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ADVANCED PROCESSES FOR PREMIUM LOW-RANK COAL/WATER FUEL PRODUCTION

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by

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ADVANCED PROCESSES FOR PREMIUM LOW-RANK COAL/WATER FUEL PRODUCTION

ABSTRACT

Four additional coals were identified as good candidates for low-rank coal/water fuel production: Beulah lignite from North Dakota, Jacobs Ranch subbituminous coal from Wyoming, Spring Creek subbituminous coal from Montana, and Usibelli subbituminous coal from Alaska. All the coals have sufficient reserve base, meet climate requirements, and show excellent amenability to initial cleaning studies.

Pilot-scale fuel preparation capabilities were developed to prepare sizable quantities of low-ash coal/water fuel from low-rank coals for advanced combustion applications. This was accomplished using a preparation scheme which included physical and chemical cleaning, hot-water drying, size optimization and, in some cases, the use of additives. Low-rank coal/water fuels were prepared with less than 1.5 wt% ash and energy densities over 8000 Btu/lb, depending on the particle size distribution desired. Bench- and pilot-scale research supported the development of the production scheme. Rheological characterization of the CWF was performed with respect to particle size distribution, additives, and temperature.

The effectiveness of process water treatment for the hot-water drying step was investigated. A single-stage activated sludge system was effective in treating process water effluent.

1.0 INTRODUCTION

This year's research focused on exploring methods to prepare low-ash, low-sulfur, coal/water fuels (CWFs) from low-rank coals (LRCs). The specific goals were to: 1) extend the hot-water drying (HWD) data base established in 1986-1987 to the production of premium-quality low-rank coal/water fuels suitable for use in light industrial, commercial, and residential heating systems; 2) investigate cleaning performance and techniques on candidate LRCs for clean CWF production; and 3) conduct rheological flow behavior studies on the hot-water-dried low-rank coals.

2.0 GOALS AND OBJECTIVES

Recent studies focused on methods of reducing the inorganic content of LRC water fuels, improving handling and flow characteristics of these fuels, and characterizing and testing wastewater treatment processes in order to maximize its reuse. The University of North Dakota Energy and Mineral Research Center (UNDEMRC) has demonstrated that high-energy-content slurry fuels can be produced from lignite and subbituminous coal by using the HWD process. However, several key issues related to maximizing solids contents, maximizing process water reuse, and improving slurry rheology were identified for further study (1).

The specific objectives of the 1987-1988 UNDEMRC Advanced Processes for Coal/Water Fuel Production project were to: 1) select four coals to extend the data base on HWD coals established in 1986-1987; 2) determine the amenability of the selected coals to physical and chemical cleaning methods and slurry fuel preparation; 3) produce a fuel with less than 1% wt ash; 4) determine the flow behavior of various coal/water slurries at conditions above ambient temperature; 5) determine the most suitable particle size distribution for a low-rank feed coal before hydrothermal treatment and identify appropriate chemical additives for stabilizing and enhancing the flow properties of the resulting coal/water fuel; 6) maximize the packing efficiency of CWFs using various blends of coarse and fine HWD particles; 7) initiate pilot-scale physical cleaning; and 8) perform pilot-scale chemical cleaning.

3.0 ACCOMPLISHMENTS

3.1 Coal Selection

The coal selection was based on raw coal analysis, washability data, mine location with respect to the number of heating degree days (HDD) greater than 6000, and mine distance from major population centers (2). A heating degree day is defined as the unit that represents one degree of decrease from a given point in the mean daily outdoor temperature, such as a mean daily temperature of less than 65°F. The target fuel properties are listed in Table 1.

TABLE 1

TARGET FUEL SPECIFICATIONS

Cost (FOB):	<\$5.00/MMBtu
Ash Content:	<1.00 lb/MMBtu
Sulfur Content:	<0.5 lb/MMBtu
Heating Value:	>0.06 MMBtu/gal (6,500 Btu/lb)
Viscosity:	<700 centipoise (100 sec^{-1} and $28^{\circ}C$)
Stability:	>One year

Flow Properties:
  Behavior - pseudoplastic, Bingham plastic, or slightly dilatant
  Yield Stress - low enough so as not to hinder gravity flow assisted by a 6-foot head

Additional Desirable Qualities:
1. Improved ignition characteristics
2. Depressed freezing point
3. Additives for in situ sulfur capture

Beulah-Zap lignite was selected as the first coal to be tested. It was selected in consultation with the DOE contracting officer and Energy International, who had selected the coal for a DOE-sponsored slurry fuel contract. In addition, preliminary cleaning of Beulah-Zap at UNDEMRC yielded a product with less than 1.0 lb ash/MMBtu, which was a target fuel specification. Beulah-Zap lignite is a Northern Great Plains Province lignite (Beulah-Zap bed, Fort Union Group, Sentinel Butte Formation(Paleocene)), from Mercer County, North Dakota (3). It is used as the feed to the Great Plains Gasification Plant and Antelope Valley Power Station.

The second coal selected was Jacobs Ranch subbituminous coal. This coal was selected in consultation with the Combustion and Environmental Systems Research Institute at UNDEMRC. It was selected because the coal comes from one of the largest mines in the Powder River Basin and the total sulfur content is less than 0.5 lb/MMBtu. Jacobs Ranch subbituminous coal is a Northern Great Plains Province coal (Wyodak bed, Powder River Basin, Tongue River Member(Paleocene)), from Campbell County, Wyoming (3).

Spring Creek subbituminous coal was chosen as the third coal based on the results of both preliminary cleaning, which produced a sample with less than 1.0 lb ash/MMBtu, a sulfur content of less than 0.5 lb/MMBtu, and the HWD process, which produced a highly solids-loaded slurry. Spring Creek subbituminous coal is a Northern Great Plains Province coal (Anderson-Dietz 1&2 bed, Powder River Basin, Tongue River Member(Paleocene)), from Big Horn County, Montana (3).

The fourth coal selected was Usibelli subbituminous coal based on preliminary cleaning results that provided a sample of less than 1.0 lb/MMBtu of ash and a sulfur content of less than 0.5 lb/MMBtu. It is a Nenana Province coal (Nenana Basin (Precambrian and Paleozoic)) from Alaska (3).

All of the samples selected were within the 6000 HDD line and are within a 400-mile radius of cities with populations greater than 25,000 (2).

Samples of Jacobs Ranch subbituminous coal were obtained from the Combustion and Environmental Systems Research Institute at UNDEMRC during May of 1987. Approximately twenty tons of Beulah-Zap lignite were procured in August 1987. In October 1987, one half ton of Spring Creek and Usibelli subbituminous coals were procured. Raw coal analyses for the four study coals are presented in Table 2. Proximate analysis is presented on a moisture-free (mf) basis and ultimate analysis is presented on a moisture-ash-free (maf) basis.

3.2 Coal Sample Preparation

3.2.1 Coal Sizing

Pilot-scale physical coal cleaning equipment has been purchased. The equipment is a Wemco dense-media cone separator and will be used to clean -1/2" (12.5 mm) x 10 mesh (2.0 mm) or -1/4" (6.35 mm) x 10 mesh coal. To be consistent between bench- and pilot-scale efforts, a continuation of static float-sink studies was performed on -1/4" x 10 mesh samples, as well as centrifugal separation on fine coal (combustion grind = 80% <200 mesh (75 micron) and micronized = 100% <325 mesh (45 micron)). The 2" (50 mm) x 0 samples were crushed to -1/4" x 0 and then classified to -1/4" x 10 mesh.

TABLE 2

PROXIMATE, ULTIMATE, AND HEATING VALUE ANALYSES FOR BEULAH-ZAP LIGNITE, AND SPRING CREEK, JACOBS RANCH, AND USIBELLI SUBBITUMINOUS COALS

Coal Sample:	Beulah-Zap	Spring Creek	Jacobs Ranch	Usibelli
Moisture, wt%	34.3	23.4	24.4	27.8
Equilibrium Moisture, wt%	28.1	23.5	29.3	24.6
Proximate Analysis, mf wt%:				
Volatile Matter	41.9	40.9	43.1	46.3
Fixed Carbon	48.7	54.9	48.7	44.7
Ash	9.4	4.2	8.2	9.0
Ultimate Analysis, maf wt%:				
Carbon	70.2	74.6	73.6	69.1
Hydrogen	4.9	5.5	5.6	5.3
Nitrogen	0.8	1.0	1.0	0.8
Sulfur	1.5	0.4	0.4	0.1
Oxygen (by diff)	22.5	18.5	19.4	24.7
Heating Value, mf Btu/lb	10,840	12,380	11,630	10,780

3.2.2 Sieve Analysis

Samples of -1/4" x 0 size coals to be studied were air-dried prior to sieve analysis which was performed to fractionate the samples. Figure 1 shows the coal size distribution for Jacobs Ranch subbituminous coal. It shows that a majority of the sample was contained in the -1/4" x 10 mesh range.

3.2.3 Ash Analysis

Ash content as a function of mesh size for the study coals is presented in Figure 2. In general, the ash content of the samples increased as the particle size decreased. This indicates that crushing liberates the ash-forming components and concentrates the ash in the fines.

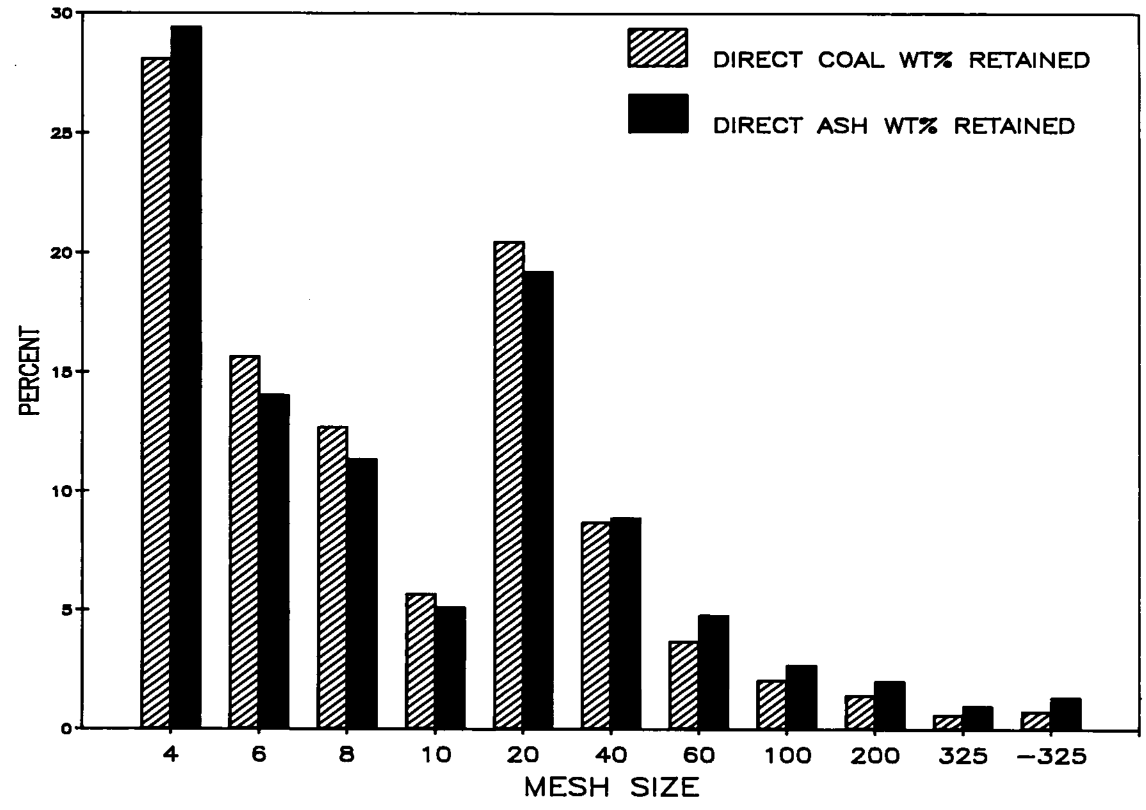

Figure 1. Sieve analysis data on 1/4" x 0 Jacobs Ranch subbituminous coal

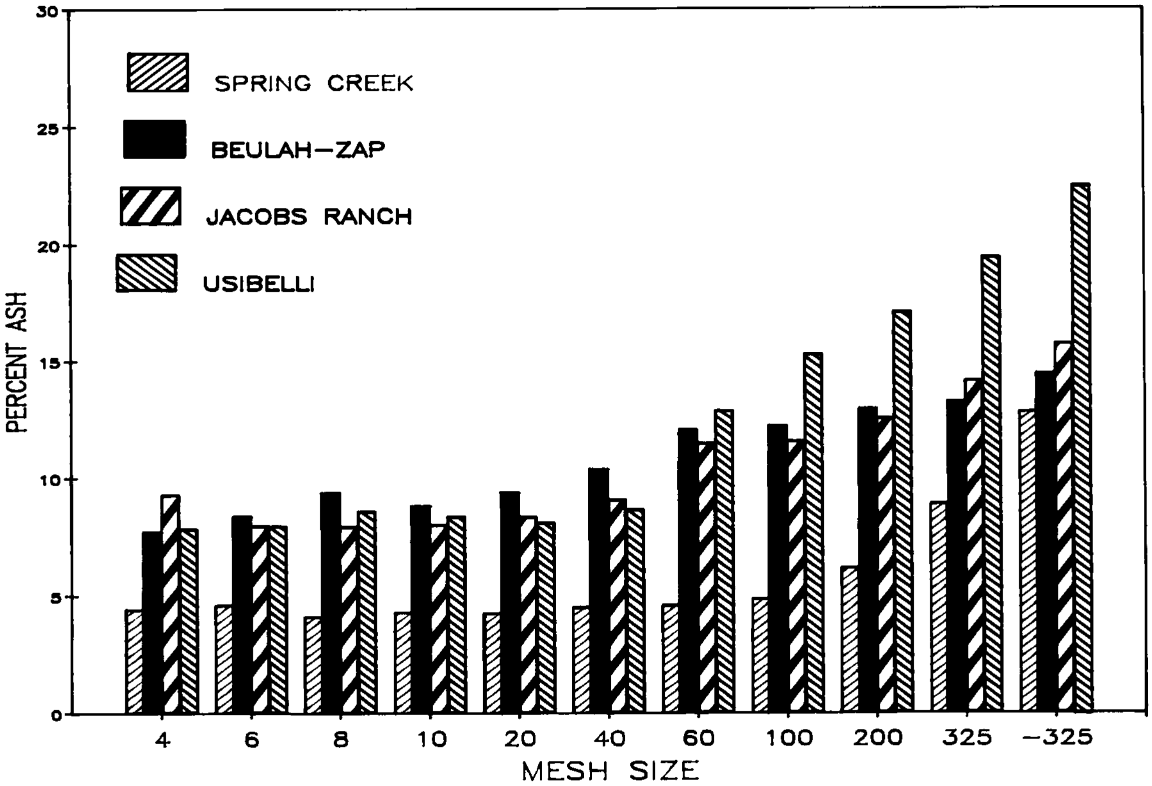

Figure 2. Mesh size vs. percent ash for 1/4" x 0 study coal samples

3.3 Physical Coal Cleaning

3.3.1 Float-Sink Analysis

3.3.1.1 Background

Float-sink testing is the standard test for determining the washability characteristics of coals. The various specific-gravity components obtained from the float-sink test represent theoretical limits attainable by gravity separation. This method can be performed either statically or centrifugally. Static separation (4) has historically been most often used for coarse-coal size fractions (3/8" (9.5 mm) - 10 mesh), although it could be used for finer-coal size fractions (as low as 100 mesh). A centrifugal separation method (5) is primarily used for fine-coal size fractions (-10 mesh).

3.3.1.2 Experimental Methods

Both static and centrifugal float-sink methods were performed using 1.3, 1.4, 1.5, and 1.6 specific gravity Certigrav solutions. Static float-sink testing involved adding 100-150 grams of coarse coal (1/4" x 10 mesh) to a float-sink flask containing 1600 milliliters of Certigrav solution. The test was completed when the coal separated into two distinct fractions. Centrifugal separation was accomplished by combining 20-30 grams of fine coal and 350 milliliters of solution into each of four centrifugal beakers and centrifuging for 20 minutes at 1500 rpm. After centrifugation and filtration, the samples were separated into float and sink fractions.

3.3.1.3 Results

Float-sink tests using Certigrav solution were completed on samples of Beulah-Zap lignite and Spring Creek, Jacobs Ranch, and Usibelli subbituminous coals. The 1/4" x 10 mesh samples were prepared by crushing the coal to -1/4 inch and then screening out the -10 mesh fraction. The combustion grind samples were prepared by using a pilot-scale pulverizer containing a 200 mesh screen. Micronized samples were made using a jet-mill pulverizer containing a 325 mesh screen. Centrifugal separation was performed only on the combustion grind and micronized samples.

Table 3 summarizes the washability results on Beulah-Zap lignite. The weight recovery for the products was initially greatest at 1.3 sp. gr. for the 1/4" x 10 mesh sample. As the particle size became smaller higher specific gravity was needed to recover 50% of the product. Fifty percent recovery was obtained with the combustion grind sample at the 1.4 sp. gr. level. For the micronized sample, 50% recovery was not obtained until between 1.4 and 1.5 sp. gr.

