	32.29	89.85	6.21	4.33	0.825	0.648
	composite	32.86	89.85					
	Feed	36.57	100.00		7.80		0.459	
10	65x200	30.36	46.21	46.21	3.06	3.06	0.644	0.644
	200x325	10.61	16.15	62.36	4.08	3.32	0.646	0.645
	-325	22.38	34.06	96.42	6.19	4.33	1.610	0.986
	composite	63.35	96.42					
	Feed	65.70	100.00		7.62		0.476	
11	65x200	15.94	45.60	45.60	2.97	2.97	0.628	0.628
	200x325	5.28	15.10	60.70	4.18	3.27	0.605	0.622
	-325	11.68	33.41	94.11	6.72	4.49	0.573	0.605
	composite	32.90	94.11					
	Feed	34.96	100.00		7.74		0.486	
12	65x200	29.58	46.48	46.48	2.90	2.90	0.632	0.632
	200x325	9.54	14.99	61.47	4.71	3.34	0.621	0.629
	-325	21.34	33.53	95.00	6.68	4.52	0.695	0.652
	composite	60.46	95.00					
	Feed	63.64	100.00		7.77		0.502	
13	65x200	15.88	46.58	46.58	2.76	2.76	0.659	0.659
	200x325	5.25	15.40	61.98	4.31	3.15	0.629	0.652
	-325	11.19	32.82	94.80	6.48	4.30	0.791	0.700
	composite	32.32	94.80					
	Feed	34.09	100.00		7.94		0.514	
14	65x200	30.04	46.57	46.57	2.67	2.67	0.670	0.670
	200x325	9.50	14.73	61.30	4.51	3.11	0.637	0.662
	-325	22.02	34.14	95.44	5.92	4.12	1.300	0.890
	composite	61.56	95.44					
	Feed	64.50	100.00		7.61		0.500	
15	65x200	16.00	46.69	46.69	2.62	2.62	0.619	0.619
	200x325	5.18	15.11	61.80	4.03	2.96	0.574	0.608
	-325	12.68	37.00	98.80	6.26	4.20	1.220	0.837
	composite	33.86	98.80					
	Feed	34.27	100.00		7.85		0.513	
16	65x200	29.48	45.58	45.58	2.68	2.68	0.657	0.657
	200x325	10.21	15.79	61.37	3.91	2.99	0.617	0.647
	-325	22.02	34.05	95.42	5.91	4.03	1.685	1.017
	composite	61.71	95.42					
	Feed	64.67	100.00		7.72		0.471	

Test No.	Size Fraction	Weight (g)	Weight (%)	Cum. Wt. (%)	Ash (%)	Cum. Ash (%)	S (%)	Cum. S (%)
17-1	65x200	22.75	45.87	45.87	2.74	2.74	0.638	0.638
	200x325	7.54	15.20	61.07	4.76	3.24	0.613	0.632
	-325	15.31	30.87	91.94	6.52	4.34	0.898	0.721
	composite	45.60	91.94					
	Feed	49.60	100.00		7.85		0.517	
17-2	65x200	22.82	46.69	46.69	2.83	2.83	0.644	0.644
	200x325	6.78	13.87	60.56	4.38	3.18	0.578	0.629
	-325	16.74	34.24	94.80	7.75	4.83	0.643	0.634
	composite	46.34	94.80					
	Feed	48.88	100.00		7.89		0.471	
17-3	65x200	23.59	47.94	47.94	3.00	3.00	0.594	0.594
	200x325	7.43	15.10	63.04	4.21	3.29	0.550	0.583
	-325	15.50	31.49	94.53	6.29	4.29	1.130	0.765
	composite	46.52	94.53					
	Feed	49.21	100.00		7.51		0.488	
18	65x200	9.09	46.61	46.61	2.84	2.84	0.623	0.623
	200x325	3.01	15.44	62.05	4.65	3.29	0.826	0.674
	-325	7.33	37.59	99.64	6.27	4.41	1.950	1.155
	composite	19.43	99.64					
	Feed	19.50	100.00		7.82		0.489	
19	65x200	39.58	50.53	50.53	2.89	2.89	0.637	0.637
	200x325	13.23	16.89	67.42	3.89	3.14	0.603	0.628
	-325	23.25	29.68	97.10	6.34	4.12	0.862	0.699
	composite	76.06	97.10					
	Feed	78.33	100.00		7.36		0.514	
20	65x200	24.45	50.08	50.08	2.50	2.50	0.573	0.573
	200x325	7.85	16.08	66.16	4.20	2.91	0.588	0.577
	-325	14.82	30.36	95.52	6.96	4.23	0.563	0.579
	composite	47.12	95.52					
	Feed	48.82	100.00		7.04		0.491	
21	65x200	24.83	50.66	50.66	2.64	2.64	0.588	0.588
	200x325	7.58	15.47	66.13	3.86	2.93	0.585	0.587
	-325	15.74	32.12	98.25	5.68	3.83	1.170	0.778
	composite	48.15	98.25					
	Feed	49.01	100.00		7.11		0.495	
22	65x200	23.07	47.01	47.01	5.90	5.90	0.497	0.497
	200x325	8.07	16.44	63.45	7.02	6.19	0.461	0.488
	-325	16.88	34.39	97.84	9.99	7.53	0.450	0.475
	composite	48.02	97.84					
	Feed	49.08	100.00		7.75		0.477	

Test No.	Size Fraction	Weight (g)	Weight (%)	Cum. Wt. (%)	Ash (%)	Cum. Ash (%)	S (%)	Cum. S (%)
23	65x200	24.42	49.89	49.89	2.27	2.27	0.630	0.630
	200x325	8.14	16.63	66.52	4.41	3.18	0.585	0.619
	-325	15.40	31.46	97.98	6.29	4.18	1.253	0.823
	composite	47.96	97.98					
	Feed	48.95	100.00		6.91		0.499	
24	65x200	24.68	49.89	49.89	3.12	3.12	0.590	0.590
	200x325	7.57	15.30	65.19	4.86	3.53	0.571	0.586
	-325	15.19	30.71	95.90	6.31	4.42	0.617	0.596
	composite	47.44	95.90					
	Feed	49.47	100.00		7.41		0.483	
25	65x200	21.89	44.84	44.84	2.73	2.73	0.638	0.638
	200x325	7.95	16.28	61.12	3.93	3.05	0.615	0.632
	-325	17.28	35.40	96.52	6.30	4.24	0.590	0.617
	composite	47.12	96.52					
	Feed	48.82	100.00		7.32		0.489	

APPENDIX 3: CECC Process Results Obtained with Wet-Screened Middle Wyodak Coal.

CECC Process Results
Obtained with Wet-Screened Middle Wyodak Coal

Test		Weight (g)	Ash (%)	Sulfur (%)
1	Product	25.84	3.15	0.543
	Reject	4.13	4.11	0.671
	Feed	30.92	6.83	0.494
2	Product	55.28	3.06	0.549
	Reject	7.04	3.87	0.791
	Feed	64.93	6.66	0.476
3	Product	29.00	3.19	0.553
	Reject	4.13	3.70	0.648
	Feed	34.91	6.72	0.488
4	Product	55.66	2.97	0.518
	Reject	6.67	5.39	1.210
	Feed	64.87	6.52	0.510
5	Product	28.22	3.42	0.576
	Reject	5.33	5.05	1.230
	Feed	35.15	6.96	0.491
6	Product	56.75	3.02	0.501
	Reject	6.44	4.54	0.755
	Feed	65.35	7.12	0.493
7	Product	28.89	2.95	0.552
	Reject	5.64	4.80	1.233
	Feed	35.01	6.33	0.467
8	Product	55.00	2.94	0.509
	Reject	9.10	5.30	1.610
	Feed	65.77	7.01	0.476
9	Product	29.67	3.78	0.545
	Reject	5.31	4.57	1.250
	Feed	35.57	7.02	0.522
10	Product	52.84	2.64	0.542
	Reject	10.02	5.25	0.863
	Feed	64.78	6.86	0.481
11	Product	29.02	2.86	0.579
	Reject	5.16	4.14	1.110
	Feed	36.23	7.09	0.465
12	Product	52.68	2.62	0.619
	Reject	10.67	5.47	1.360
	Feed	66.28	6.71	0.523
13	Product	29.05	2.74	0.565
	Reject	4.82	5.12	1.680
	Feed	35.11	6.96	0.553

Test		Weight (g)	Ash (%)	Sulfur (%)
14	Product	53.95	2.76	0.554
	Reject	8.81	5.38	1.430
	Feed	65.80	6.79	0.477
15	Product	29.95	2.74	0.672
	Reject	3.85	3.81	1.260
	Feed	35.02	6.83	0.496
16	Product	54.81	2.77	0.591
	Reject	10.02	5.23	0.833
	Feed	65.20	6.68	0.495
17-1	Product	42.44	2.86	0.570
	Reject	5.56	4.78	1.600
	Feed	50.25	6.62	0.494
17-2	Product	42.94	2.99	0.603
	Reject	5.15	4.33	1.570
	Feed	50.18	6.66	0.513
17-3	Product	42.78	2.98	0.567
	Reject	5.65	5.02	1.605
	Feed	50.18	6.14	0.505
18	Product	17.24	2.98	0.564
	Reject	2.14	4.54	1.770
	Feed	20.38	6.95	0.540
19	Product	69.13	2.84	0.574
	Reject	8.82	5.33	0.850
	Feed	79.80	6.75	0.529
20	Product	41.71	3.01	0.522
	Reject	8.89	4.33	1.510
	Feed	51.62	6.73	0.515
21	Product	39.76	3.12	0.543
	Reject	9.33	4.04	1.590
	Feed	50.18	6.72	0.520
22	Product	44.55	6.75	0.446
	Reject	6.55	8.90	0.532
	Feed	51.42	7.00	0.469
23	Product	43.89	2.91	0.611
	Reject	3.94	4.11	0.691
	Feed	51.45	6.81	0.493
24	Product	40.61	3.28	0.505
	Reject	7.75	6.49	0.723
	Feed	50.07	6.79	0.504
25	Product	43.22	2.76	0.597
	Reject	5.08	4.93	0.599
	Feed	51.81	6.92	0.501

APPENDIX 4: Response Surface Plots for the Effects of Different Parameters on the Product Ash Content (% wt) for the Middle Wyodak Coal.

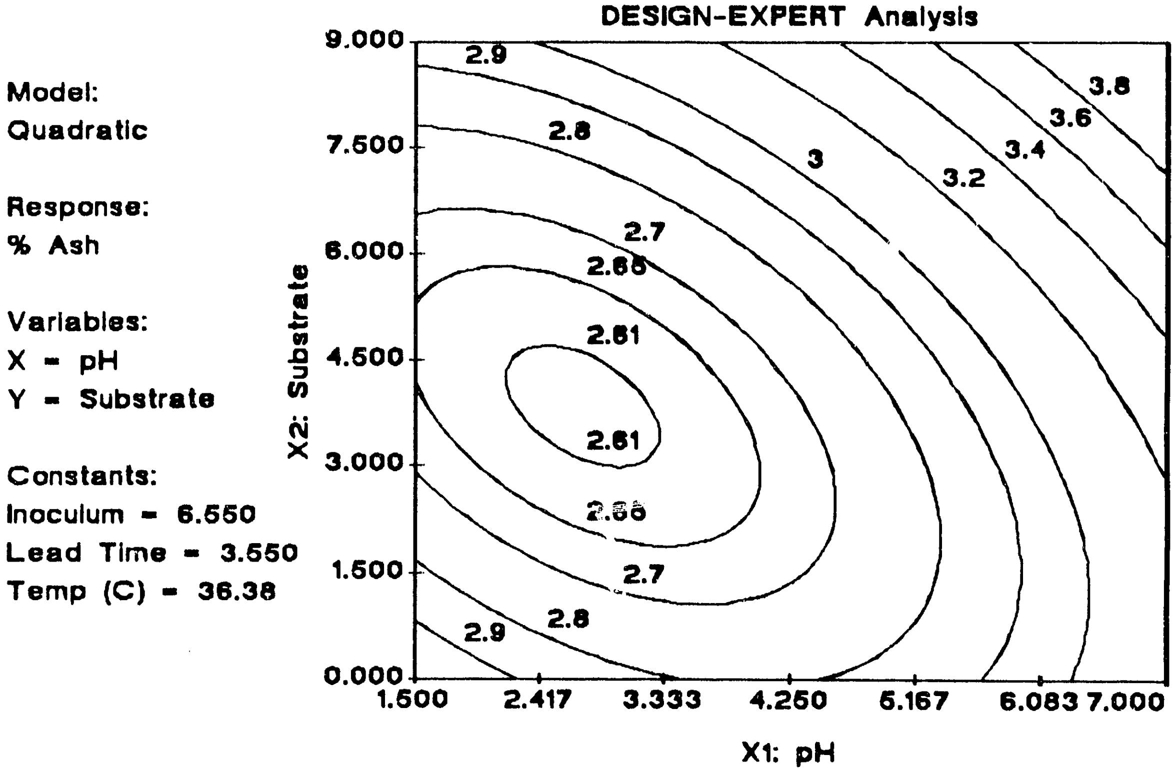

Figure 1. The effect of pH and substrate concentration on the product ash content (% wt) for the Middle Wyodak coal.