Table 4 contains the washability results of Spring Creek subbituminous coal. This coal has a raw ash content of approximately 4%. When float-sink analysis was performed, liberation of the ash was at a minimum. The weight recovery of the sample did not fluctuate from one particle size to the next; the main difference in weight recovery occurred at 1.3 sp. gr. for the 1/4" x 10 mesh sample. This coal did not benefit significantly from grinding to smaller particle sizes.

TABLE 3

CUMULATIVE RESULTS FOR FLOAT-SINK ANALYSIS ON BEULAH-ZAP LIGNITE

Sample	Product	Cumulative Yield (%)	Ash (%)	Ash Reduction (%)
1/4" x 10 mesh	1.30-Float	66.01	6.35	28.00
	1.40-Float	81.78	6.75	23.47
	1.50-Float	93.66	7.27	17.57
	1.60-Float	96.47	7.55	14.40
	Total	100.00	8.82	---
80% <200 mesh	1.30-Float	4.78	4.56	46.60
	1.40-Float	50.06	5.56	34.89
	1.50-Float	90.39	6.28	26.46
	1.60-Float	95.89	6.66	22.01
	Total	100.00	8.54	---
100% <325 mesh	1.30-Float	0	0	0
	1.40-Float	41.96	4.92	41.29
	1.50-Float	91.37	5.90	29.59
	1.60-Float	96.06	6.10	27.21
	Total	100.00	8.38	---

TABLE 4

CUMULATIVE RESULTS FOR FLOAT-SINK ANALYSIS ON SPRING CREEK SUBBITUMINOUS COAL

Sample	Product	Cumulative Yield (%)	Ash (%)	Ash Reduction (%)
1/4" x 10 mesh	1.30-Float	55.24	3.5	12.94
	1.40-Float	98.89	3.76	6.47
	1.50-Float	100.00	4.02	---
	1.60-Float	100.00	4.02	---
	Total	100.00	4.02	---
80% <200 mesh	1.30-Float	8.84	3.44	16.82
	1.40-Float	68.73	3.27	20.83
	1.50-Float	98.28	3.46	16.28
	1.60-Float	100.00	4.14	---
	Total	100.00	4.14	---
100% <325 mesh	1.30-Float	0	0	0
	1.40-Float	87.36	3.50	18.42
	1.50-Float	98.47	3.60	16.16
	1.60-Float	100.00	4.29	---
	Total	100.00	4.29	---

The results of washability of Jacobs Ranch subbituminous coal are summarized in Table 5. This sample exhibited float-sink characteristics similar to those of 1/4" x 10 mesh Beulah-Zap. Although the Jacobs Ranch sample achieved greater than fifty percent weight recovery at 1.3 sp. gr., it did not show the ash liberation that appears for Beulah-Zap. The smaller particle size float-sink results showed a contrast in results. The combustion grind Jacobs Ranch sample appeared to benefit from the float-sink treatment more than the micronized sample, indicating no benefit due to smaller particle sizing.

TABLE 5

CUMULATIVE RESULTS FOR FLOAT-SINK ANALYSIS
ON JACOBS RANCH SUBBITUMINOUS COAL

Sample	Product	Cumulative Yield (%)	Ash (%)	Ash Reduction (%)
1/4" x 10 mesh	1.30-Float	52.69	5.8	21.62
	1.40-Float	95.55	6.24	15.68
	1.50-Float	97.69	6.49	12.30
	1.60-Float	98.45	6.67	9.86
	Total	100.00	7.40	---
80% <200 mesh	1.30-Float	3.24	4.97	38.94
	1.40-Float	35.77	4.96	39.07
	1.50-Float	93.53	5.79	28.87
	1.60-Float	96.43	6.01	26.17
	Total	100.00	8.14	---
100% <325 mesh	1.30-Float	0	0	0
	1.40-Float	72.69	5.20	26.24
	1.50-Float	94.66	5.26	25.39
	1.60-Float	100.00	7.05	---
	Total	100.00	7.05	---

Table 6 summarizes the float-sink results for Usibelli subbituminous coal. This coal required a higher specific gravity in order to obtain 50 wt% recovery for the 1/4" x 10 mesh sample. It appeared to have the same characteristics as Beulah-Zap. The finer particle sizes showed a greater ash liberation than the 1/4" x 10 mesh sample.

Table 7 contains washability results that were performed on 1/4" x 10 mesh samples of Kemmerer subbituminous coal and Velva lignite, which were studied at smaller particle sizes in previous work (6). Kemmerer showed no benefit in physical cleaning at this size. However, Velva presented more of a distribution in its physical cleaning characteristics.

TABLE 6

CUMULATIVE RESULTS FOR FLOAT-SINK ANALYSIS ON USIBELLI SUBBITUMINOUS COAL

Sample	Product	Cumulative Yield (%)	Ash (%)	Ash Reduction (%)
1/4" x 10 mesh	1.30-Float	10.81	4.45	48.26
	1.40-Float	84.35	5.65	34.30
	1.50-Float	93.98	6.33	26.40
	1.60-Float	96.64	7.03	18.26
	Total	100.00	8.60	---
80% <200 mesh	1.30-Float	0	0	0
	1.40-Float	54.01	5.34	44.78
	1.50-Float	88.78	6.44	33.40
	1.60-Float	93.70	7.17	25.85
	Total	100.00	9.67	---
100% <325 mesh	1.30-Float	0	0	0
	1.40-Float	48.05	4.80	40.00
	1.50-Float	94.36	5.82	27.25
	1.60-Float	96.93	6.13	23.38
	Total	100.00	8.00	---

TABLE 7

CUMULATIVE RESULTS FOR FLOAT-SINK ANALYSIS ON 1/4" X 10 MESH KEMMERER SUBBITUMINOUS COAL AND VELVA LIGNITE

Sample	Product	Cumulative Yield (%)	Ash (%)	Ash Reduction (%)
Kemmerer subbituminous	1.30-Float	41.93	2.41	9.59
	1.40-Float	100.00	2.67	---
	1.50-Float	100.00	2.67	---
	1.60-Float	100.00	2.67	---
	Total	100.00	2.67	---
Velva lignite	1.30-Float	45.53	6.34	34.18
	1.40-Float	74.91	6.78	29.62
	1.50-Float	94.65	7.77	19.37
	1.60-Float	97.67	8.13	15.65
	Total	100.00	9.63	---

Utilization of 1/4" x 10 mesh fraction data will assist in implementation of recently purchased, pilot-scale, coarse-coal cleaning equipment. The data showed that Beulah-Zap, Jacobs Ranch, Usibelli, and Velva had a distinct separation at different specific gravity levels. Low ash contents of Spring Creek and Kemmerer created less separation between the denser and lighter fractions, making float-sink separation less beneficial.

3.3.2 Froth Flotation

3.3.2.1 Background

Although the role and effectiveness of flotation reagents is better understood in higher-rank coals, it has not been determined which reagents are most suited for effective flotation of LRCs. Our research has shown that fuel oil (FO) an alkane mixture (CH_{12}-CH_{18} and aromatics) has beneficiating properties when used in froth flotation (6), but its effectiveness is highly coal specific. To complete froth flotation on LRCs, a collecting agent must be added to the coal/water mixture to coat specific water-repellent minerals through adsorption on the mineral surface. As reported for higher-rank coals, the collecting agent coats the coal particles, making them even more hydrophobic and floatable (7). In addition to the collector, a frothing agent must be added to the solution. MIBC (methyl isobutyl carbinol) is often successfully used as a frothing agent with higher-rank coals. The frother stabilizes the bubble attachment to the hydrophobic particles. One reason froth flotation was attempted with low-rank coals was to determine the effect of various frothers and collectors on the cleaning efficiency. Shur-Coal 164A(SC164A) from the Sherex Chemical Co. was found to improve the cleaning capabilities more than MIBC. The poor performance of MIBC can be attributed to the fact that LRC surfaces are more hydrophilic than bituminous coal surfaces.

In addition to testing with SC164A, testing was performed on one sample of coal using a different additive. In an effort to find a better froth flotation collector for LRCs, or one in which the collecting properties of fuel oil would be enhanced, a brief literature search was performed. An alkane with a similar or shorter methylene (CH_2) chain and containing a quaternary ammonium group was used in addition to fuel oil. It was reasoned that the methylene chains would have collecting properties similar to those of fuel oil, and the ammonium groups would ionically bond to carboxyl groups on coal surfaces. Adogen (methyltrialkyl(C_8-C_{10})-ammonium chloride) was selected for testing.

3.3.2.2 FO:SC164A Experimental Methods

The two components, fuel oil and Shur-Coal 164A, were mixed in a ratio of four parts of fuel oil to one part of the frother-promoter on recommendation of the Sherex Chemical Co. This solution was then added in varied dosages to a mixture of 8 wt% coal and water. Froth flotation testing was completed on combustion grind and micronized coals using a Denver froth flotation cell. The test matrix included Beulah-Zap lignite and Spring Creek, Jacobs Ranch, and Usibelli subbituminous coals. Dosages used were 4, 6, 8, 16 lbs of fuel oil: SC164A/ton of coal.

3.3.2.3 FO:SC164A Results

For comparative purposes, Table 8 provides froth flotation results of the coals between combustion grind and micronized.

TABLE 8

FROTH FLOTATION RESULTS FOR COMBUSTION GRIND AND MICRONIZED SAMPLES USING FO:SC164A

Coal Sample	Combustion Grind Results		Micronized Results	
Dosage, lbs/ton	Yield, (wt%)	Ash Reduction, (wt%)	Yield, (wt%)	Ash Reduction, (wt%)
Beulah-Zap:				
4	38.4	10.9	39.5	12.6
6	44.2	14.4	60.6	10.9
8	60.8	17.2	74.4	9.1
16	70.1	18.8	80.4	10.1
Spring Creek:				
4	55.6	23.3	46.5	19.4
6	67.1	21.3	76.3	16.2
8	72.8	20.8	83.3	12.8
16	90.5	11.5	89.0	10.1
Jacobs Ranch:				
4	47.9	21.4	75.4	5.0
6	77.9	19.2	77.0	2.5
8	78.9	20.7	71.9	2.5
16	82.3	18.1	82.4	6.3
Usibelli:				
4	76.0	21.5	66.8	10.5
6	76.3	21.5	85.3	7.1
8	82.3	18.6	87.1	7.2
16	83.1	12.0	86.3	3.3

Combustion grind Beulah-Zap lignite showed positive relationships between yield, dosage, and ash reduction. The relationship between dosage and ash reduction was not expected because when the dosage was increased, the percent recoveries of the sample increased, thus the amount of ash should also have increased in the product fractions. However, the results indicate a decrease in ash content in the product as the dosage of collector/frother increased. Further analysis must be done before any distinct conclusions can be set for the Beulah-Zap sample. These results do indicate a more efficient removal of the ash than expected. When micronized samples were subjected to froth flotation, the yield was similar but the ash removal was not as effective. This shows that the finer the coal was pulverized, the less effective the flotation. This occurred because of the collection of the finer ash-containing particles in the froth.

Froth flotation of Spring Creek exhibited no significant difference between the combustion grind and micronized samples. This would suggest that the ash was too finely distributed throughout the coal structure, resulting in no ash liberation in the micronizing process.

Jacobs Ranch showed cleaning characteristics for the combustion grind material that were similar to those obtained for the Spring Creek sample. Froth flotation of the micronized sample also showed similar yield recoveries, but there was a difference in the ash reduction. Micronized Jacobs Ranch had a much lower ash reduction than combustion grind, which was another indication that the liberated ash was being collected in the froth rather than the tailings.

Results for Usibelli indicated that percent recoveries were similar for the combustion grind compared to the micronized grind. However, Usibelli had lower ash reduction percentages when using a micronized sample. Therefore, flotation of micronized Usibelli coal was not beneficial to the product coal quality.

An overall summary of froth flotation using the fuel oil:Shur-Coal mixture shows that a substantial yield can be obtained, but it does not increase the reduction of ash content significantly. It also shows that, for the majority of coals tested, the best results were obtained with a combustion grind sample in comparison to a micronized sample.

3.3.2.4 Adogen Experimental Methods

A Box-Behnken Design (BBD) was chosen as the statistical design strategy to use for testing adogen in combination with fuel oil and MIBC. The BBD is a part of the general approach used for Response Surface Methodology, i.e., a package of statistical design and analysis tools which generally are used for: 1) design and collection of experimental data which allows fitting of a general quadratic equation for smoothing the data and making predictions, 2) multiple regression analysis of the data to select the best equation to describe the data, and 3) presentation of the results in a graphical form, usually via contour plots.

3.3.2.5 Adogen Results

BBD calls for collection of experimental data at low (-1), mid-range (0), and high (+1) concentrations of each factor. In the selection of concentrations, maintenance of symmetry is important and experiments must be performed in random order. Table 9 lists the selected concentrations used (-1, 0, +1; log linear). Combustion grind Jacobs Ranch was used as the test coal. Froth flotation experiments were performed in the same manner as other froth flotation experiments discussed previously. Table 10 lists the run order, concentrations, yield, and ash reduction.

TABLE 9

REAGENT CONCENTRATIONS (LBS/TON) USED IN THE BOX-BEHNKEN DESIGN FROTH FLOTATION EXPERIMENTS

Concentration Level	MIBC X1	Fuel Oil X2	Adogen X3
(-1) Low	0.1	0.6	0.5
(0) Mid-range	0.4	2.5	1.5
(+1) High	1.6	10.0	4.5

TABLE 10

YIELD AND ASH REDUCTION USING DIFFERENT REAGENT CONCENTRATIONS SELECTED ACCORDING TO BOX-BEHNKEN DESIGN

Randomized Run Order	MIBC X1	Fuel Oil X2	Adogen X3	Yield (wt%)	Ash Reduction (wt%)
2	+1	+1	0	58.32	10.06
12	-1	+1	0	54.71	10.17
7	+1	-1	0	7.33	-7.51
15	-1	-1	0	3.60	-12.83
4	+1	0	+1	39.46	3.03
1	-1	0	+1	30.85	2.42
10	+1	0	-1	21.25	2.18
14	-1	0	-1	2.86	-1.69
8	0	+1	+1	61.17	13.32
3	0	-1	+1	18.94	-11.03
13	0	+1	-1	11.89	7.75
6	0	-1	-1	3.33	-9.81
5	0	0	0	10.24	1.33
11	0	0	0	25.87	1.45
9	0	0	0	21.96	-1.21

The experiments were analyzed via multiple regression to determine an equation for the prediction of ash reduction at varying concentrations of MIBC, fuel oil, and adogen. Graphs showing the relationship between ash reduction and varying concentrations of fuel oil, MIBC, and adogen were prepared and a regression equation that defines ash reduction is:

$$\text{Ash Reduction} = 1.07 + 1.21X1 - 10.31X2 + 1.16X3 - 1.06X4 - 1.36X5 + 1.70X6 \quad [1]$$

where X1 = +1,0,-1 for the MIBC concentrations
X2 = +1,0,-1 for the Fuel Oil concentrations
X3 = +1,0,-1 for the Adogen concentrations
X4 = X2*X2
X5 = X1*X2
X6 = X2*X3

In the best case, there is only a 13% reduction and in some cases, there is actually an increase in ash. One would probably not use this technique to clean coals.

3.3.3 Dispersion of Clean Coal in Oil

3.3.3.1 Background

The objective of this coal cleaning task was to make a preliminary evaluation of the effectiveness and desirability of using the Dispersion of Clean Coal in Oil Technique (DCCOT) (8,9) for reducing ash contents in low-rank coals. The suitability and application of this technique was identified by a literature search and communication with other investigators. The description of the DCCOT is contained in the patent (8). This patent lists two ingredient mixtures which gave significant results, hereafter referred to as DCCOT Mixture 1 and DCCOT Mixture 2.

3.3.3.2 Experimental Methods

Table 11 lists the ingredients, dosage used per ton of as-received raw coal, and the type and role of the ingredient. DCCOT Mixture 1 uses all of the ingredients listed below, whereas DCCOT Mixture 2 uses all of the ingredients except Aerofroth-65.

Kemmerer, Velva, Beulah-Zap(7/15/87), and Jacobs Ranch were selected as test coals so that general comparisons could be made between DCCOT and other cleaning techniques being carried out at EMRC. These coals and the frothing equipment and setup are the same as those used for frothing experiments reported in other parts of this report. The raw coals were pulverized to combustion grind. Raw coal on an oven-dry basis to water ratios were set at 25:75, 15:85, and 5:95.