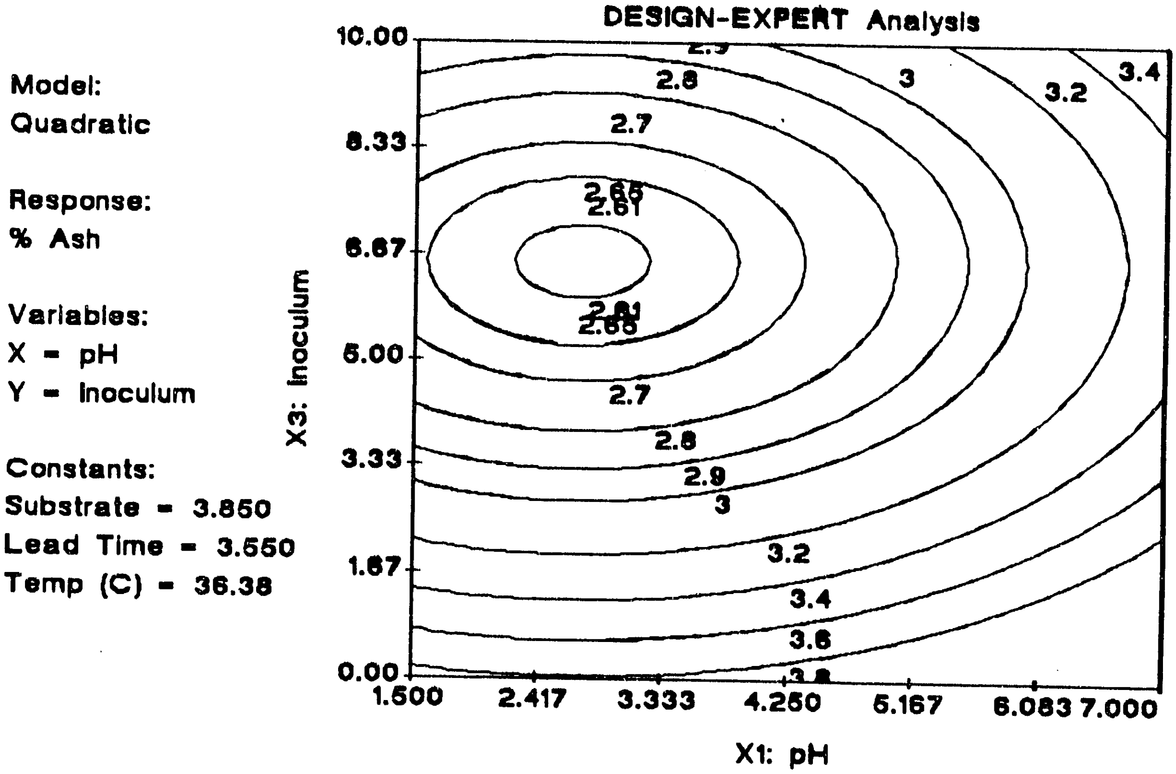

Figure 2. The effect of pH and inoculum concentration on the product ash content (% wt) for the Middle Wyodak coal.

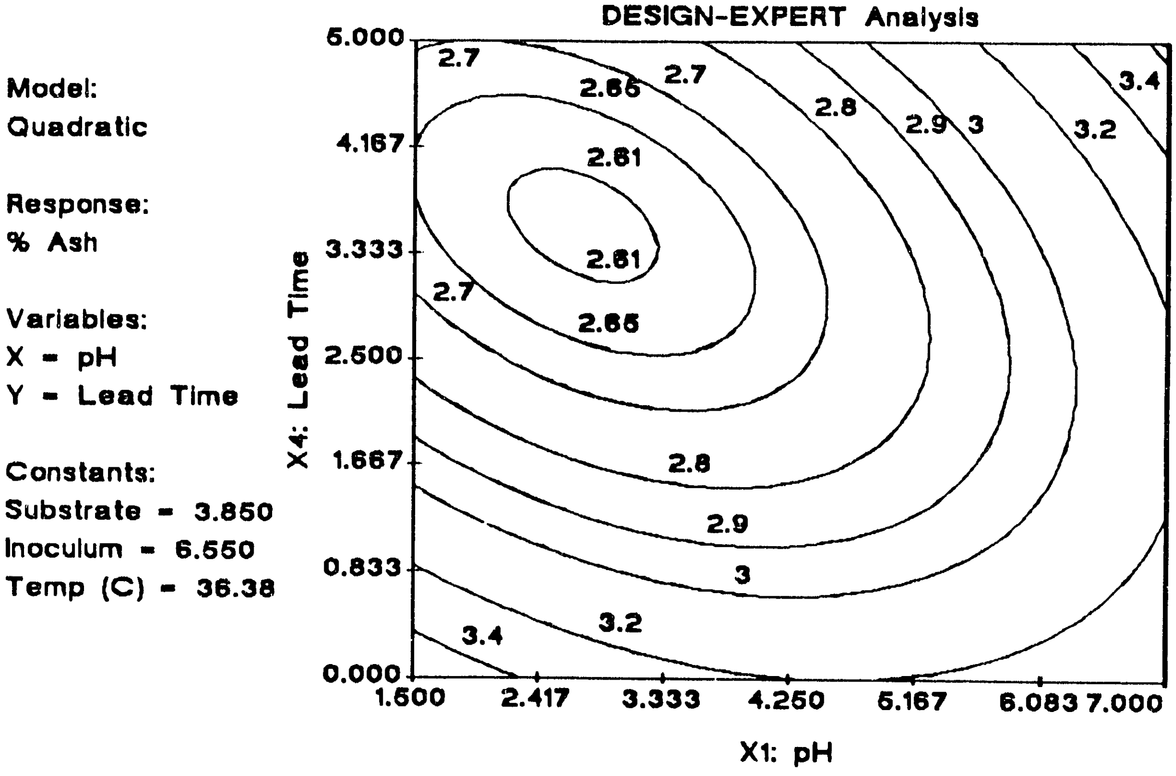

Figure 3. The effect of pH and lead time on the product ash content (% wt) for the Middle Wyodak coal.

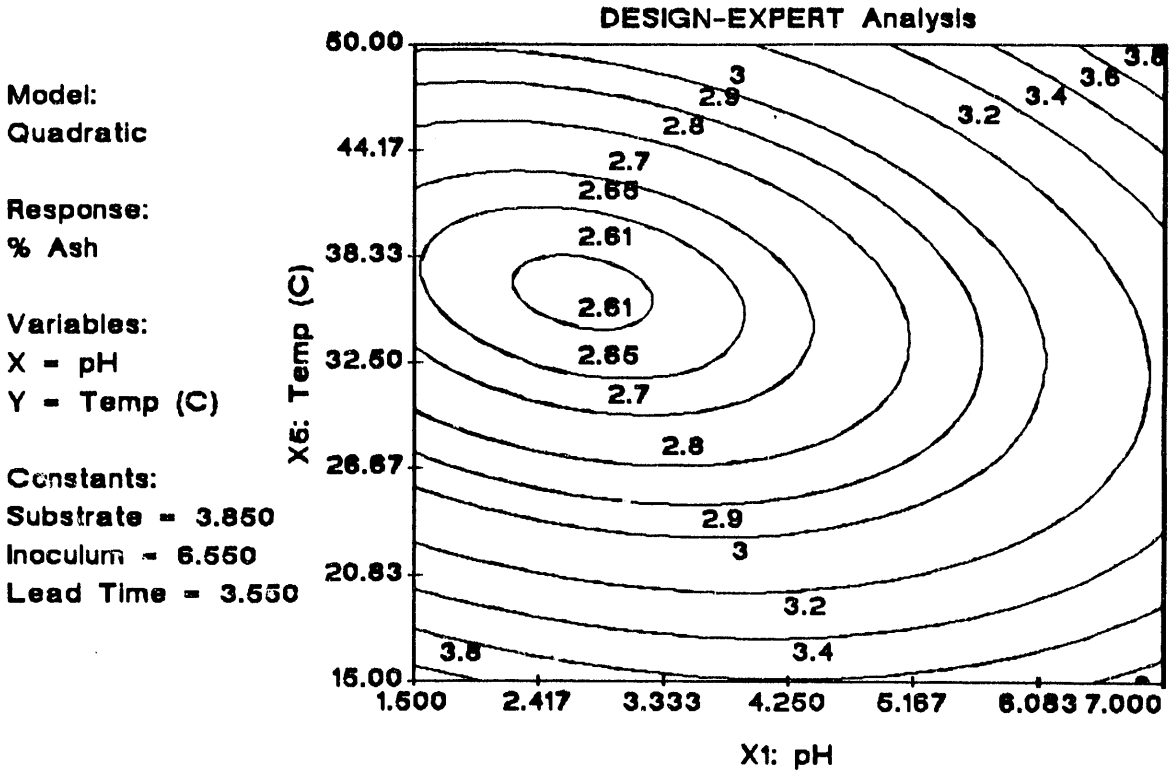

Figure 4. The effect of pH and temperature on the product ash content (% wt) for the Middle Wyodak coal.

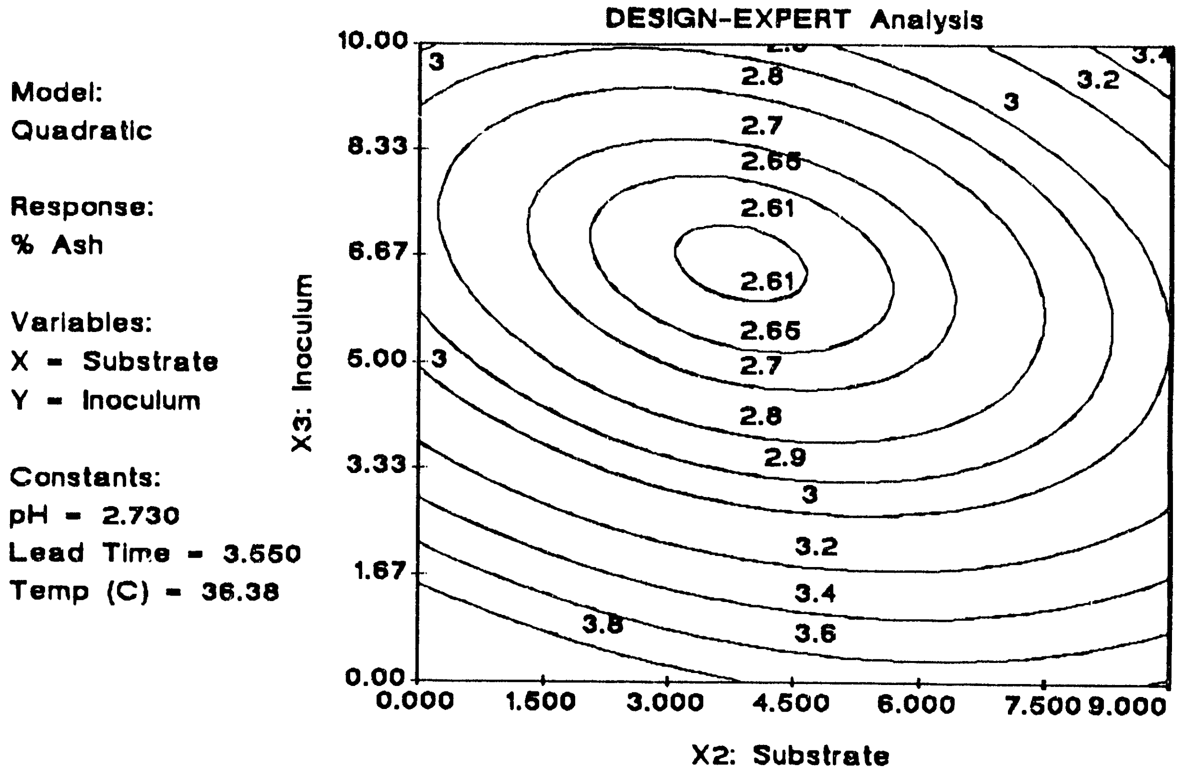

Figure 5. The effect of substrate and inoculum concentration on the product ash content (% wt) for the Middle Wyodak coal.

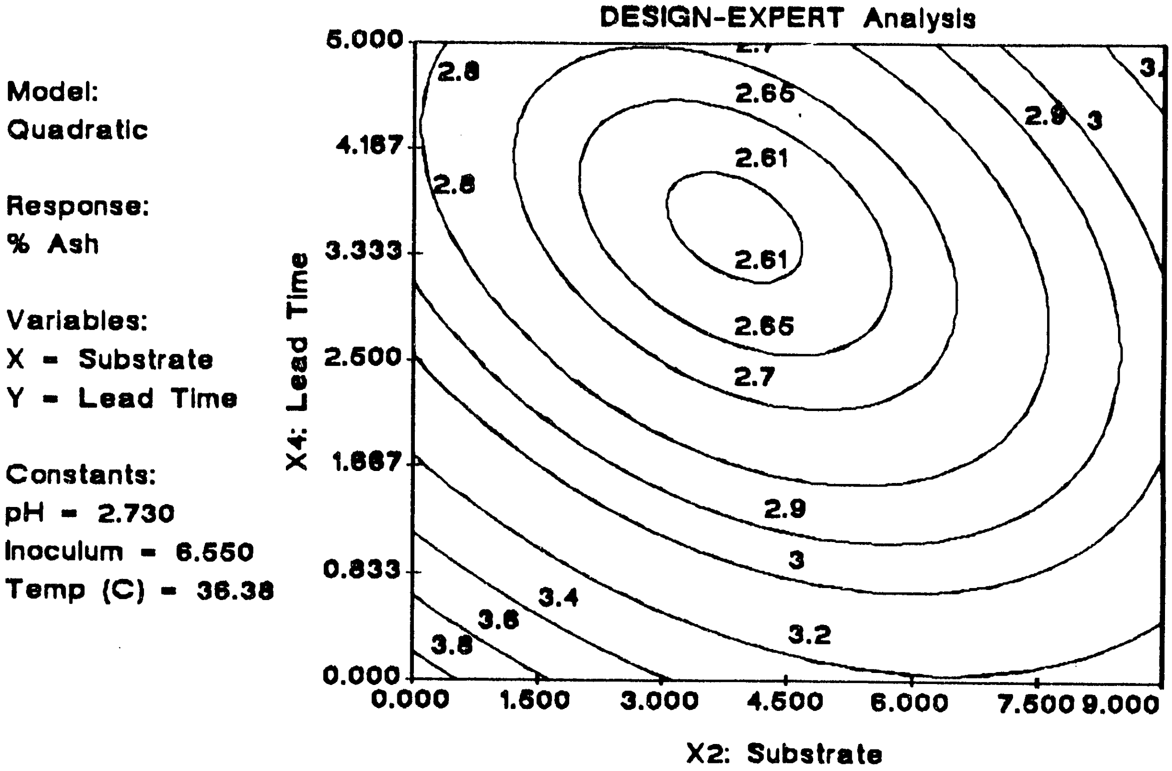

Figure 6. The effect of substrate concentration and lead time on the product ash content (% wt) for the Middle Wyodak coal.