TABLE 11

DCCOT INGREDIENTS, DOSAGE, AND TYPE OF INGREDIENT AND ROLE

Ingredients	Dosage (lb/ton)	Type of Ingredient and Role
$Na_4P_2O_7$	5.0	Promoter (surfactant); renders ash more hydrophilic for ease of separation.
H_2O_2	0.5	Initiator/Catalyst; affects coal surface which aids in polymerization reactions.
$Cu(NO_3)_2$	1.0	Initiator; helps initiate free radical reactions.
Corn Oil	5.0	Initiator/Catalyst; affects coal surface which aids in polymerization reactions.
Flotation Oil No. 634	100.0	Carrier; covers coal and renders surface hydrophobic for ease of separation.
Pine Oil	9.3	Frother; polymerizable monomer which aids frothing.
Aerofroth-65	0.4	Frother; primary frothing ingredient.

3.3.3.3 Results

Results of these experiments were given in previous reports (10). The following statements summarize important observations about ash reductions and yields using the DCCOT Mixture 1:

1) More dilute coal/water mixtures result in improved yield.

2) Kemmerer and Jacobs Ranch subbituminous coals have higher yields than Velva and Beulah-Zap(7/15/87) lignites.

3) In most cases, there was a greater ash reduction in the yields of the subbituminous coals. The highest ash reduction (33.3%) was with Kemmerer, at a coal:water ratio of 5:95.

4) Ash reductions, for the subbituminous coals, appears to be related to high water-to-coal mixtures.

5) Inconsistent ash reductions were evident with the lignites.

A summary of important observations about ash reductions and yields, using DCCOT Method 2, follows:

1) The yield for Kemmerer was very high at all coal:water ratios and ash reductions were relatively good.

2) There was slightly less yield, compared to DCCOT Method 1, for Jacobs Ranch, while ash reductions were about the same.

3) Velva and Beulah-Zap(7/15/87) showed decreasing and extremely poor yields with increasingly wider coal:water ratios.

Although the DCCOT shows promise as a viable method of obtaining high yields with some ash reduction potential, the DCCOT needs to be further researched to understand the interactions of ingredients, especially Aerofroth-65. However, because other coal cleaning methods given in this report are as good as or better than the DCCOT, further research on the DCCOT was discontinued.

3.4 Chemical Coal Cleaning

3.4.1 Acid Leaching

3.4.1.1 Background

Acid leaching has been used, in combination with caustic leaching and physical cleaning, to clean bituminous coals to low ash levels (11). Previous work has shown that acid leaching of LRCs, after physical cleaning, can produce less than 1 wt% ash product (6,10,12). Caustic leaching with LRCs has proven to be futile because the humic acids in LRCs dissolve in caustic solutions, making recovery of the coal difficult (6).

3.4.1.2 Experimental Methods

The leaching procedure consisted of treating 15 grams (dry basis) of coal in a 4 wt% solution of nitric acid for one hour at 80°C. The 23 wt% coal slurry was filtered and then reslurried with deionized water and mixed for another hour at 80°C. The results of acid-leaching are presented in Tables 12 through 16.

3.4.1.3 Results

Acid-leaching tests were performed on raw and physically cleaned samples of Beulah-Zap, Spring Creek, Jacobs Ranch, Usibelli, Kemmerer, and Velva. Acid leaching was performed on 1/4" x 10 mesh samples of all the coals. Testing was also performed on combustion grind and micronized samples of Beulah-Zap, Spring Creek, Jacobs Ranch, and Usibelli. In order to acid-leach the 1/4" x 10 mesh samples, the coal had to be pulverized to a combustion grind.

Beulah-Zap acid-leaching data is contained in Table 12. The results of acid-leaching 1/4" x 10 mesh raw coal show an ash reduction of 68%. When acid-leaching was done on the physically cleaned products, the ash level was less than 2 wt% ash (moisture-free basis). For the 1.30 sp. gr. float fraction, a yield of 61% was obtained with a 91% reduction in the feed ash level. The 1.40 sp. gr. float fraction had a slightly higher product recovery and greater than 1 wt% ash. Acid-leaching on the combustion grind had to be done at the 1.40 and 1.50 sp. gr. levels in order to produce results similar to those obtained for the 1/4" x 10 mesh sample. The data indicated that the liberation of ash-forming components takes place at a higher specific gravity for the smaller particles than for the larger particles.

Table 13 contains the results from acid leaching Spring Creek subbituminous coal. Acid-leaching of the raw coal samples produced a product with approximately 2 wt% ash (moisture-free basis) for all particle sizes tested. Leaching the float fractions produced the same trends as found with Beulah-Zap, with the higher specific gravity being necessary to produce higher yields of clean products at the smaller particle sizes. For the 1/4" x 10 mesh sample, a yield of 53% was obtained with 69% ash reduction at 1.30 sp. gr. At 1.40 sp. gr., a similar ash reduction was obtained, but the percent recovery was approximately 96%. With the combustion grind product at 1.40 sp. gr., a yield of 66% and 1 wt% ash level was obtained. At 1.50 sp. gr., the product had an ash content of 1.45 wt% and yielded 96% of the original product. Dry micronized Spring Creek at 1.40 sp. gr. resulted in a product with approximately 1.1 wt% ash and a cumulative yield of 85%. When acid-leaching was done on the 1.50 sp. gr. float product results similar to those of the other two samples. For this coal, the results indicate that particle size showed a fairly even distribution of ash-forming components throughout the coal.

TABLE 12

ACID LEACHING RESULTS FOR THE TREATMENT OF RAW AND PHYSICALLY CLEANED SAMPLES OF BEULAH-ZAP LIGNITE

Sample	Product	Cumulative Yield (%)	Ash (%)	Feed Ash Reduction (%)
1/4" x 10 mesh	Raw	93.28	3.18	67.88
	1.30-Float	60.56	0.90	90.91
	1.40-Float	75.50	1.61	83.74
80% <200 mesh	Raw	93.75	4.19	59.87
	1.40-Float	45.25	0.82	92.15
	1.50-Float	88.29	1.11	89.37
100% <325 mesh	Raw	94.08	3.74	56.00
	1.40-Float	38.54	1.50	82.35
	1.50-Float	87.33	1.81	78.71

Jacobs Ranch subbituminous coal did not yield a product with less than 1 wt% ash. The results of acid leaching this coal are contained in Table 14. Acid leaching on 1/4" x 10 mesh samples of this coal showed the advantages of physically cleaning prior to leaching. When raw coal was acid leached, there was only a 50% reduction in the ash, but acid leaching of the physically cleaned products showed overall ash reductions of approximately 80%. This indicates that in order to more efficiently remove the ash-forming components this coal needs to be physically cleaned before acid leaching. In general, the acid leaching results on the combustion grind sample followed the same trend as the 1/4" x 10 mesh sample, an exception being the use of a higher specific gravity of Certigrav to obtain similar results. Acid leaching of micronized Jacobs Ranch exhibited lower ash levels than the other two samples. This indicates that the finer particle size liberated more

TABLE 13

ACID LEACHING RESULTS FOR THE TREATMENT OF RAW AND PHYSICALLY CLEANED SAMPLES OF SPRING CREEK SUBBITUMINOUS COAL

Sample	Product	Cumulative Yield (%)	Ash (%)	Feed Ash Reduction (%)
	Raw	97.68	1.98	53.95
1/4" x 10 mesh	1.30-Float	53.07	1.33	69.07
	1.40-Float	96.12	1.32	69.30
	Raw	96.80	2.00	61.54
80% <200 mesh	1.40-Float	65.94	0.95	81.73
	1.50-Float	96.17	1.45	72.12
	Raw	97.22	2.16	56.28
100% <325 mesh	1.40-Float	84.99	1.13	77.13
	1.50-Float	96.36	1.45	70.65

ash-forming components, thus lowering the ash content of the sample. This also occurred at a specific gravity of 1.4 to 1.5, which is similar to the combustion grind sample.

Table 15 contains the results of acid leaching on Usibelli subbituminous coal. Acid leaching on the raw coals did not result in large reductions in ash content. However, leaching of the physically cleaned products showed a significant reduction in ash content. Acid leaching on 1/4" x 10 mesh 1.40 float product produced a sample with less than 1 wt% ash at a yield of 80%. Yields of 50% and 45% were obtained at 1.4 sp. gr. with ash contents of 1.4 and 1.8 wt% for the combustion grind and micronized samples, respectively. Acid leaching on the 1.50 sp. gr. samples resulted in a slightly higher ash content with over 80% yield for both combustion grind and micronized coal.

TABLE 14

ACID LEACHING RESULTS FOR THE TREATMENT OF RAW AND PHYSICALLY CLEANED SAMPLES OF JACOBS RANCH SUBBITUMINOUS COAL

Sample	Product	Cumulative Yield (%)	Ash (%)	Feed Ash Reduction (%)
	Raw	95.78	4.65	50.00
1/4" x 10 mesh	1.30-Float	48.79	1.90	79.57
	1.40-Float	91.89	2.43	73.87
	Raw	96.29	5.09	42.16
80% <200 mesh	1.40-Float	32.84	2.03	76.93
	1.50-Float	91.00	2.85	67.61
	Raw	94.45	2.95	65.29
100% <325 mesh	1.40-Float	68.59	1.10	87.06
	1.50-Float	87.21	2.03	76.12

TABLE 15

ACID LEACHING RESULTS FOR THE TREATMENT OF RAW AND PHYSICALLY CLEANED SAMPLES OF USIBELLI SUBBITUMINOUS COAL

Sample	Product	Cumulative Yield (%)	Ash (%)	Feed Ash Reduction (%)
1/4" x 10 mesh	Raw	95.66	4.06	51.67
	1.40-Float	80.05	0.70	91.72
80% <200 mesh	Raw	96.11	6.84	36.25
	1.40-Float	50.07	1.40	86.95
	1.50-Float	84.34	1.50	86.02
100% <325 mesh	Raw	95.73	4.58	48.25
	1.40-Float	45.21	1.78	79.89
	1.50-Float	88.11	2.51	71.64

Acid leaching was also performed on 1/4" x 10 mesh samples of Velva lignite and Kemmerer subbituminous coal. This data is contained in Table 16. Acid leaching on raw Velva lignite produced a sample with 5 wt% ash. When the 1.30 sp. gr. float product was acid leached, the ash level was lowered to less than 2 wt% ash with a 41% yield. Leaching performed on the 1.40 sp. gr. float product exhibited an ash level of 3.5 wt% and 71% yield. Acid leaching of the physically cleaned 1/4" x 10 mesh product of Kemmerer subbituminous coal did not result in a significant improvement in ash reduction. Comparing these results with the results of treatment of combustion grind and micronized samples which was performed last year (6) shows that Velva benefitted by using 1/4" x 10 mesh in that a lower specific gravity was needed to obtain a cleaner product. Results from last year indicate that finer grinding of Kemmerer liberated more ash-forming components (6).

TABLE 16

ACID LEACHING RESULTS FOR THE TREATMENT OF 1/4" X 10 MESH RAW AND PHYSICALLY CLEANED SAMPLES OF VELVA LIGNITE AND KEMMERER SUBBITUMINOUS COAL

Sample	Product	Cumulative Yield (%)	Ash (%)	Feed Ash Reduction (%)
Velva	Raw	95.04	4.96	54.83
	1.30-Float	41.44	1.83	84.52
	1.40-Float	71.40	3.51	69.82
Kemmerer	Raw	98.25	1.75	47.60
	1.30-Float	40.51	1.41	54.83

The 1.30 float acid-leached product of the 1/4" x 10 mesh fractions of all the coals, except Usibelli, were evaluated further for sulfur reduction and heat recovery. For Usibelli, the 1.40 sp. gr. product was used due to the low recovery at 1.30 sp. gr.

3.4.2 Colloidal Coal Cleaning

3.4.2.1 Background

Methods for the solubilization of low-rank coals, under ambient conditions, were extensively investigated in recent research projects at UNDEMRC (13,14). In these projects, the conversion of low-rank coals into a stable, dispersed form (latex) was investigated. Humic material recovered from the latex had very low mineral content. This coal cleaning process was called the colloidal coal cleaning technique.

A preliminary assessment of the potential of using the colloidal coal cleaning technique on selected LRCs was evaluated. The objective was to study the conversion of several LRCs to humic acids, under conditions of high mass flow, and to evaluate the effectiveness of the process as a coal cleaning technique. The evaluation was concerned primarily with the amount of humic acid recovered, ash reduction, and time and complexity of the extraction procedure.

Because the humic material had such low mineral content, UNDEMRC researchers believed that the process had high potential for the preparation of ultra-clean coal (15).

3.4.2.2 Experimental Methods

The process essentially consists of the production of a latex from a mixture of coal, water, and 5% sodium hydroxide. The mixture is processed in a kitchen-style blender, and then centrifuged. Temperature of blending was less than 45°C. As developed, the procedure takes approximately six hours to complete, with an initial starting sample of ten grams.

3.4.2.3 Results

Five coals were selected for analysis: two Gulf Coast lignites (Martin Lake, TX, and Panola County, MS) and three North Dakota lignites (Beulah-Zap, Velva, and Indian Head). These coals were selected because UNDEMRC has acid-leaching data (16) on these coals, thereby allowing a comparative evaluation of the cleaning effectiveness of the colloidal coal cleaning technique. The procedure for extracting humic acids was developed by E. S. Olson, et al. (13,14).

Table 17 presents the percentage of ash present in the five coals before and after treatment and the percentage recovery for the colloidal coal cleaning method. The raw coal ash contents ranged from 9.1 to 20.2 wt%. Ash contents of the extracted humic acids ranged from 1.1 wt% (Velva) to 3.4 wt% (Beulah-Zap and Indian Head). Recovery ranged from a low of 19.5 wt% (Panola Co.) to 57.4 wt% (Velva). Total ash reduction was highly significant for all coals.

TABLE 17

RESULTS OF COLLOIDAL COAL CLEANING TECHNIQUE

Coal	Raw Coal Ash (wt%)	Dried Prod. Ash (wt%)	% Recovery	Tot. Ash Red. (wt%)	Acid-Leach Ash (wt%)
Martin Lake	11.1	3.4	46.3	65.4	9.8
Panola Co.	20.2	2.8	19.5	86.4	9.7
Beulah-Zap	15.7	3.4	47.5	78.6	7.0
Velva	9.2	1.1	57.4	87.6	4.6
Indian Head	9.1	2.2	51.3	75.5	8.0

The major drawback of the colloidal coal cleaning technique is the considerable amount of time it takes to complete the humic acid extraction step and the small amount of initial coal sample which can be used in the technique. The potential for this technique would be better evaluated in a scaled-up scenario (15).

3.5 Analytical Studies

3.5.1 Background

Results from chemical cleaning made it desirable to analyze 1/4" x 10 mesh samples in further detail. Sulfur content and heating values were evaluated for the coals. In addition to this testing on the coal, bulk chemical analysis of ash was determined by X-ray fluorescence. High-temperature ashing (HTA) methods were used to prepare ash samples for X-ray analysis.

3.5.2 Experimental Methods

Total sulfur analysis was performed on a LECO Sulfur Analyzer. Heating value analysis was achieved using a Parr bomb calorimeter. Values for sulfur forms were determined by ASTM-D2492-80 procedures. A Kevex 0700 dispersive spectrometer was used for X-ray fluorescence analysis. HTA preparation was done at 750^{o}C following ASTM-D3147-73 procedures.

3.5.3 Results

3.5.3.1 Sulfur and Heating Value Analysis

Results from both sulfur and heating value analyses are shown in Table 18 for the 1/4" x 10 mesh fraction of the data base samples. All the data were determined for 1.30 float fractions of the coal, except for Usibelli of which the 1.40 float fraction was used. The percent sulfur reduction was based on the removal of total sulfur rather than the sulfur forms. Since target sulfur levels are 0.5 wt% or less, it is important to reach this level.

TABLE 18

SUMMARY OF SULFUR AND HEATING VALUE ANALYSIS ON DATA BASE SAMPLES SIZED TO 1/4" X 10 MESH

Analysis (mf, wt%)	Beulah-Zap	Spring Creek	Jacobs Ranch
Sulfur Reduction:			
Acid-leached	38	36	29
Physically cleaned	56	19	15
Physically cleaned:[a]	70	48	37
Heat Recovery:			
Acid-leached	96	96	99
Physically cleaned	72	54	54
Physically cleaned:[a]	67	54	61
	Usibelli	Kemmerer	Velva
Sulfur Reduction:			
Acid-leached	--[b]	7	13
Physically cleaned	--[b]	10	20
Physically cleaned:[a]	--[b]	23	33
Heat Recovery:			
Acid-leached	99	93	95
Physically cleaned	84	41	55
Physically cleaned:[a]	89	38	49

[a] Acid-leached

[b] Not determined

Beulah-Zap contains greater than 1% total sulfur (Table 2), indicating that sulfur reductions must occur in order to meet emission standards. Acid leaching of raw Beulah-Zap lignite indicated the removal of a small amount of organic sulfur. Sulfur reduction was also achieved for the physically cleaned sample, indicating that inorganic sulfur was removed. Table 18 shows the sulfur reduction for both the physically cleaned and the physically cleaned-acid leached samples. The 70% reduction in the physically cleaned-acid leached sample indicates that a small amount of organic and possibly pyritic sulfur were removed. Without the sulfur form analysis of the sample, it was not possible to isolate the specific sulfur form removed.

Since there was a substantial reduction of sulfur for Beulah-Zap, sulfur forms present in the 1.30 sp. gr. float sample were investigated. Analysis of the sulfur forms shown in Table 19 indicates a reduction in pyritic sulfur of 95%. The results do not indicate a significant removal of any other sulfur form. No other coal exhibited this type of removal.

Heat recovery in Table 18 is defined by the following equation:

$$((BtuC * \%Y)/BtuR) * 100 = \text{Percent Heat Recovery} \quad [2]$$

where BtuC = Btu/lb of cleaned coal,
%Y = Percent yield for that cleaned fraction/100,
and BtuR = Btu/lb of raw coal

Note: Calculations done on moisture-free basis

As the equation shows, percent yield of the product has an effect on the amount of heat recovery. For the acid-leached samples, the heat recovery was over 90% due to the high yield of greater than 90%. The recoveries of the physically cleaned samples and the physically cleaned-acid leached samples were lower due to the yields of the physically cleaned samples being somewhat lower. The exception being Usibelli which was cleaned at a higher specific gravity and therefore has a higher yield.

TABLE 19

SULFUR FORMS ANALYSIS FOR 1/4" X 10 MESH
RAW AND 1.3 FLOAT BEULAH-ZAP SAMPLES

Sulfur Form (mf, wt%)	Raw	1.3 Float	% Removal
Sulfate	<0.01	<0.01	--[a]
Pyritic	0.60	0.03	95.00
Organic	0.53	0.47	11.32
Total	1.13	0.50	55.75

[a] Not determined

3.5.3.2 X-ray Fluorescence Analysis of Coal Ash

Results from X-ray fluorescence analysis on high-temperature ash samples of data base coals are presented in Tables 20 through 22. The results are listed on a moisture-free, percent oxide basis. The analyses were performed on both 1/4" x 0 and 1/4" x 10 mesh coal as well as products from physical and chemical cleaning tests on the 1/4" x 10 mesh fractions.

Table 20 contains the results of X-ray fluorescence for Velva and Beulah-Zap lignites. Ash analysis on Velva indicates that low silica and aluminum minerals are removed with the fines. The results in a higher proportion of silica and aluminum is the ash of the 1/4" x 10 mesh size fraction. An overall summary of the results showed that the acid leaching process removed mainly sodium, calcium, magnesium oxide, and a small amount of silica. Sodium, calcium, and magnesium were removed by acid leaching because they primarily occur as ion-exchangeable cations. Acid-leaching tends to increase (relatively) aluminum and ferric oxide and, to a smaller extent, titanium and potassium oxide. Concentrations of these components indicate that particles such as clay minerals or quartz, are finely disseminated throughout the coal and not easily removed.

TABLE 20

RESULTS OF X-RAY FLUORESCENCE ANALYSIS ON SAMPLES OF VELVA AND BEULAH-ZAP LIGNITES

VELVA

High Temperature Ash Results (% of ash)	Raw 1/4"x0 Mesh	Raw 1/4"x10 Mesh	1/4" x 10 mesh Acid-leached	1/4" x 10 mesh 1.3 Float	1/4" x 10 mesh 1.3 Float Acid-leached
Silica	10.2	71.5	62.5	18.8	59.6
Aluminum Oxide	10.1	15.2	17.9	11.2	23.8
Ferric Oxide	7.3	0.8	12.3	5.4	6.8
Calcium Oxide	42.0	8.4	1.9	34.5	2.2
Sodium Oxide	3.0	0	0	0.7	0
Magnesium Oxide	11.2	3.3	0.9	8.6	1.2
Sulfur Trioxide	14.7	0.4	1.0	19.0	2.1
Titanium Oxide	0.7	0.3	1.5	0.8	2.6
Phosphorous Pentoxide	0.6	0	0	0.8	0.3
Potassium Oxide	0.1	0	2.1	0.1	1.4
Percent Ash	9.9	11.0	5.0	5.7	2.2

BEULAH-ZAP

High Temperature Ash Results (% of ash)	Raw 1/4"x0 Mesh	Raw 1/4"x10 Mesh	1/4" x 10 mesh Acid-leached	1/4" x 10 mesh 1.3 Float	1/4" x 10 mesh 1.3 Float Acid-leached
Silica	17.8	12.6	38.1	23.0	41.4
Aluminum Oxide	9.9	9.0	17.9	16.5	31.3
Ferric Oxide	9.3	13.5	35.5	4.1	8.3
Calcium Oxide	19.9	19.1	2.5	25.3	4.0
Sodium Oxide	8.6	10.0	0	6.0	0
Magnesium Oxide	6.2	5.6	0.2	7.4	1.7
Sulfur Trioxide	25.6	27.7	2.5	13.8	4.5
Titanium Oxide	1.2	1.0	2.5	1.3	4.0
Phosphorous Pentoxide	1.4	1.4	0.7	1.2	3.9
Potassium Oxide	0.1	0.1	0.3	1.3	0.1
Percent Ash	9.4	9.3	3.7	6.4	0.9

TABLE 21

RESULTS OF X-RAY FLUORESCENCE ANALYSIS ON SAMPLES OF USIBELLI AND JACOBS RANCH SUBBITUMINOUS COALS

USIBELLI

High Temperature Ash Results (% of ash)	Raw		1/4" x 10 mesh		
	1/4"x0 Mesh	1/4"x10 Mesh	Acid-leached	1.3 Float	1.3 Float Acid-leached
Silica	31.2	29.0	59.7	12.1	20.7
Aluminum Oxide	12.3	12.6	22.7	8.9	12.8
Ferric Oxide	8.8	8.2	6.1	12.6	16.1
Calcium Oxide	34.1	35.5	3.6	52.2	21.8
Sodium Oxide	2.0	1.3	0	0.7	0
Magnesium Oxide	3.9	4.2	1.4	5.7	1.0
Sulfur Trioxide	5.9	7.3	3.2	6.5	25.3
Titanium Oxide	1.2	1.3	1.8	1.3	1.1
Phosphorous Pentoxide	0	0.1	0.1	0	0.9
Potassium Oxide	0.6	0.5	1.4	0	0.3
Percent Ash	9.1	8.4	4.1	5.7	0.7

JACOBS RANCH

High Temperature Ash Results (% of ash)	Raw		1/4" x 10 mesh		
	1/4"x0 Mesh	1/4"x10 Mesh	Acid-leached	1.3 Float	1.3 Float Acid-leached
Silica	27.7	29.8	45.0	19.6	49.4
Aluminum Oxide	17.5	16.9	19.3	15.0	25.1
Ferric Oxide	5.8	12.0	23.3	8.6	9.5
Calcium Oxide	25.0	19.4	4.4	29.4	5.7
Sodium Oxide	1.6	1.6	0	0.9	0
Magnesium Oxide	5.5	4.7	1.1	6.5	1.5
Sulfur Trioxide	14.0	12.3	3.6	17.0	3.2
Titanium Oxide	1.9	1.6	2.2	1.6	3.8
Phosphorous Pentoxide	0.6	1.3	0.5	1.2	1.3
Potassium Oxide	0.4	0.4	0.5	0.1	0.4
Percent Ash	8.2	9.3	4.7	5.8	1.6

Physical cleaning removes silica and aluminum oxide and concentrates calcium, magnesium oxide, and sulfur trioxide. Physical cleaning increases the amount of ferric oxide but not to the level that acid-leaching does. This behavior indicates the presence of inorganically bound iron such as pyrite. The combined physically and chemically cleaned samples showed results similar to acid leaching for silica, aluminum, and ferric oxide concentrations. The combined process removed calcium, sodium, magnesium oxide, and sulfur trioxide. These results suggest the presence of finely disseminated clay minerals and pyrite particles which are too small to be removed by these processes.

The results of fines removal for Beulah-Zap, listed in Table 20, shows an increase in ferric oxide and a slight increase in sodium oxide. As with Velva, acid-leaching concentrated silica, aluminum, and ferric oxide. It also removed a large amount of calcium oxide and the sodium oxide, which is important in reducing the potential for ash-fouling. Physical cleaning on 1/4" x 10 mesh samples of Beulah-Zap showed an increase in silica, aluminum oxide, calcium and magnesium oxide, and sulfur trioxide. The decrease in ferric oxide for this sample indicates the presence of pyrite which is removable by physical cleaning processes. Acid leaching of 1.3 Float shows a concentration in the amount of silica, aluminum oxide, and ferric oxide. A similar behavior occurred with the acid-leached, raw 1/4" x 10 mesh sample of Beulah-Zap. It also exhibits a decrease in the ion-exchangeable cations. The results obtained for this coal also indicated the presence of finely disseminated clay minerals, as well as the removal of pyrite in this coal by physical and chemical cleaning.

The results of X-ray fluorescence analyses performed on Usibelli and Jacobs Ranch subbituminous coals are contained in Table 21. Usibelli exhibited little removal or concentration of the components when the fines were removed. Acid leaching of this coal followed the same trends as indicated with the previous samples. Physical cleaning of Usibelli was similar to that of Velva in the component distributions. Acid leaching of the physically cleaned product showed a significant concentration in the amount of sulfur trioxide and the other components were distributed in much the same way as previously discussed. These results indicate a fairly even distribution of all the elements present for the Usibelli sample.

Jacobs Ranch results presented in Table 21, show that the removal of fines produced results similar to the other coals. Acid leaching of the Jacobs Ranch did result in the concentration and reduction of the same oxides as the previous coals. Physical cleaning followed the same pattern as that observed with Usibelli, except for a reduction in ferric oxide. Acid leaching on the physically cleaned product followed the same trend as previous coals tested.

Results of X-ray fluorescence on Spring Creek and Kemmerer are contained in Table 22. Both coals have a raw percent ash content of less than 5%. The removal of fines in the Spring Creek sample showed no significant changes in any oxides present. Acid leaching of Spring Creek indicated a concentration in the amount of silica, aluminum oxide, ferric oxide, and titanium oxide present and a decrease in the calcium, sodium, magnesium oxide, and sulfur trioxide. The only significant changes in ash content observed for physically cleaning Spring Creek were a slight decrease in silica and an increase in calcium oxide. The other oxides present did not show any significant changes in the composition of their ash. Acid leaching on the physically cleaned product indicated the same results as described with previous samples.

TABLE 22

RESULTS OF X-RAY FLUORESCENCE ANALYSIS ON SAMPLES OF SPRING CREEK AND KEMMERER SUBBITUMINOUS COALS

SPRING CREEK

High Temperature Ash Results (% of ash)	Raw		1/4" x 10 mesh		
	1/4"x0 Mesh	1/4"x10 Mesh	Acid-leached	1.3 Float	1.3 Float Acid-leached
Silica	21.3	25.5	59.4	19.3	45.0
Aluminum Oxide	16.1	16.6	21.2	16.5	29.0
Ferric Oxide	4.3	4.4	6.5	4.3	7.1
Calcium Oxide	19.6	19.4	4.1	22.5	5.2
Sodium Oxide	8.3	7.4	0	6.5	0
Magnesium Oxide	5.1	4.9	1.2	5.7	2.1
Sulfur Trioxide	22.3	18.6	3.3	21.9	6.7
Titanium Oxide	2.0	1.9	3.6	2.1	4.2
Phosphorous Pentoxide	1.0	0.8	0.2	0.8	0.6
Potassium Oxide	0.2	0.5	0.5	0.3	0.1
Percent Ash	4.2	4.3	2.1	3.5	1.1

KEMMERER

High Temperature Ash Results (% of ash)	Raw		1/4" x 10 mesh		
	1/4"x0 Mesh	1/4"x10 Mesh	Acid-leached	1.3 Float	1.3 Float Acid-leached
Silica	39.5	38.5	57.2	36.5	58.5
Aluminum Oxide	22.8	16.9	22.3	16.4	20.3
Ferric Oxide	1.9	2.0	2.7	6.2	1.3
Calcium Oxide	12.9	17.1	7.3	13.4	1.7
Sodium Oxide	0.6	0.4	0	0.8	0
Magnesium Oxide	5.4	5.5	2.4	5.1	2.8
Sulfur Trioxide	15.1	17.3	6.1	18.6	7.6
Titanium Oxide	0.9	1.0	1.5	1.0	1.7
Phosphorous Pentoxide	0.8	1.1	0.5	1.0	0.6
Potassium Oxide	0.1	0.1	0	0	0.1
Percent Ash	3.7	2.9	1.8	2.4	1.4

Results of X-ray fluorescence analysis on Kemmerer indicated that the removal of fines slightly reduced the percent of silica and aluminum oxide, causing an increase in calcium oxide and sulfur trioxide concentrations. Acid leaching of a raw 1/4" x 10 mesh sample resulted in an increase in silica, aluminum oxide, ferric oxide, and titanium oxide. The sample also showed reduced amounts of calcium oxide, sodium oxide, magnesium oxide, and sulfur trioxide.

Physical cleaning of Kemmerer did not show any significant reduction in the oxides. Noticeable effects were a decrease in the level of calcium oxide and increase in ferric oxide concentration. The ferric oxide increase presumably indicates low pyritic sulfur levels in the coal. The 1.3 Float, acid-leached sample follows a pattern similar to that observed with the acid-leached raw sample with further reduction in calcium oxide and also a reduction in ferric oxide. This reduction in ferric oxide by acid leaching indicates the presence of ion-exchangeable iron rather than inorganically bound iron.

A summary for results on X-ray fluorescence analysis indicates that removal of fines can benefit the cleaning of the coal depending on the distribution of the ash in the coal matrices. Acid leaching removes the ion-exchangeable cations such as calcium, sodium, and magnesium. Physical cleaning removes some of the more erosive materials such as silica, aluminum oxide, and titanium oxide and to a lesser extent, depending on the form present, it removes ferric oxide.

3.6 Process Development Unit (PDU) Operation

3.6.1 Introduction

UNDEMRC has been developing a hydrothermal low-rank coal treatment process since 1983. A continuous Process Development Unit (PDU) capable of producing 2.5 tons of slurry per day has been built and operated to demonstrate the technical feasibility of the process and to generate data useful in engineering and economic studies (17). PDU Runs 25, 26, 27, 28, 30, and 31 were made in support of the DOE projects during the year. PDU Run 29 was completed for a private contractual agreement.

3.6.2 PDU Run 25

Run 25 was made under a subcontract with AMAX Extractive Research & Development Center. The objective of their subcontract to United Technologies, through a DOE project at Morgantown Energy Technology Center, was to prepare gas turbine-quality fuel using Velva lignite. This work resulted from successful tests at the bench scale and pilot scale with Eagle Butte subbituminous coal (18). UNDEMRC's role was to hot-water dry the coal after AMAX had cleaned it. As long as AMAX was preparing pilot-scale quantities of clean Velva, UNDEMRC purchased one barrel of clean coal to be hot-water dried and studied for fuel preparation at UNDEMRC.

The coal was cleaned from 9.2 wt% ash to 1.9 wt% ash at AMAX. Standard gravity separation using a magnetite slurry was used to clean 1/4" x 10 mesh raw Velva lignite. The physically cleaned coal was then ball milled to minus 20 mesh (850 microns) and cleaned with nitric acid using the same procedure UNDEMRC uses in the laboratory.

Sulfur content was reduced throughout the treatment steps, with a final content of 0.43 wt%, which was below the target of 0.5 wt%. The heating value of the coal, on a dry basis, was increased from 11,200 Btu/lb to 11,900 Btu/lb after hot-water drying treatment at 330°C. Results of fuel preparation with this product will be discussed in the rheology section of this report.

3.6.3 PDU Runs 26 & 27

These runs were made with the same coal, Jacobs Ranch, to produce hot-water-dried fuel for an extended fluid bed combustion run. Approximately 18,000 lbs of Jacobs Ranch (Wyoming) subbituminous coal/water fuel (CWF) were prepared for Atmospheric Fluidized-Bed Combustion (AFBC) utilization using a preparation process including hydrothermal treatment. The hydrothermal treatment was performed in the 2.5-ton/day UNDEMRC continuous Process Development Unit (PDU) at 330°C for five minutes (1). Three different particle sizes were processed for the AFBC combustion testing: coarse, medium, and fine sizes, allowing the testing of combustion performance and rheology as a function of particle size. The coarse size had an average particle size of approximately 120 microns (130 mesh); the medium size had an average size of 80 microns (200 mesh) and the fine size which had an average size of approximately 40 microns (400 mesh), was used as the baseline fuel.

During Run 26, medium-sized coal feed was attempted unsuccessfully and the system was quickly returned to fine-grind feed. The processing problem was anticipated and occurred in the check valves of the high-pressure pumps, blocking movement of the balls in the check valves. To prevent this from occurring, the medium and coarse samples had been sieved at 20 mesh (850 microns). After attempting to feed the -20 mesh medium sample, both samples were sieved at 40 mesh (425 microns), since a 30 mesh screen was not available, to prevent further problems in feeding the slurry.

The particle size distributions for the three raw coal grinds are shown in Figure 3. Both the medium and coarse sizes are shown after sieving at 20 mesh. A considerable amount of -40 mesh material was hung up on the 40 mesh screen for both grinds; 88% of total oversize for medium and 85% of total oversize for coarse, but the processing problem was solved. The particle size distributions for the three grinds after hot-water drying at 330°C in the PDU and centrifuging are shown in Figure 4.