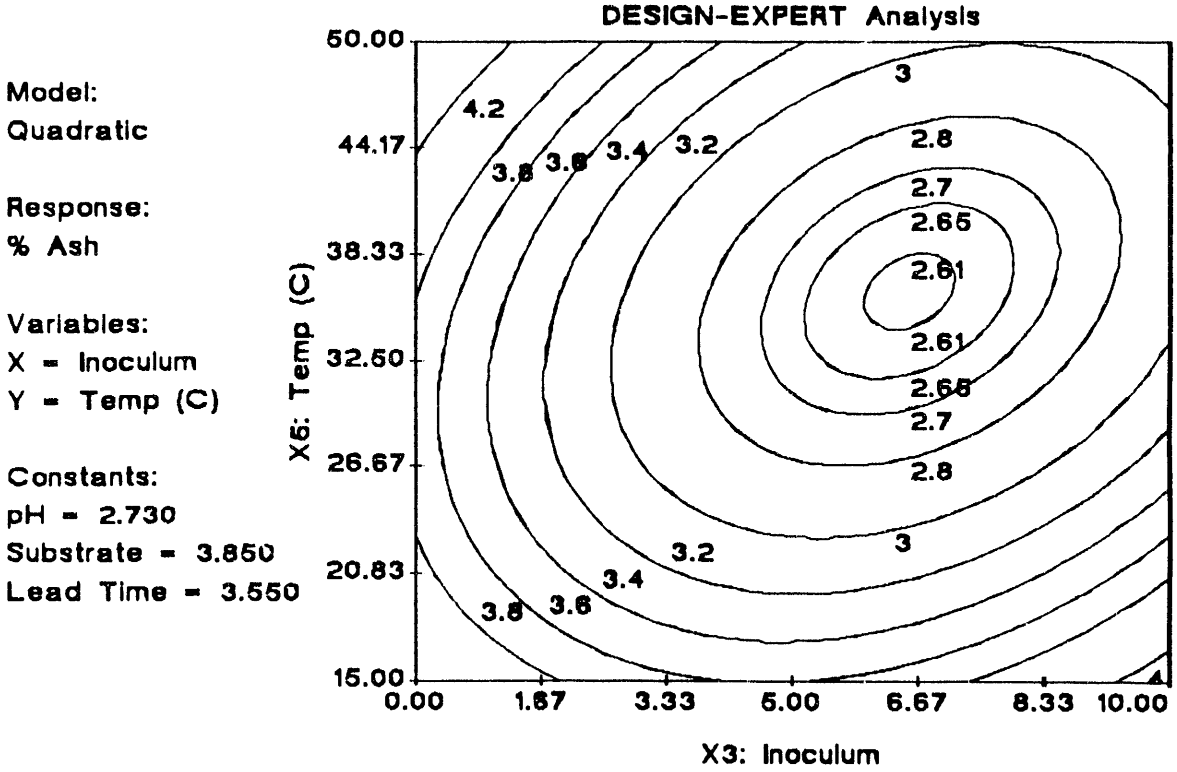

Figure 9. The effect of inoculum concentration and temperature on the product ash content (% wt) for the Middle Wyodak coal.

APPENDIX 5: Response Surface Plots for the Effects of Different Parameters on the Product Ash Content (% wt) for the Pittsburgh No. 8 Coal.

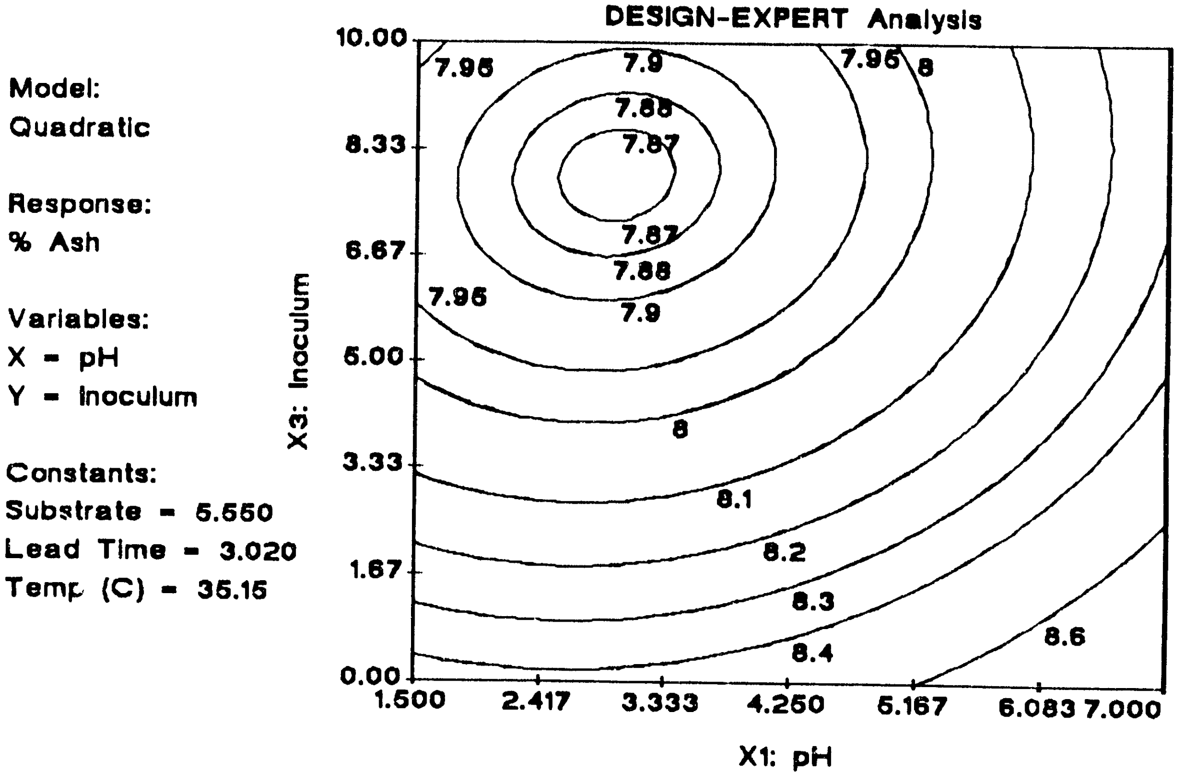

Figure 1. The effect of pH and inoculum concentration on the product ash content (% wt) for the Pittsburgh No. 8 coal.

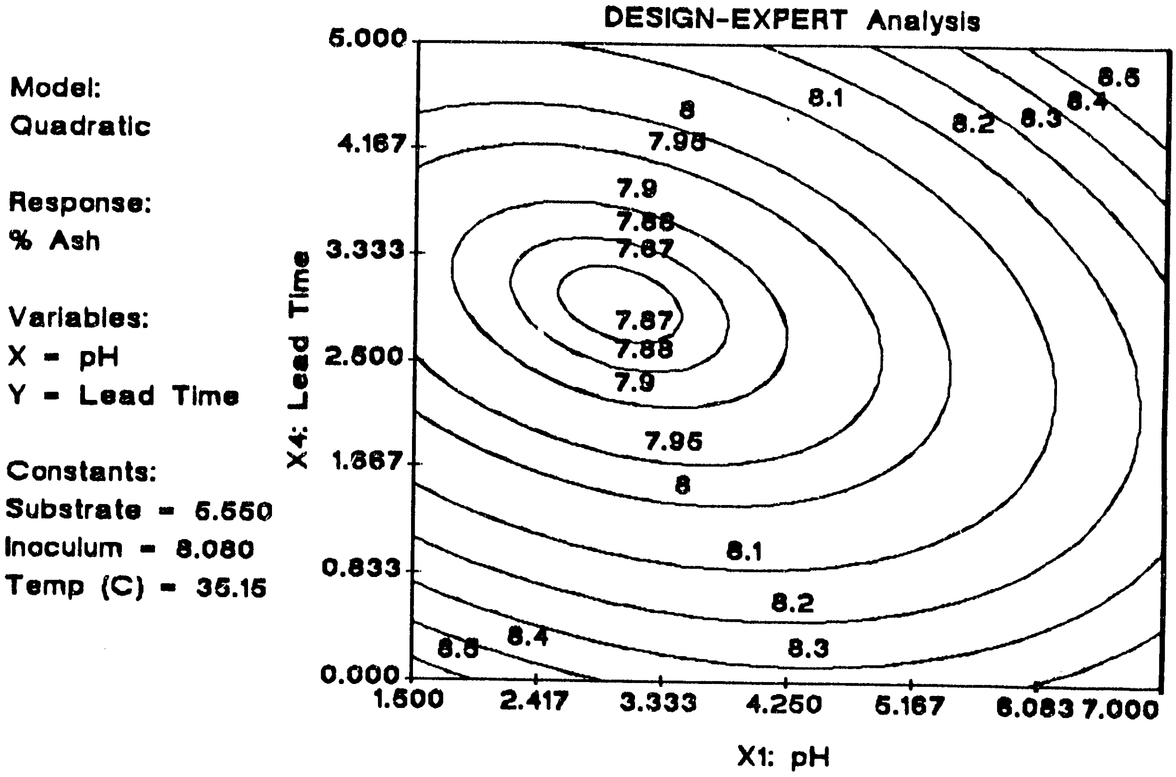

Figure 2. The effect of pH and lead time on the product ash content (% wt) for the Pittsburgh No. 8 coal.