3.6.4 PDU Run 28

Cleaned samples of Kemmerer (4.6 lbs dry weight) and Jacobs Ranch (7.7 lbs dry weight) subbituminous coals were hot-water dried at 330°C during PDU Run 28. The samples were apparently contaminated with ash-forming material during the hydrothermal treatment since ash levels increased. The Kemmerer ash level increased from 1.3 wt% for the clean product to 2.5 wt% and Jacobs Ranch showed an increase from 2.5 wt% to 3.1 wt% ash. With more attention paid to cleaning the PDU and centrifuge, this contamination will hopefully be prevented in future small-scale tests.

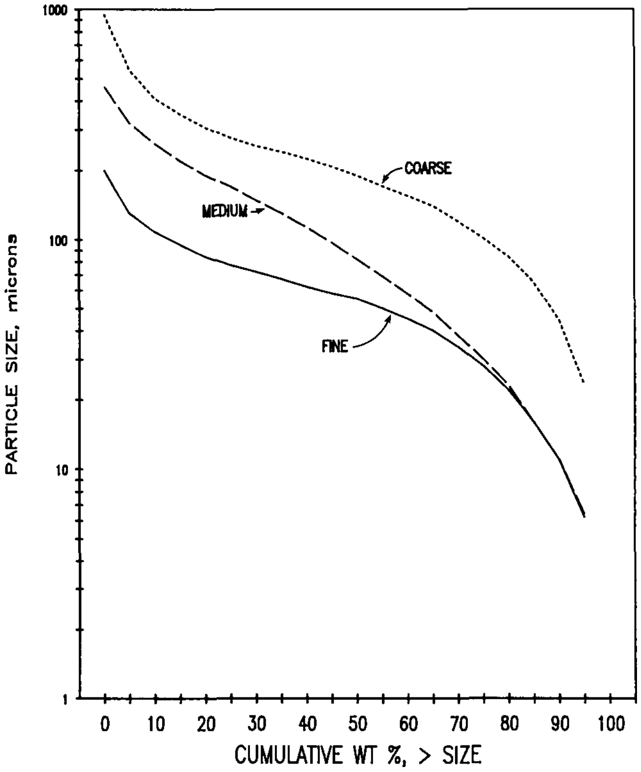

Figure 3. Particle size distributions for raw, fine, medium, and coarse Jacobs Ranch subbituminous coal

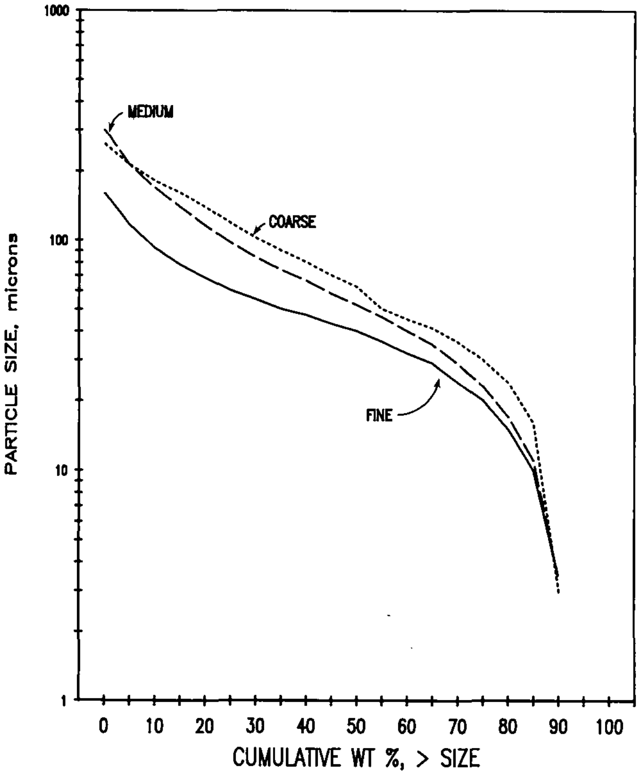

Figure 4. Particle size distributions for HWD, fine, medium, and coarse Jacobs Ranch subbituminous coal

Two raw samples of Jacobs Ranch subbituminous coal were also processed during PDU Run 28. They were treated at 270° and 300°C to complete the data base for this coal. In addition, a sample of Gibbons Creek lignite from Texas was also processed at 330°C. This coal was included in the screening of coals for cleaning, and it was included in the PDU run to determine its potential of producing a slurry fuel.

3.6.5 PDU Run 30

The objective of PDU Run 30 was to process 700 pounds of pulverized Beulah lignite, 300 pounds of Spring Creek subbituminous coal, and 300 pounds of Usibelli subbituminous coal. A nitrogen purge on the mix tank was used to minimize coal oxidation, which can contribute to calcium sulfate deposition in the Dowtherm heater coils. Various HWD temperatures and pressures were examined for each coal. A summary of the results from Run 30 is listed in Table 23.

TABLE 23

CWF PERFORMANCE FOR COALS PROCESSED IN PDU RUN 30
APPARENT VISCOSITY AT 800 CP AND 100 SEC^{-1}

Coal Sample	% Solids	% Ash	% S	Btu/lb	Energy Density Btu/lb
1. Spring Creek:					
a. Raw	46.4	4.21	0.36	12382	5745
b. HWD @ 270°C	56.1	4.34	0.34	12497	7011
c. HWD @ 300°C	57.0	4.31	0.36	12538	7147
d. HWD @ 330°C	57.5	4.46	0.34	12711	7309
2. Beulah-Zap Lignite:					
a. Raw	43.2	9.41	1.37	10837	4703
b. HWD @ 270°C	56.2	7.57	0.81	11185	6286
c. HWD @ 300°C	56.4	8.02	0.63	11378	6417
d. HWD @ 330°C	57.2	8.14	0.92	11385	6512
3. Usibelli:					
a. Raw	46.8	9.05	0.02	10778	5044
b. HWD @ 270°C	56.4	11.40	0.02	10728	6051
c. HWD @ 300°C	56.8	10.70	0.04	10975	6234
d. HWD @ 330°C	57.4	12.30	0.00	10900	6257

Note: all data presented on a moisture-free basis

An increase in achievable solids contents and energy densities was noted for CWF produced with the HWD products compared to that produced with the raw coal. There was also a general increase in heating value for the coal products on a moisture-free basis with temperature. The low sulfur levels remained relatively unchanged for the various temperatures and pressures.

Figures 5, 6, and 7 show the rheological performances of the three test coals. Lower than expected solids concentrations may be attributed to high HWD feed rates ranging from 220 to 300 lbs/hr due to control difficulties caused by small batch operation. Rheological results showed yield pseudoplastic flow behavior for the three coals. Pseudoplasticity tended to increase with increasing HWD temperature.

Production modifications were made to streamline product collection for Run 30. The hot, dilute products from the PDU were continuously fed into a product-handling tank and then transferred directly to the centrifuge.

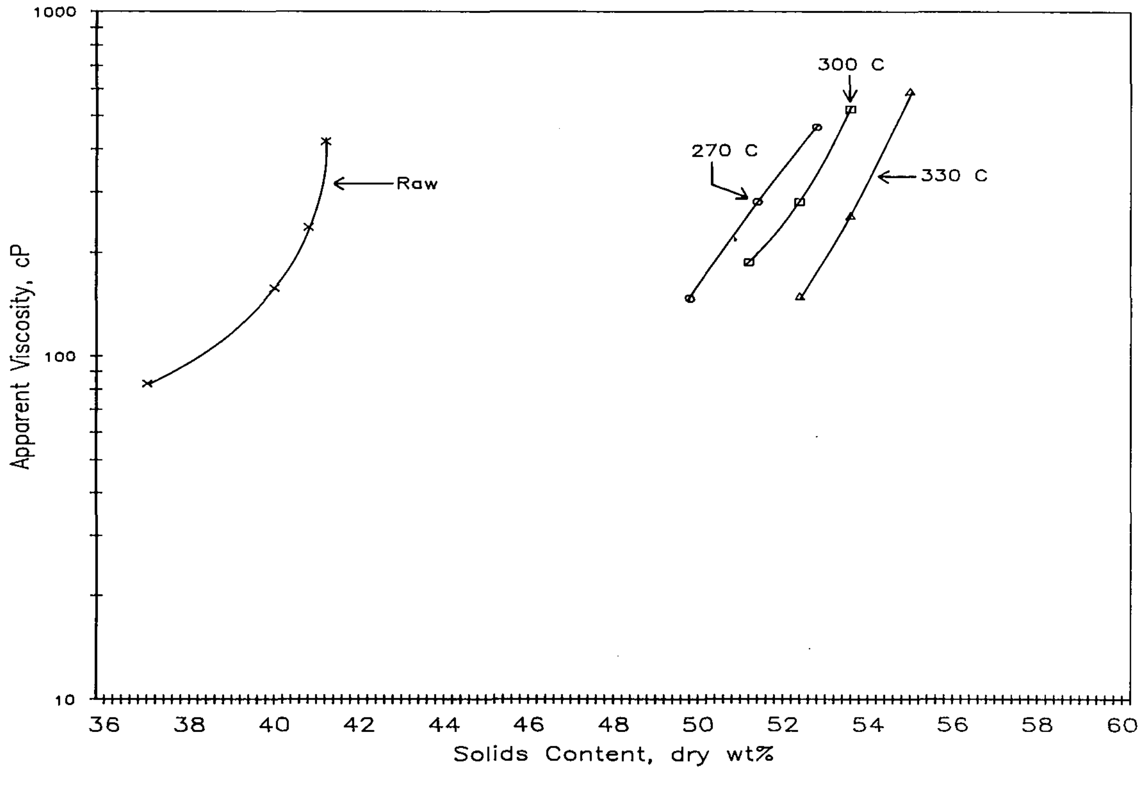

Figure 5. Rheological performance for CWF made from raw and hot-water-dried Beulah-Zap lignite at 100 sec^{-1} and 25^{o}C

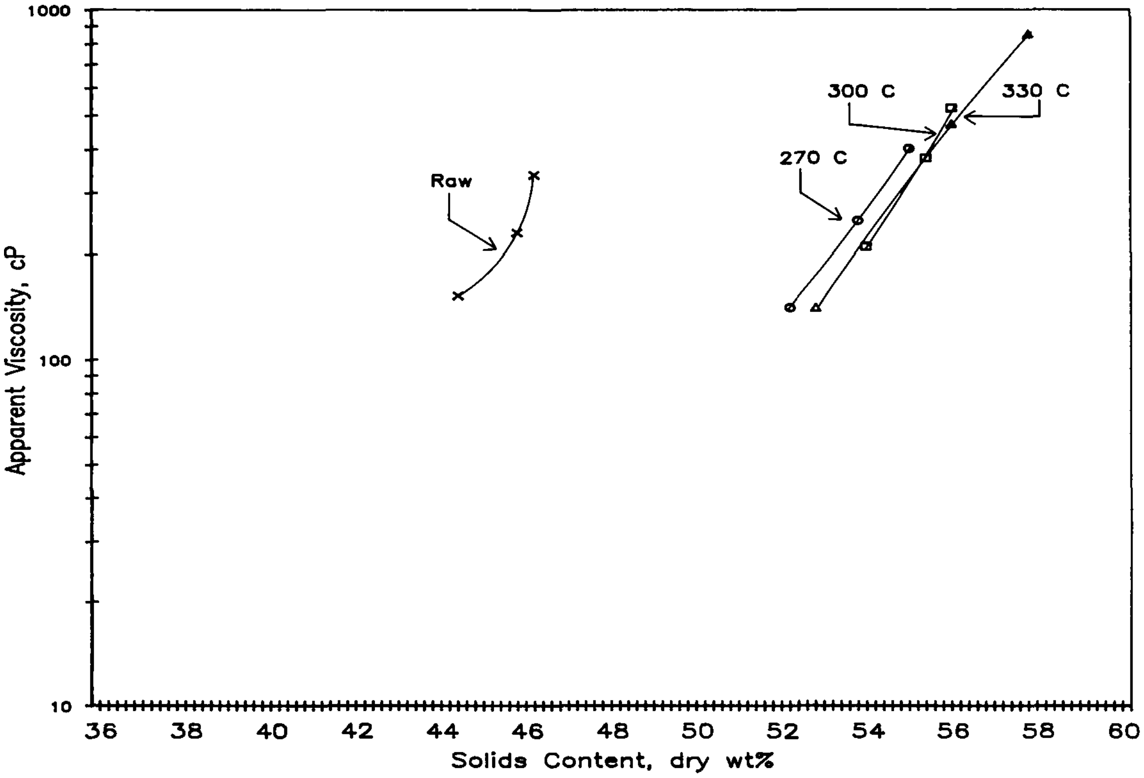

Figure 6. Rheological performance for CWF made from raw and hot-water-dried Usibelli subbituminous coal at 100 sec^{-1} and 25°C

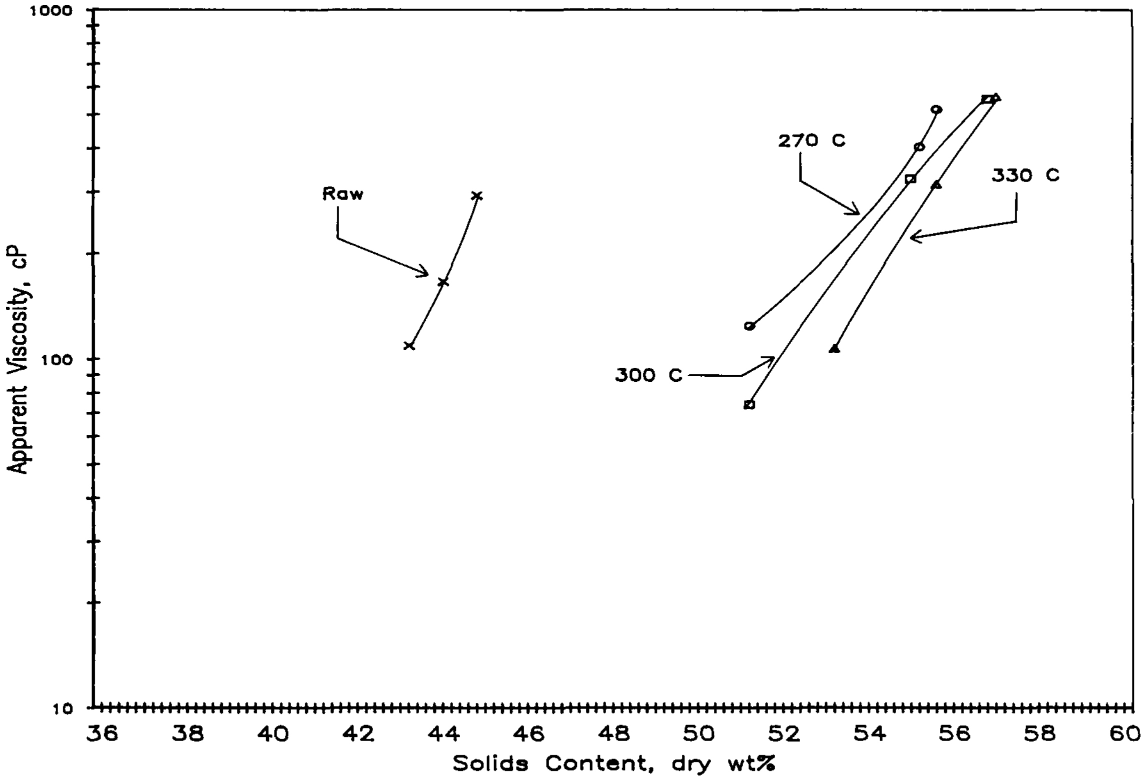

Figure 7. Rheological performance for CWF made from raw and hot-water-dried Spring Creek subbituminous coal at 100 sec^{-1} and 25°C

3.6.6 PDU Run 31

The objective of Run 31 was to HWD 1500 pounds of clean, micronized Beulah lignite at 330°C, and 1200 pounds pulverized Beulah Zap at 330°C. The run was performed to satisfy contractual commitments with Advanced Fuels Research, to provide fuel for the EMRC gas turbine program, and to provide fuel for a contractual agreement with Penn State University.

Before running the clean coal through the PDU, a 50 wt% coal mixture was prepared and then micronized using a new Attritor wet grinding mill at 200 lbs/hr. After processing the clean coal, the product was run through the centrifuge using 50% excess water to wash soluble cations from the coal.

Raw, pulverized Beulah lignite was processed similarly to Run 30, except that the feed rate was set at 200 lbs/hr. Higher solids concentrations were obtained as a result of the lower feed rates.

3.7 Particle Size Analysis and Rheological Characteristics of PDU Hydrothermally Treated Coals at Ambient Conditions

3.7.1 Particle Size Analysis

One of the key technologies required to obtain highly loaded, low-viscosity mixtures is the particle size distribution of the coal. Optimum particle size distributions for hydrothermally treated coal/water fuels can be approximated by blending two different-sized fractions together in the proper ratio, increasing the packing density of the fuel (6). This principle is shown in Figure 8 as apparent viscosity versus dry solids content for a 120-micron average size, hydrothermally treated, Kemmerer subbituminous coal and fuel made from the same coal product with optimized particle size of 20% 10-micron average size and 80% 120-micron average size. Note the significant increase in solids content for a comparable viscosity, from 59.4 wt% to a 61.6 wt% at 800 cP. Figure 8 also shows that, as the packing efficiency for the coal/water fuel increases, the reduced void space resulted in a greater additive effectiveness. After the addition of 1 wt% non-ionic surfactant, the solids content increased from 61.6 wt% to 64.4 wt% solids at 800 cP. Further comparison of the benefits of these preparation techniques are given in Table 24 for solids content and energy density for a fuel viscosity of 800 cP at 100 1/sec.

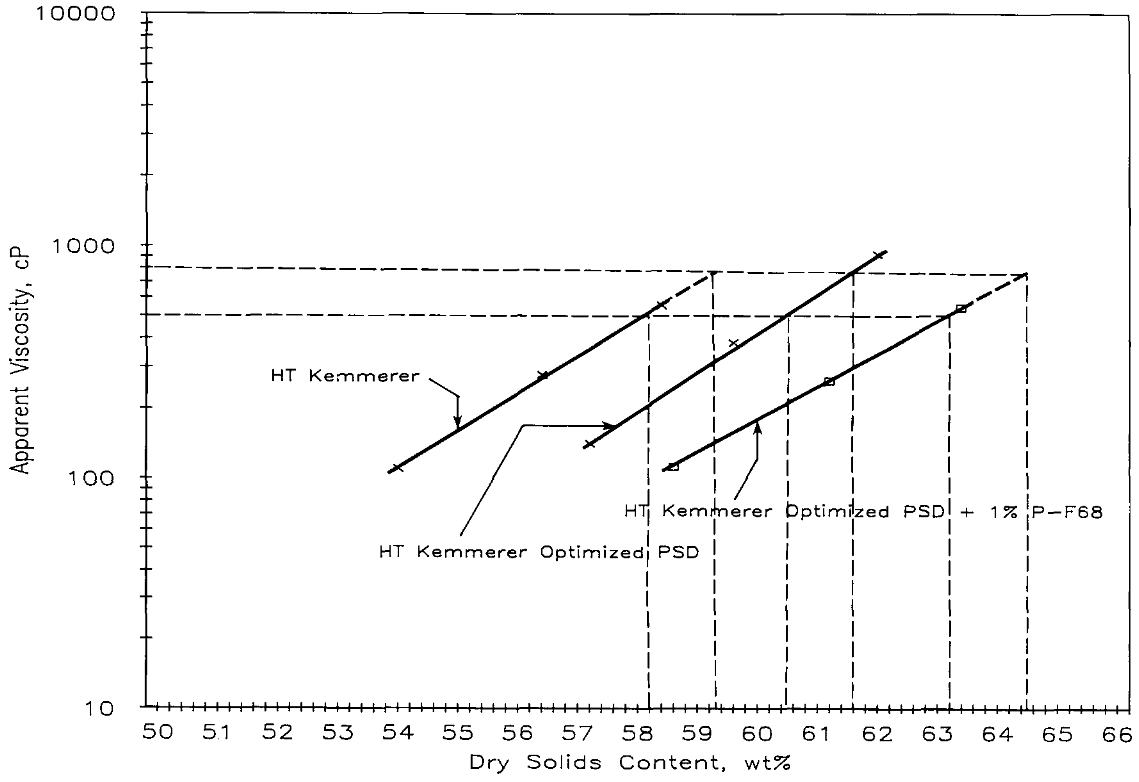

Figure 8. Rheological performance for CWF made from hydrothermally treated Kemmerer subbituminous coal

TABLE 24

RHEOLOGICAL PERFORMANCE COMPARISON OF ENERGY DENSITY AND SOLIDS CONTENT FOR VARIOUS PREPARATIONS OF CWF USING 330^{o}C HYDROTHERMALLY TREATED (HT) KEMMERER SUBBITUMINOUS COAL

Preparation Sizing and Treatment (Avg. Particle Size)	CWF apparent viscosity of 800 cP @ 100 sec^{-1}	
	Solids Content (mf, wt%)	Energy Density (Btu/lb slurry basis)
19 micron: Raw	44.2	5700
10 micron: 330^{o}C HT	52.3	6760
120 micron: Raw	50.9	6570
120 micron: 330^{o}C HT	59.4	7680
200 micron: Raw	49.5	6380
72 micron: 330^{o}C HT	64.2	8330
20%: 19 micron, Raw & 80%: 120 micron Raw	54.4	7030
20%: 10 micron, 330^{o}C HT & 80%: 120 micron, 330^{o}C HT	61.6	8000
Optimized Mix, 330^{o}C HT + 1% Non-ionic additive	64.4	8360

In an effort to achieve optimum rheological performance, coal with a MMD of 200 microns was prepared for hydrothermal treatment due to its broad-ranged particle size distribution. After screening out the +850 microns (20 mesh) size portion of the feed, the actual average size of the coal sent through the PDU was only 72 microns. Table 24 and Figure 9 show the favorable rheological performance compared to the 80:20 blend. This shows that optimum particle size distribution can be achieved for feed to the PDU. In Figure 9, the particle size distribution of the hydrothermally treated product is compared to an optimum distribution range for maximum packing as predicted by a relation developed by Furnas and restated by Henderson (6,19). Although the coarse fraction of the particle size is skewed, the fit for the 72-micron hydrothermally treated product is arguably as good a fit as for the optimum grind mix shown in Figure 10. These results show that it is possible to obtain a sufficiently broad PSD hydrothermally treated coal product from a single grind raw feed to produce CWF with near-optimum packing.

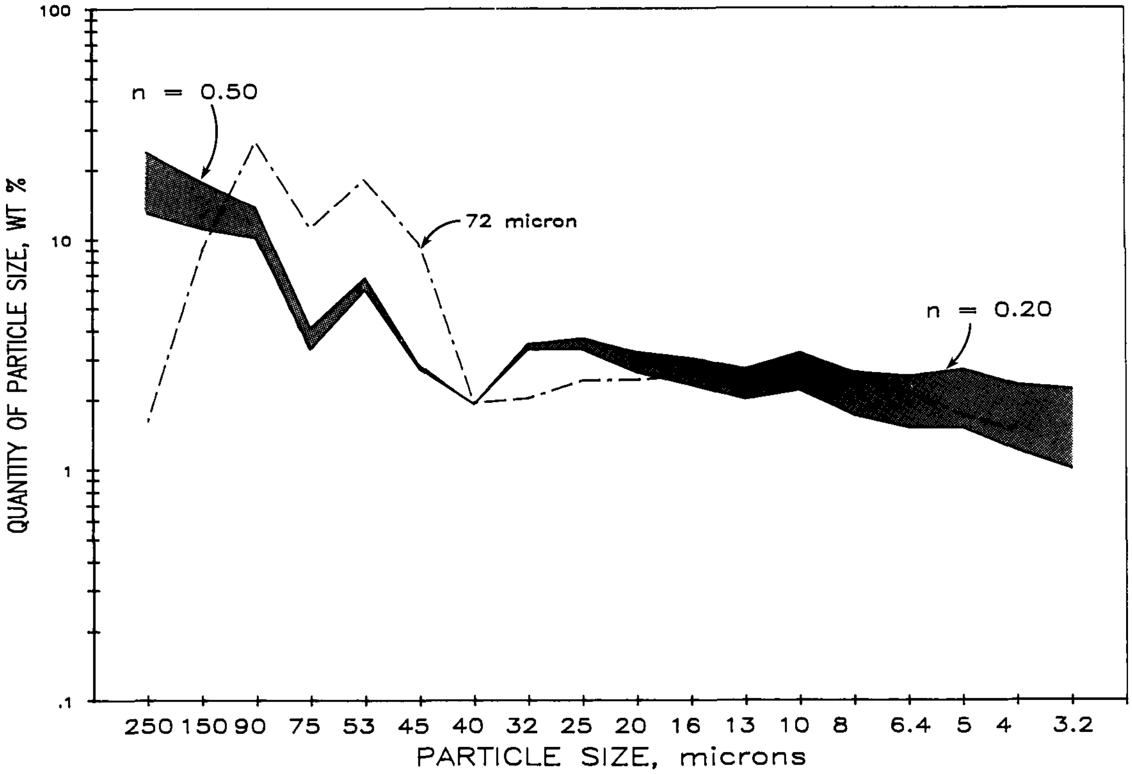

Figure 9. Particle size distribution for 72-micron HWD Kemmerer subbituminous coal as compared to an optimum size range, top size 425 microns

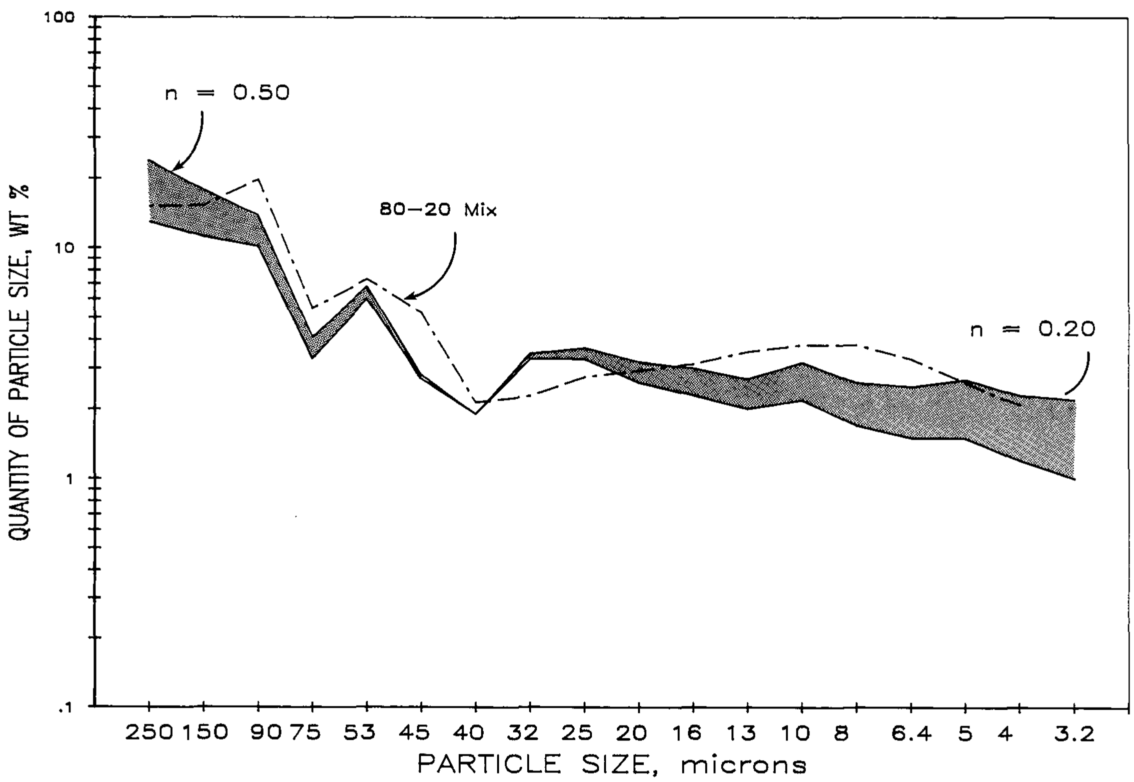

Figure 10. Particle size distribution for HWD Kemmerer subbituminous coal as compared to an optimum size range, Top Size 425 microns

The Furnas relation used above is widely accepted for mineral particle sizing. However, it has problems fitting the actual particle size distribution of pulverized coal and coal:water mixtures (20). The Rosin-Rammler formula (Equation 3) better defines the particle size distributions realized in coal processing and allows for graphical interpretation (21).

$$R = 100 \exp^{-(D/Dm)^{N}} \qquad [3]$$

R = cumulative weight percentage oversize
D = particle diameter in microns
Dm= the particle diameter at R = 36.7%
N = size distribution constant

Table 25, containing PDU data from Run 28 for combustion ground and micronized samples of four cleaned coals, indicates that Kemmerer and Velva micronized portions had high mean diameters of 19 microns. To increase packing efficiencies of CWF, the ideal micronized mean diameters should range from 8 to 10 microns to provide for an 8-to-1 size ratio when preparing a bimodal mixture (22). The Jacobs Ranch PSD fractions more closely approach this desired ratio.

TABLE 25

MASS MEAN DIAMETERS FOR VARIOUS COAL SAMPLES

	Cum. Data MMD (microns)		
	Jacobs Ranch	Velva	Kemmerer
Combustion Ground and Cleaned	41	38	41
Micronized and Cleaned	8	19	19
80% Comb. Ground and 20% Micronized	32	--	--
Optimum Grind[a]	31	--	--

[a] As predicted by the Rosin-Rammler equation with size distribution constant N = 0.9.

Figure 11 shows cumulative Jacobs Ranch coal data as a function of the natural log of particle size. A mixture of 80% combustion grind and 20% micronized coal was used to obtain the data. Optimum conditions were determined using the Rosin-Rammler equation with the size distribution constant equal to 0.9. This plot confirms that an 80:20 mix provides a near-optimum particle size distribution for the bimodal mixture. The mass mean diameter of the 80:20 mix was determined to be 32 microns compared to an optimum of 31 microns.

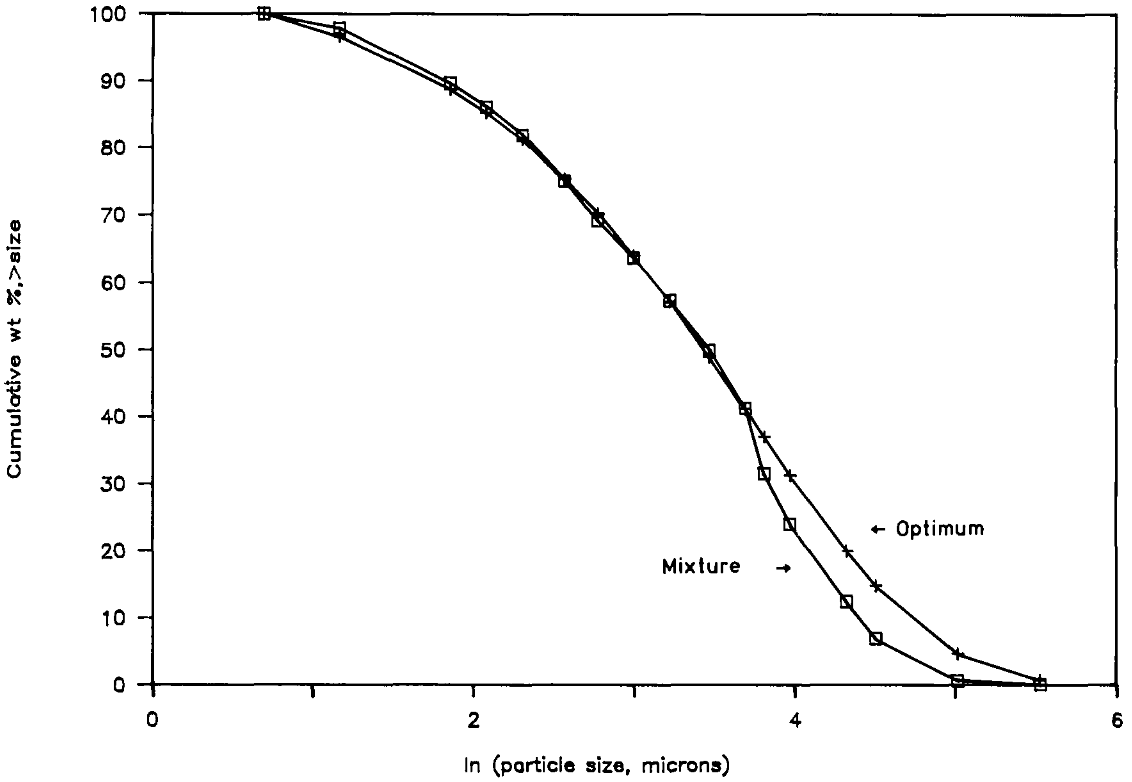

Figure 11. Rosin-Rammler plot for Jacobs Ranch 80:20 mix

It is important to note the poor solids content and energy densities for the micronized fuels, because of the narrow particle size distributions that are produced. Since reaction time and carbon burnout are critical in advanced combustion systems for residential applications, micronizing is necessary for bituminous coals and CWFs. This may not be the case for the highly reactive low-rank coals and coal/water fuels.

3.7.2 Rheological Characteristics

3.7.2.1 Background

The sensitivity of coal/water fuel flow behavior and appropriate viscosity to solids content and temperature are important parameters in designing storage and pumping circuits for slurry-fed combustors and gasifiers. Changes in slurry viscosity and other flow properties because of variations in solids content and temperature can drastically alter the energy requirements for pumping and the pressure requirements for atomization. Therefore, the primary objective has been to measure the influence of solids content and temperature on the flow properties (i.e., viscosity, yield stress, thixotropy) of slurries and fuels prepared from raw and beneficiated (through hydrothermal treatment and/or cleaning) low-rank coal.