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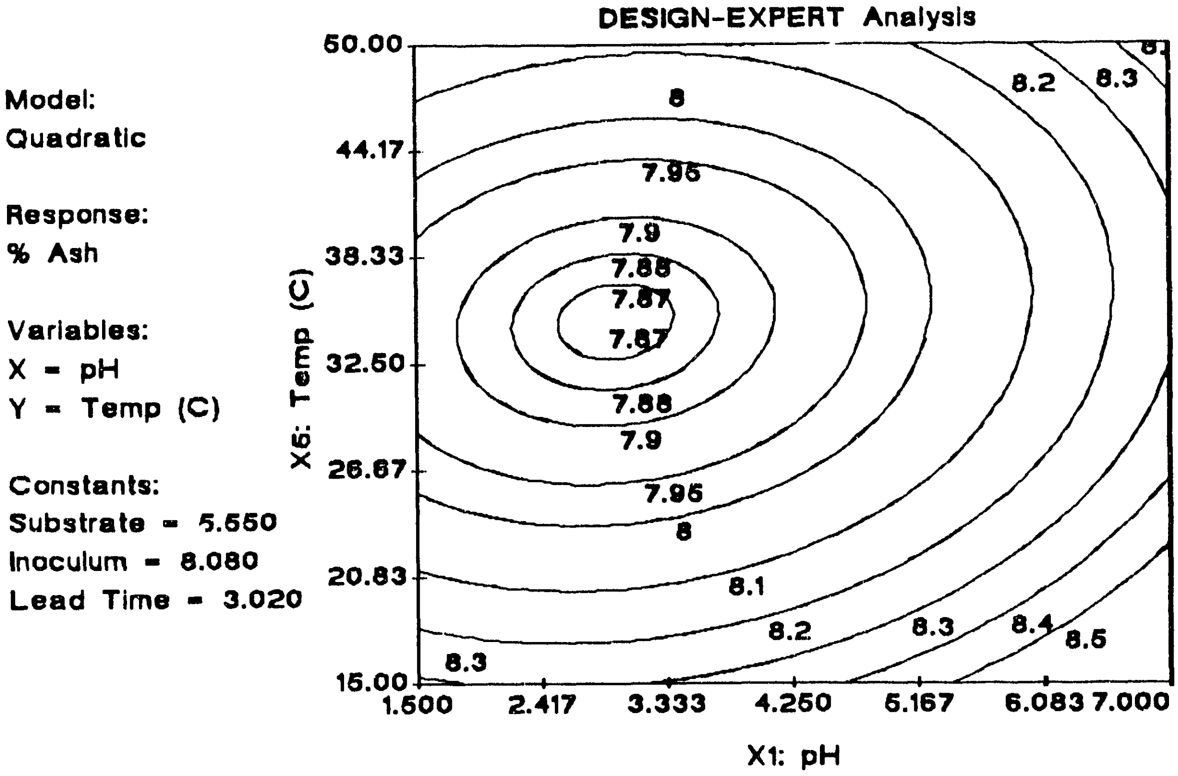

Figure 3. The effect of pH and temperature on the product ash content (% wt) for the Pittsburgh No. 8 coal.

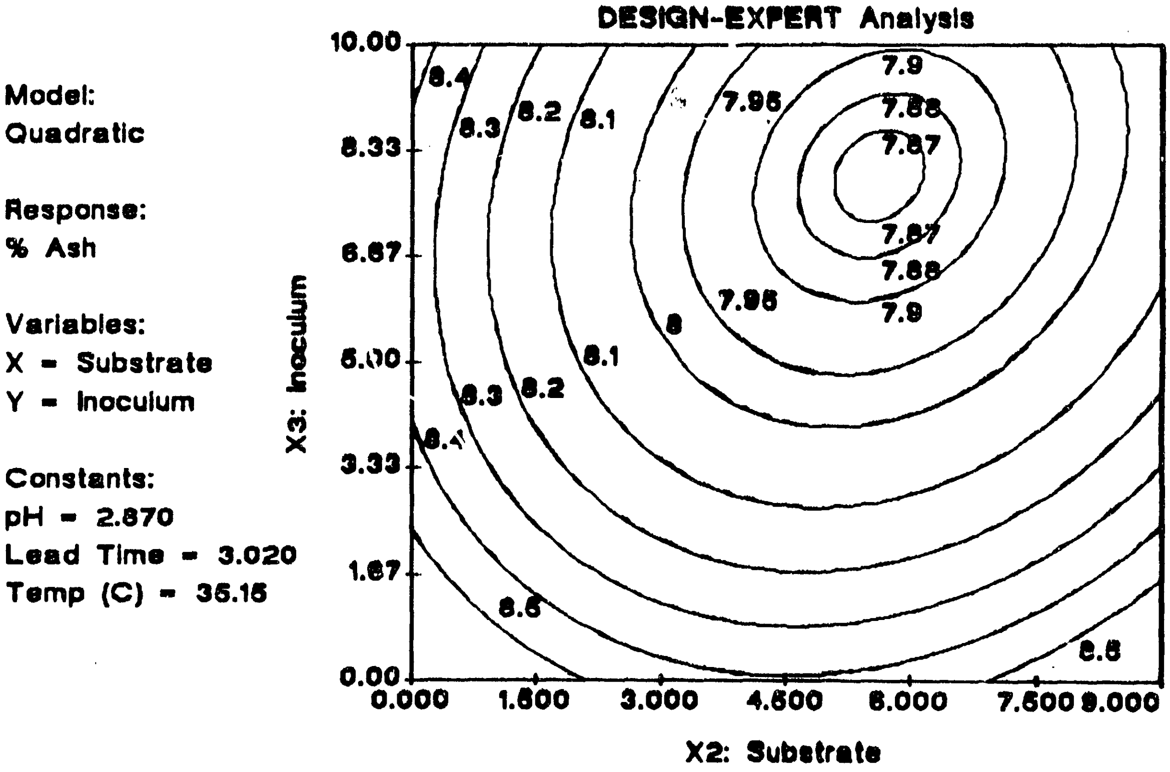

Figure 4. The effect of substrate and inoculum concentration on the product ash content (% wt) for the Pittsburgh No. 8 coal.