3.7.2.2 Experimental Methods

The coal/water slurries produced in this study generally behaved as non-Newtonian fluids. The data produced during rheological studies ranged from single point values of shear stress at a shear rate to continuous rheograms of shear stress versus both increasing and decreasing shear rate. The experimentally observed data allowed the determination of the pseudo or apparent viscosity as the ratio of the measured shear stress divided by the shear rate. The rotational viscometer used to determine the flow characteristics of the coal/water slurries and fuels for this work was the Haake RV100 viscometer (6).

3.7.3 Results

3.7.3.1 Additive Study

Rheological studies were performed on physically and chemically cleaned PDU hydrothermally treated coals. Solids contents of 56.8, 57.6, and 56.5 wt% solids were achieved for the Velva, Kemmerer, and Jacobs Ranch low-rank coals, respectively, at a viscosity of 800 cP. These solids contents are as high or higher than those achieved for hydrothermally treated products which were not cleaned. This is significant because ash weight is included in solids content values and a significant portion of the ash was removed, thus increasing the fuel energy density for the samples.

A screening study was performed to determine the effectiveness of chemical additives for increasing the solids loadings for the clean CWFs. Table 26 lists the type and brand name of the additives screened and the dry solids contents that resulted for CWF made with cleaned, hydrothermally treated Velva lignite and 1 wt% additive for a viscosity of 800 cP.

TABLE 26

ADDITIVE SCREENING STUDY ON CWF MADE FROM VELVA LIGNITE WITH 1 WT% ADDITIVE ADDITION

Brand Name	Type	Dry Solids Content
No-additive	---	56.8
Norlig TSFL	anionic	56.6
A-23	anionic	56.2
T-Mulz	non-ionic	59.8
BASF-Pluronic L61	non-ionic	ineffective
BASF-Pluronic L64	non-ionic	ineffective
BASF-Pluronic F38	non-ionic	58.3
BASF-Pluronic F68	non-ionic	58.3
BASF-Pluronic F108	non-ionic	59.2
GAF Igepal-CO 990	non-ionic	58.7

Note: CWF viscosity was 800 cP at 100 sec^{-1}.

Generally, the non-ionic surfactants were more effective than the anionic dispersants tested. Addition of the anionic dispersants was ineffective, as no increase in solids content was realized for the two tested. The anionic additives disperse and stabilize solids by the principles of electrostatic dispersion or positive-negative charge. This phenomena was adversely affected by the ionic strength of the CWF aqueous medium. The ionic strength was possibly caused by residual acid from the chemical cleaning and other water-soluble ions in the aqueous medium of the CWF. The pH of the CWF from the clean products ranged from 4 to 5, rendering the anionic additives ineffective. The non-ionic surfactants behave on the principles of steric dispersion and stabilization, which are physical phenomena. Therefore, the non-ionic additives are generally insensitive to pH changes or ionic strength in aqueous medium. The high molecular weight BASF F series additives were effective on the clean Velva lignite in the screening tests. These additives are copolymers of ethylene-oxide and propylene-oxide. A higher series number relates to higher overall molecular weight. Figure 12 summarizes the screening study on the concentration performance of various non-ionic surfactants after being added to clean, HWD Velva lignite. The data shows that the BASF copolymers were the most effective, with F-108 slightly more effective than F-68. It is evident from Figure 12 that the additive consumption was higher for these samples than for the optimally packed CWFs (17). Particle optimization, by decreasing the additive dosages, increases the economic attractiveness of processing low-rank CWFs. The test matrix for the additive study was then extended to include Jacobs Ranch and optimum particle blends for the three coals. Results similar to those achieved for Velva were achieved for Jacobs Ranch and the 80:20 mixes. A complete summary of the additive study for the three test CWFs is listed in Table 27.

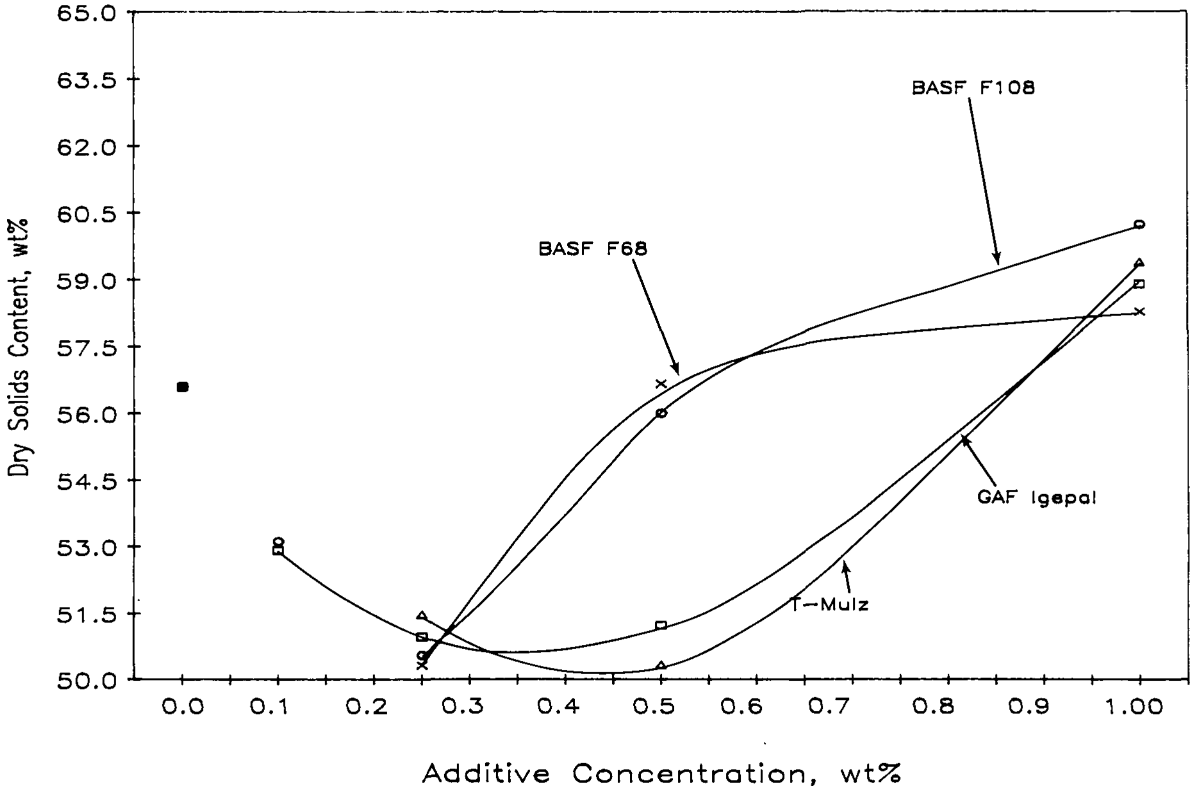

Figure 12. Additive performance of various non-ionic surfactants on CWF made from clean, hydrothermally treated Velva lignite

3.7.3.2 Stability Study

Long-term stability is a concern with coal/water fuel, especially when considering the fuel for residential, commercial, or industrial combustion applications. Depending on the percentages of soluble, multivalent cations in the coal, hot-water drying promotes stability in coal/water fuels prepared from low-rank coals by leaching available cations out of the coal. Physical and chemical cleaning of these low-rank coals removes the majority of these ions. To correct the lack of stability, it is necessary to use an additive to achieve the six-month stability desired in residential and commercial space heating.

Four CWFs were prepared with clean, hot-water-dried Velva lignite with xanthan gum concentrations of 0, 0.1, 0.2, and 0.3 wt%. The solids contents and viscosities of the mixtures were maintained at a level of approximately 56 wt% dry solids and 500 cP. The slurries have been observed qualitatively for stability for six months (Table 28).

TABLE 27

ADDITIVE PERFORMANCE OF VARIOUS NON-IONIC SURFACTANTS ON CLEAN, 330°C HYDROTHERMALLY TREATED LOW-RANK COALS AT AN APPARENT VISCOSITY OF 800 CP

Coal Type	Additive Type	Additive Conc. (wt%)	Mean Particle Diameter (microns)	Solids Conc. (dry wt%)	Energy Density (Btu/lb)
Velva	None	0.0	37	56.6	6340
	None	0.0	26*	55.4	6210
	BASF F68	0.25	37	50.4	5650
		0.5	37	56.7	6360
		1.0	37	58.3	6540
		1.0	26*	58.4	6550
	BASF F108	0.1	37	53.1	5950
		0.25	37	50.6	5670
		0.5	37	56.0	6280
		1.0	36	60.3	6760
		1.0	26*	61.2	6860
	BASF Pluradyne	0.1	37	56.6	6350
		0.25	37	56.2	6300
		0.5	37	58.4	6550
		1.0	37	59.4	6660
		1.0	26*	59.6	6680
	T-Mulz	0.25	37	51.5	5770
		0.5	37	50.4	5650
		1.0	36	59.4	6660
		1.0	26*	50.8	5700
	GAF CO-990	0.1	37	52.9	5930
		0.25	37	51.0	5720
		0.5	37	51.2	5740
		1.0	37	58.9	6600
Kemmerer	None	0.0	40	57.2	7280
	None	0.0	33.45*	60.4	7680
	BASF F68	1.0	40	57.7	7340
	BASF F108	1.0	40*	62.6	7960
	BASF Pluradyne	1.0	33.45*	60.5	7710
	T-Mulz	1.0	40	62.4	7940
Jacobs Ranch	None	0.0	41	56.0	6880
	BASF F68	1.0	41	58.2	7150
	BASF F108	1.0	32*	62.8	7710
	BASF Pluradyne	1.0	41	57.2	7020
	T-Mulz	1.0	41	58.2	7150

* 80% coarse (100 microns) and 20% fine (10 microns) coal mixture.

TABLE 28

STABILITY TESTING OF XANTHAN GUM ON CLEAN, HYDROTHERMALLY TREATED VELVA LIGNITE CWF

<table>
<tr><th>Xanthan Gum Conc.</th><th colspan="8">No. of Weeks Stored</th></tr>
<tr><th>(wt%)</th><th>3</th><th>6</th><th>9</th><th>12</th><th>15</th><th>18</th><th>21</th><th>24</th></tr>
<tr><td>0.0</td><td colspan="4">{soft packed}</td><td colspan="4">{significant hard packing}</td></tr>
<tr><td>0.1</td><td colspan="4">{some soft pack}</td><td colspan="4">{significant soft packing}</td></tr>
<tr><td>0.2</td><td colspan="6">{stable, slight yield stress}</td><td colspan="2">{soft packed}</td></tr>
<tr><td>0.3</td><td colspan="6">{stable, high yield stress}</td><td colspan="2">{soft packed}</td></tr>
</table>

After three weeks, a significant amount of soft pack settling was noticed in the sample without xanthan gum. The sample without xanthan gum then developed significant hard packing at the 15-week stage. Some soft packing was noticed in the 0.1 wt% sample after three weeks, developing into a soft pack after 12 weeks. The 0.2 and 0.3 CWFs remained stable throughout most of the observation period, developing slight soft packing at the end of the six months. Testing of the 0.2 and 0.3 wt% samples showed the 0.3 wt% had a significantly higher yield stress, which indicates that it was overdosed. This study indicates that the 0.2 wt% xanthan gum loading is sufficient for six-month storage stability of the cleaned Velva lignite CWF. In addition to stabilization compounds, formaldehyde added at 0.1 wt% is necessary to prevent mold growth.

3.8 Overall Fuel Performance

EMRC has begun compiling an additive package which would allow the low-rank CWFs to meet DOE energy density, flow behavior, and storage life specifications. Figures 13, 14, and 16 show apparent viscosity versus solids content at 100 sec^{-1} and 25°C for CWF made from the three cleaned and HWD coals. The rheological performance of the various formulations in all three cases shows that the F108 was effective in reducing viscosity for a given solids concentration when using an 80:20 mixture of fine coal to micronized coal. However, as stated under particle size results, the micronized portions of the Kemmerer and Velva CWFs were not small enough to benefit the particle packing significantly.

The most significant factor was that the stabilizer lowered the achievable viscosities at the 0.2% level, indicating that the stabilizer was slightly overdosed in all three cases. Work will continue in an effort to identify ways in which the additive package can be further developed in terms of performance and cost savings. Long-term stability was also affected by interaction between the stabilizer and the surfactant. Table 29 summarizes the fuel qualities realized to date for CWF at the 800 cP viscosity and 100 sec^{-1}.

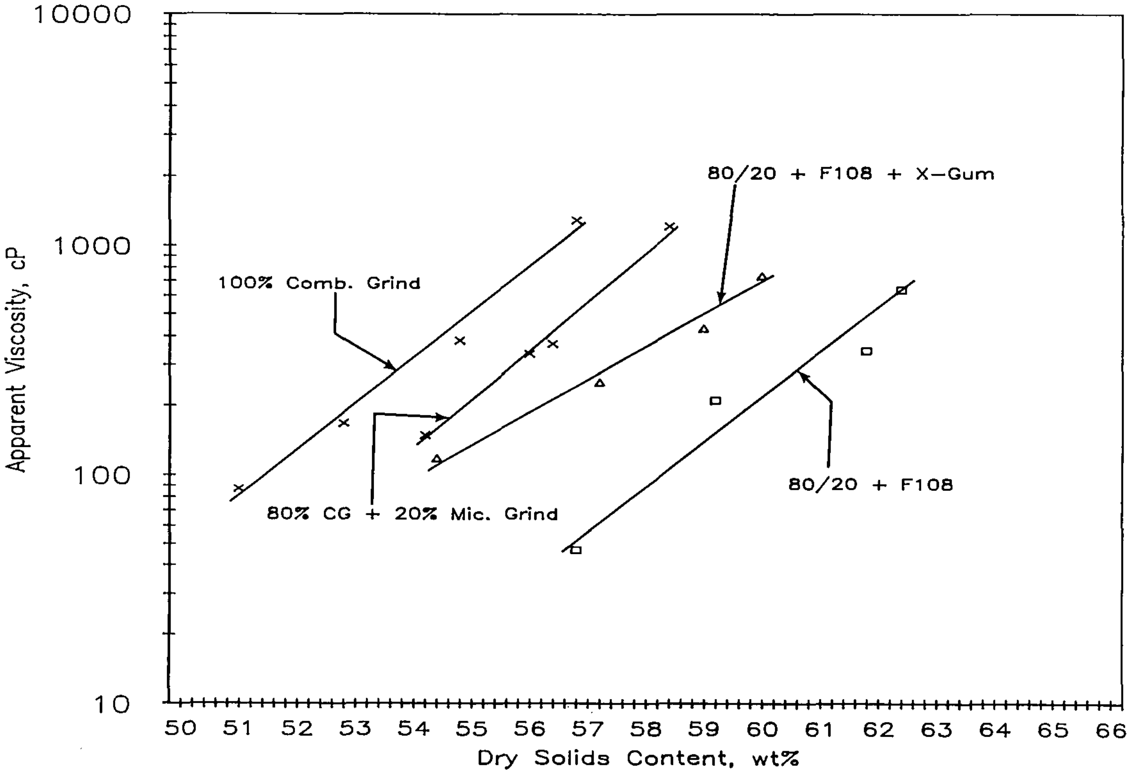

Figure 13. Rheological performance of CWF made from clean, HWD Jacobs Ranch subbituminous coal