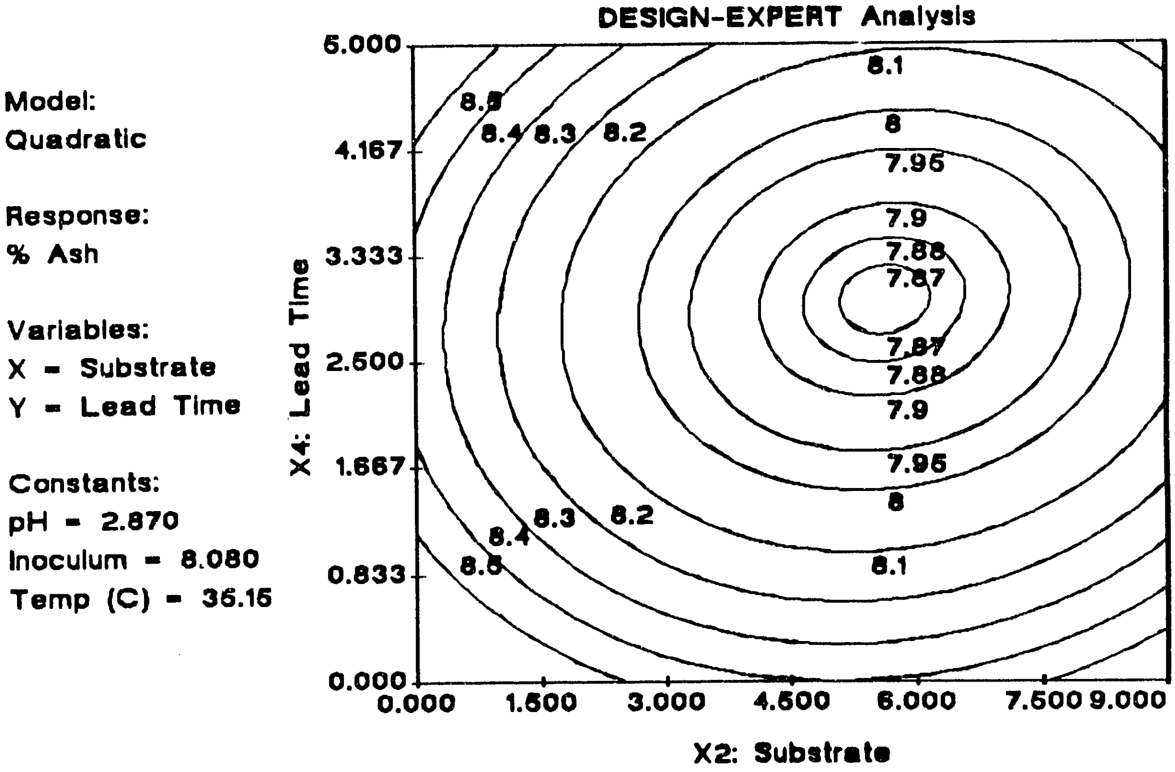

Figure 5. The effect of substrate concentration and lead time on the product ash content (% wt) for the Pittsburgh No. 8 coal.

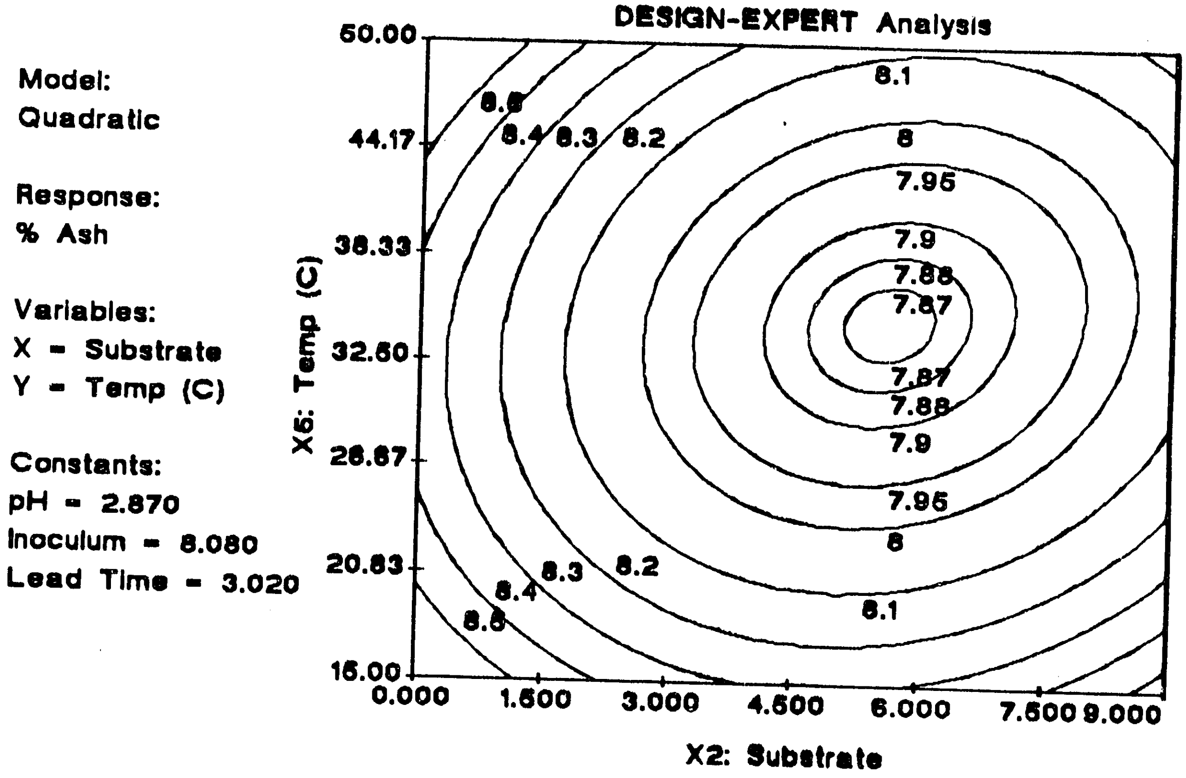

Figure 6. The effect of substrate concentration and temperature on the product ash content (% wt) for the Pittsburgh No. 8 coal.

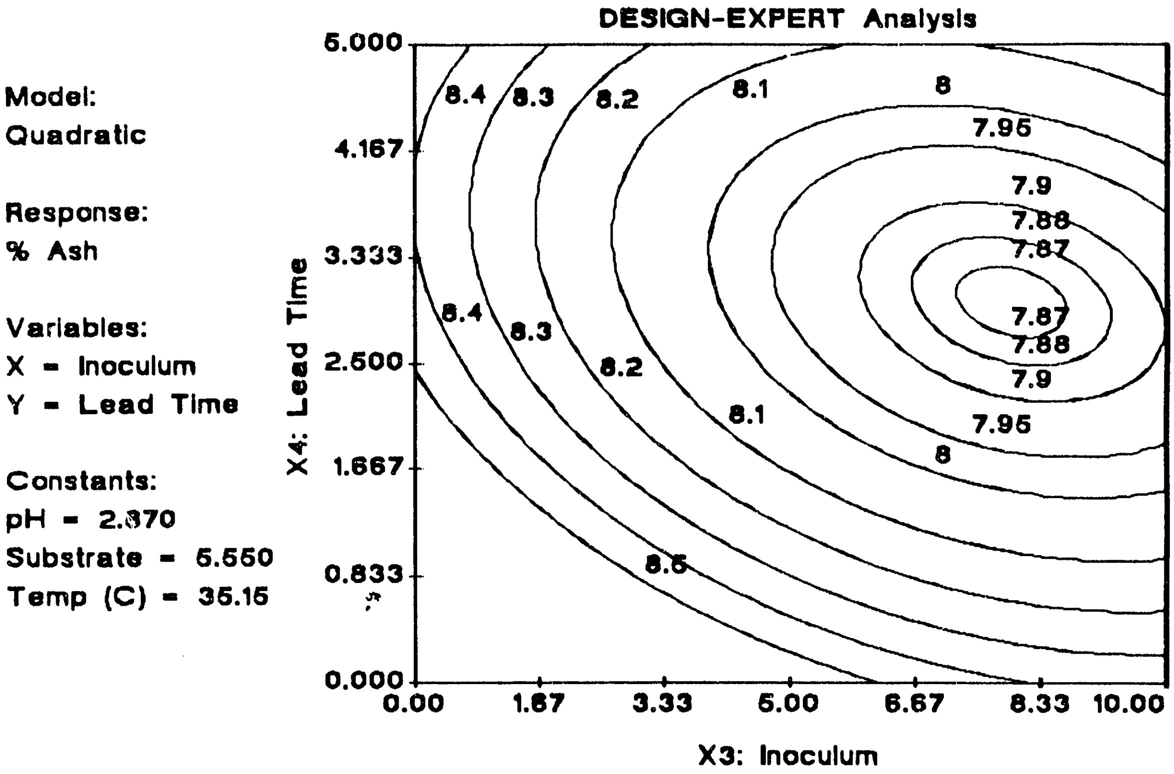

Figure 7. The effect of inoculum concentration and lead time on the product ash content (% wt) for the Pittsburgh No. 8 coal.

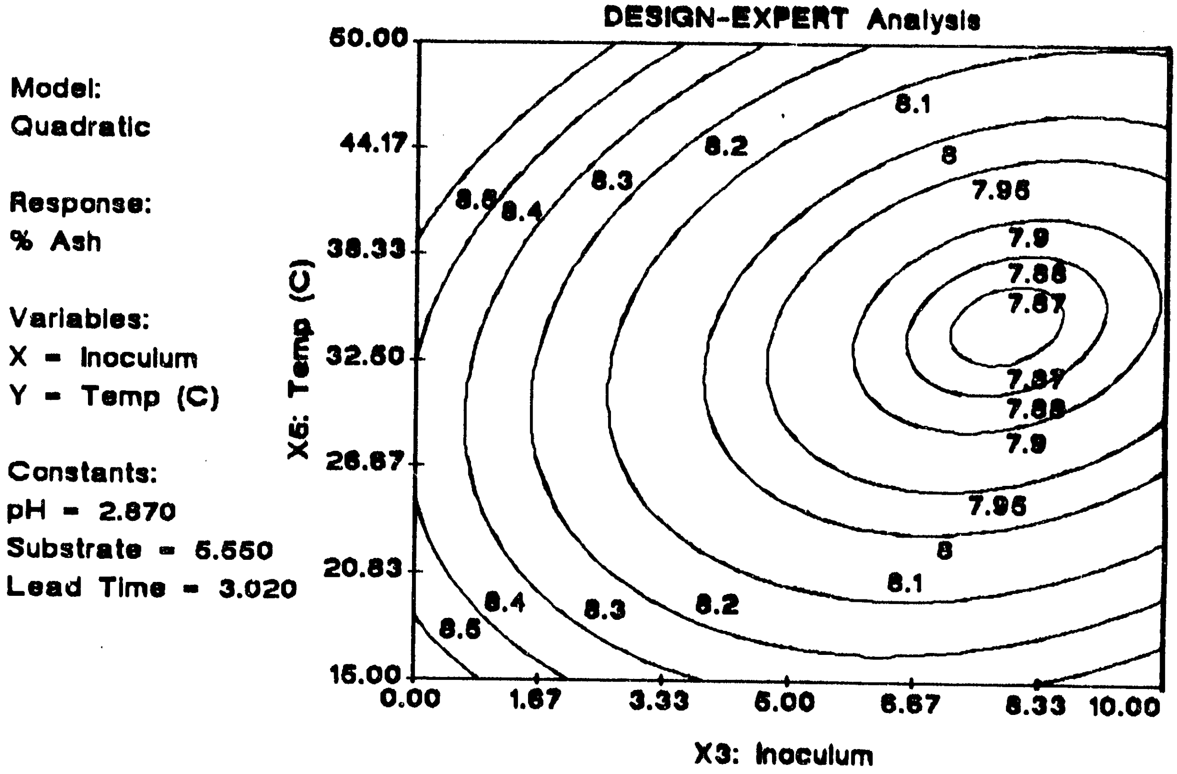

Figure 8. The effect of inoculum concentration and temperature on the product ash content (% wt) for the Pittsburgh No. 8 coal.

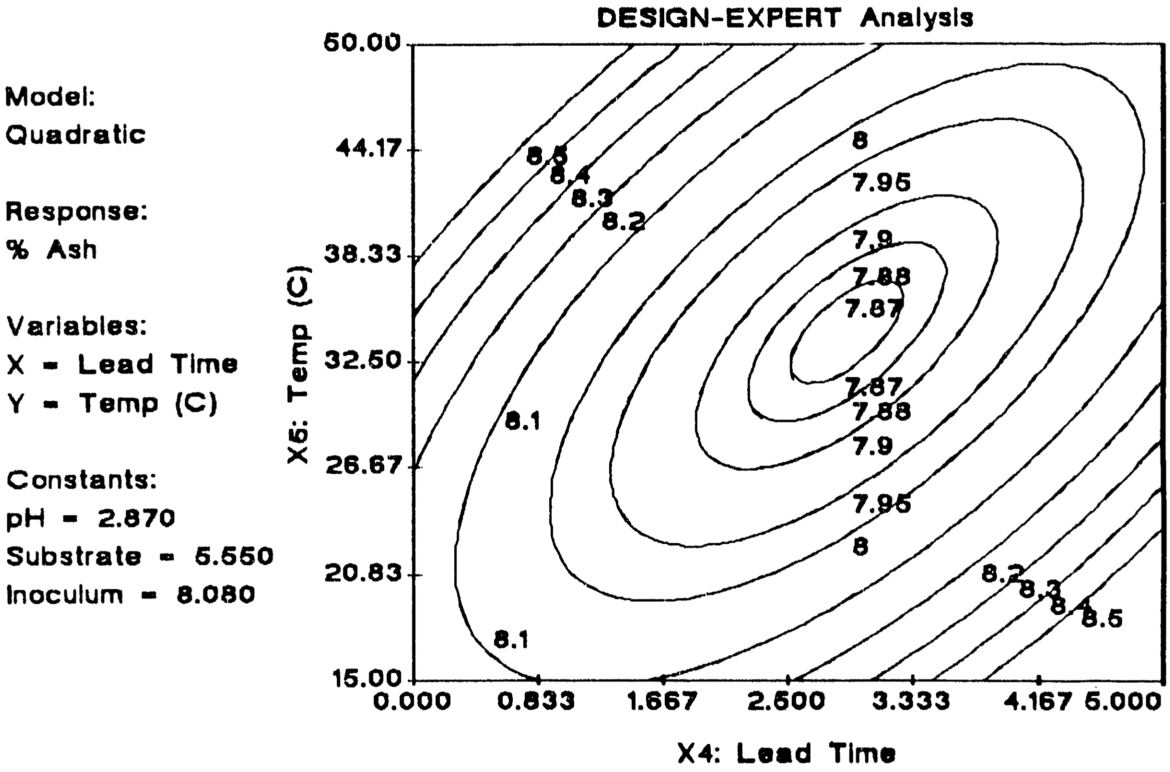

Figure 9. The effect of lead time and temperature on the product ash content (% wt) for the Pittsburgh No. 8 coal.

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