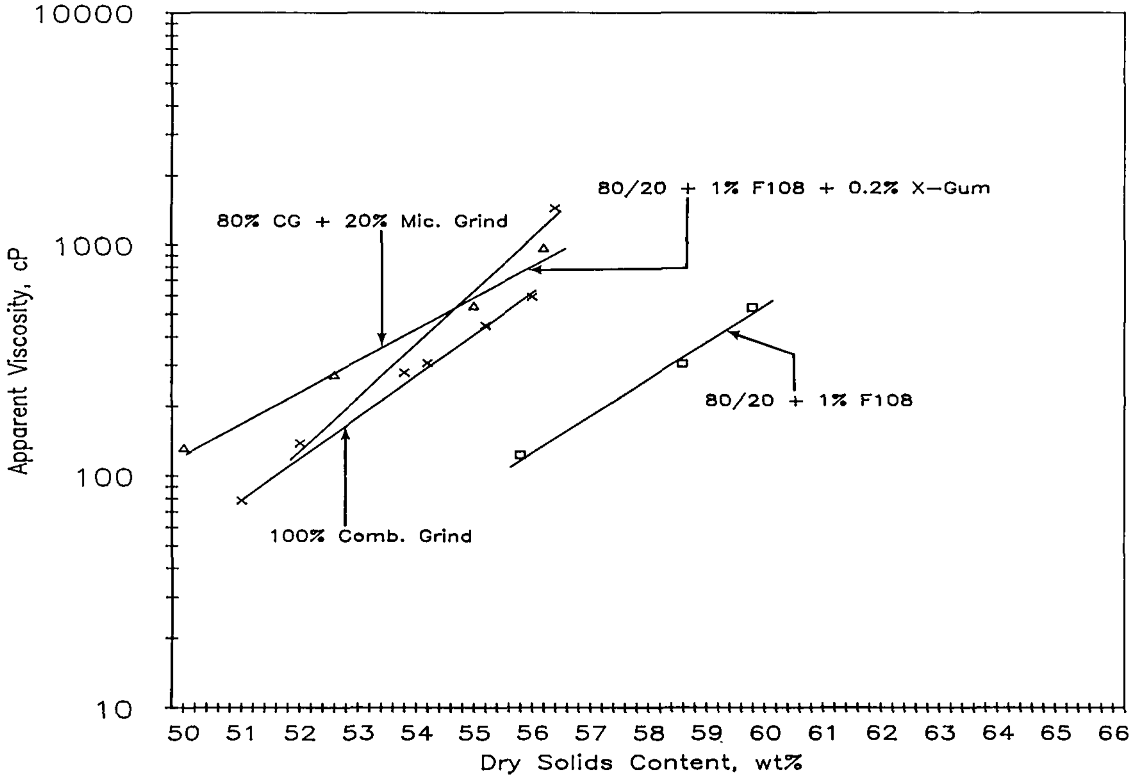

Figure 14. Rheological performance of CWF made from clean, HWD Velva lignite

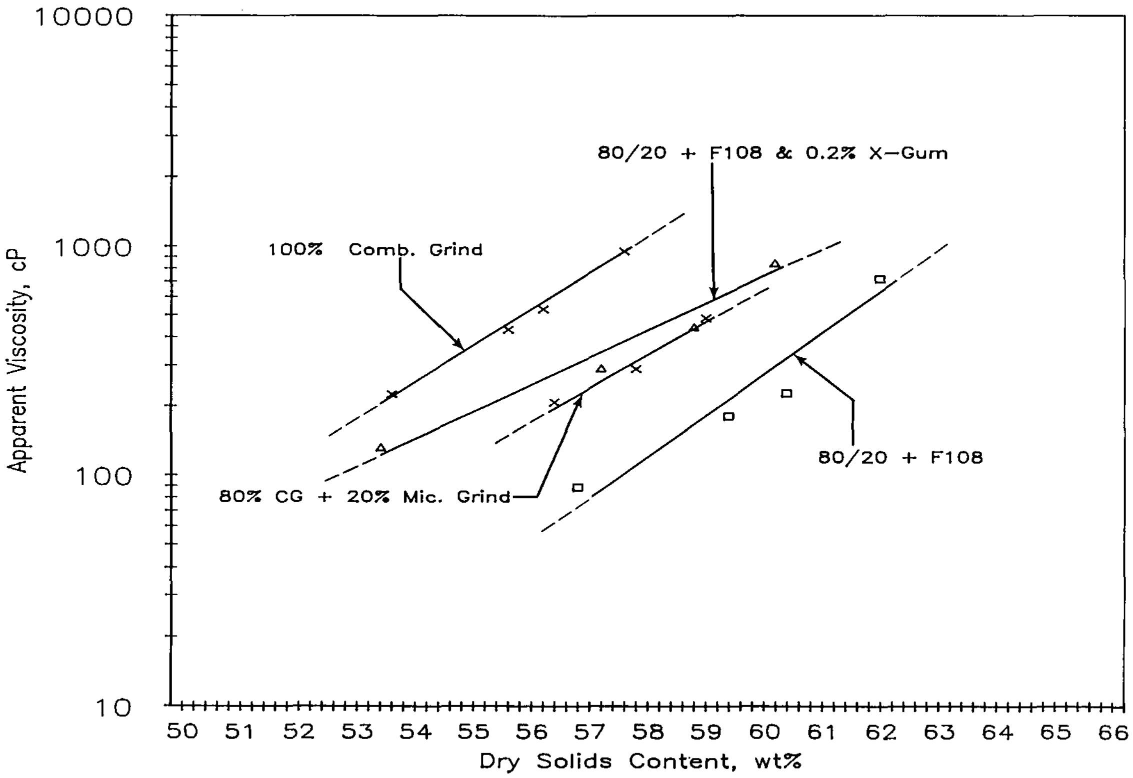

Figure 15. Rheological performance of CWF made from clean, HWD Kemmerer subbituminous coal

TABLE 29

SPECIFICATIONS FOR CWF PREPARED FROM CLEAN, HWD VELVA, KEMMERER, AND JACOBS RANCH LOW-RANK COALS

	Clean, HWD CWF Type		
Specification	Velva	Kemmerer	Jacobs Ranch
Wt% dry Solids @ 800 cP & 100 sec^{-1}			
(w/o stabilizer)	61.0	62.6	62.8
(w/ stabilizer)	56.2	60.4	60.4
Energy Density (Btu/lb)			
(w/o stab.)	7280	7960	7710
(w/ stab.)	6710	7680	7420
(mois. free)	11935	12714	12277
Wt% Ash Cont.			
(w/o stab.)	1.16	0.81	1.57
(w/ stab.)	1.07	0.79	1.51
(mois. free)	1.90	1.30	2.50

Depending on which additive is used, the flow behavior of the fuels can be generally characterized as yield pseudoplastic (viscosity reduction with increased shear rate after an initial yield stress), or near Newtonian. An example of the flow behavior exhibited for the Jacobs Ranch CWFs is shown in Figure 16 as shear stress versus shear rate rheograms over the shear rate range of 0 to 450 $\sec^{-1}$. However, the flow behavior of the fuels with the surfactant added alone were slightly dilatant (viscosity increase with increased shear rate). Similar flow behavior results were also obtained for the Kemmerer and Velva CWFs. The shear stress versus shear rate data was fit to the yield power law model according to the equation:

$$Y = Y_0 + KX^N \qquad [4]$$

where Y is the shear stress in Pascals, Y_0 is the yield stress in Pascals, K is the consistency factor in cP, x is the shear rate in $\sec^{-1}$ and N is the dimensionless flow factor (23). The flow factor is a barometer of the flow behavior of the fluid. If the flow factor is greater than 1, the fluid is dilatant, if less than 1 it is pseudoplastic, and if it is equal to 1 it is Newtonian. Table 30 summarizes the data for the CWFs studied.

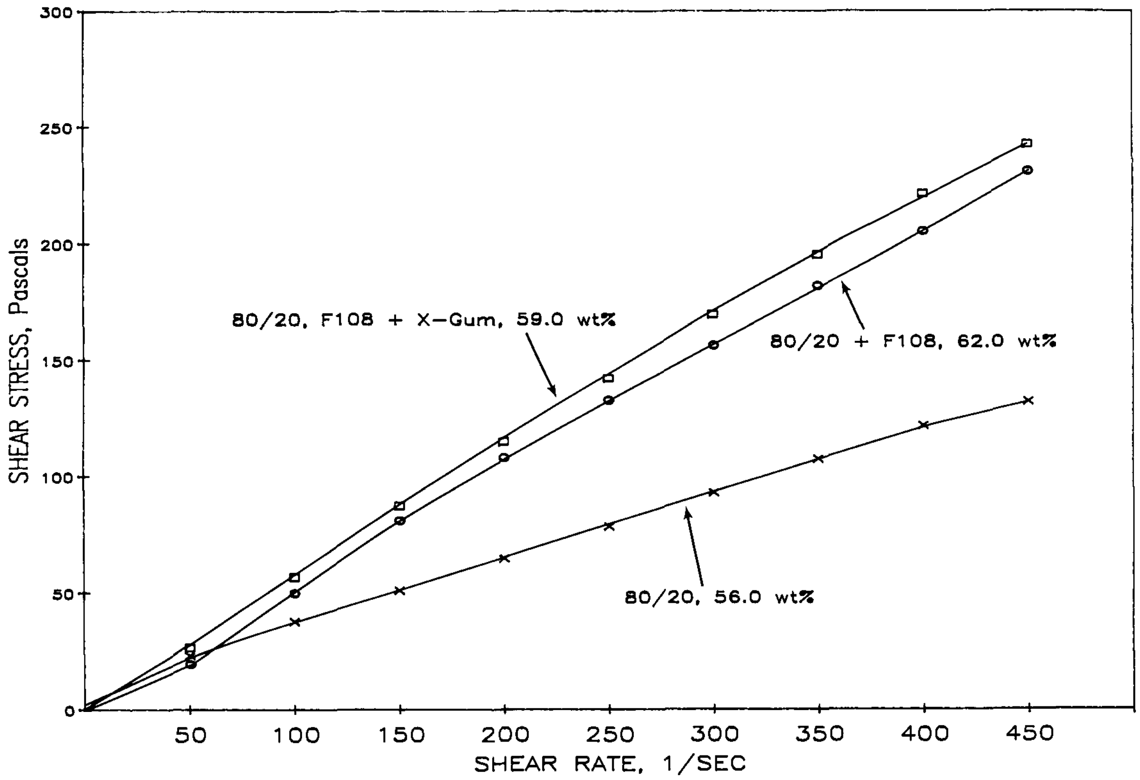

Figure 16. Shear stress vs. shear rate for CWF made from clean, HWD Jacobs Ranch subbituminous coal

TABLE 30

YIELD POWER LAW FLOW BEHAVIOR FOR CLEAN, HWD VELVA, KEMMERER AND JACOBS RANCH CWFS AT 25°C

CWF Type	Solids Content (wt% MF)	Yield Stress (Pascals)	Consis. Factor (cP)	Flow Index	Corr. Coeff.
Jacobs Ranch CWF					
80:20 mix, no add.	56.0	5.64	431.5	0.931	1.000
80:20 mix, + F108	62.0	0.79	182.0	1.18	0.999
80:20, F108 + X-gum	59.0	0.32	331.2	1.08	1.000
Kemmerer CWF					
80:20 mix, no add.	57.8	5.64	668.7	0.862	0.999
80:20 mix, + F108	60.4	0.00	102.1	1.24	0.999
80:20, F108 + X-gum	58.8	0.26	497.3	0.987	1.000
Velva CWF					
80:20 mix, no add.	56.0	5.64	431.5	0.931	1.000
80:20 mix, + F108	59.8	0.00	152.4	1.31	0.998
80:20, F108 + X-gum	55.0	5.00	467.0	1.01	0.999

3.9 Rheological Studies at Conditions Above Ambient

Significant efforts were made to develop a more continuous means of conducting rheological testing with the D100/300 sensor system (6). A new configuration allows continuous measurements of temperature and viscosity.

A screening test on various CWF dispersing agents yielded F108 as the most effective additive according to solid loadings of clean CWFs. Figure 17, a plot of apparent viscosity versus temperature, indicates that surfactant F108 additive degrades the raw Velva sample as the temperature increases from 30° to 90°C. However, by adding a stabilizing agent, xanthan gum, to the raw Velva and F108, the fuel was stabilized for the complete temperature range of 30° to 270°C. This is indicated by Figure 18. It should be noted that, by adding anionic dispersants, no noticeable degradation occurred with increasing temperature for raw coal samples (6).

Figures 19 and 20 show the effect of temperature on HWD CWFs. From the figures, a distinct increase in viscosity occurs from 210° to 240°C for the HWD Velva and HWD Beulah. This is due to surface tars that have formed in the HWD samples and the plasticity characteristics of the tars.

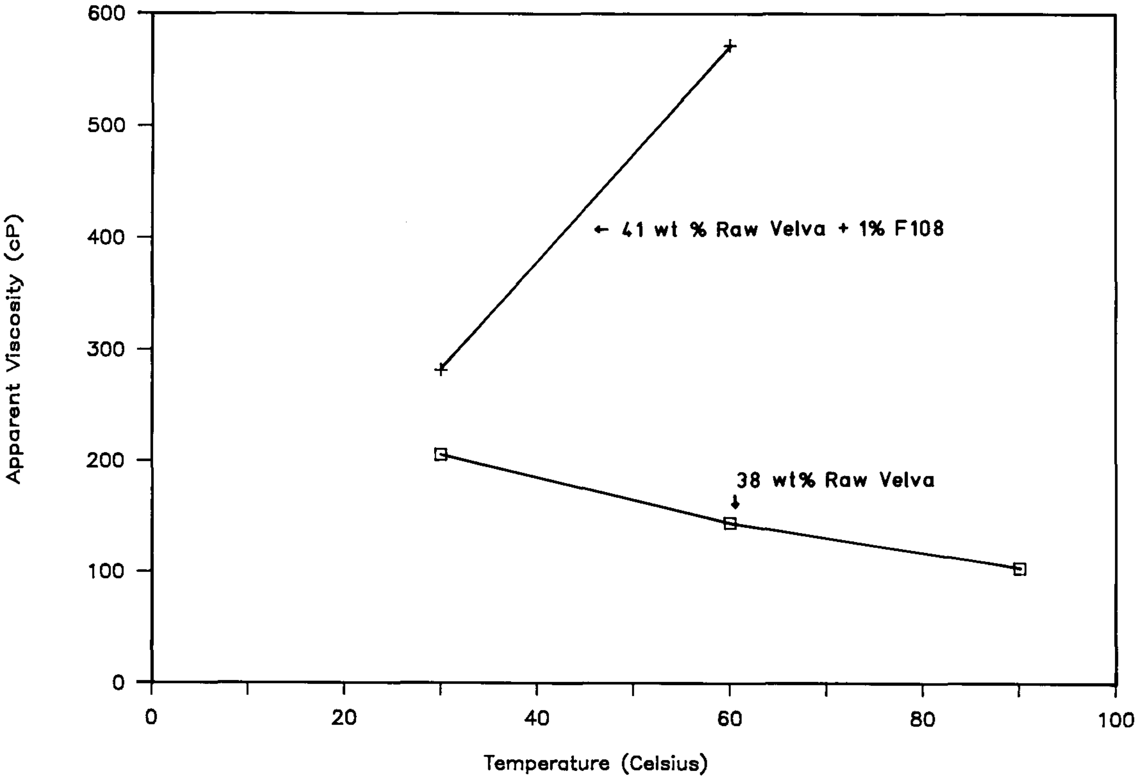

Figure 17. High temperature/high presssure for raw Velva lignite and raw Velva plus 1 wt% F108

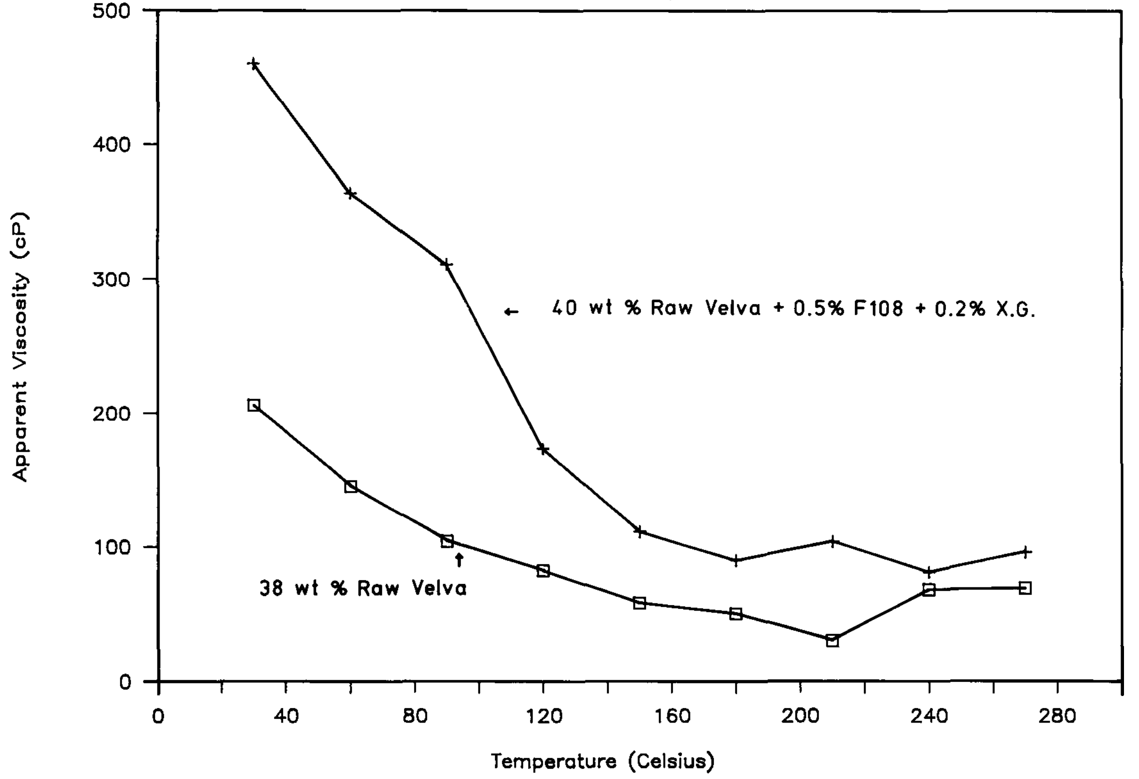

Figure 18. High temperature/high pressure for raw Velva lignite and raw Velva plus additives

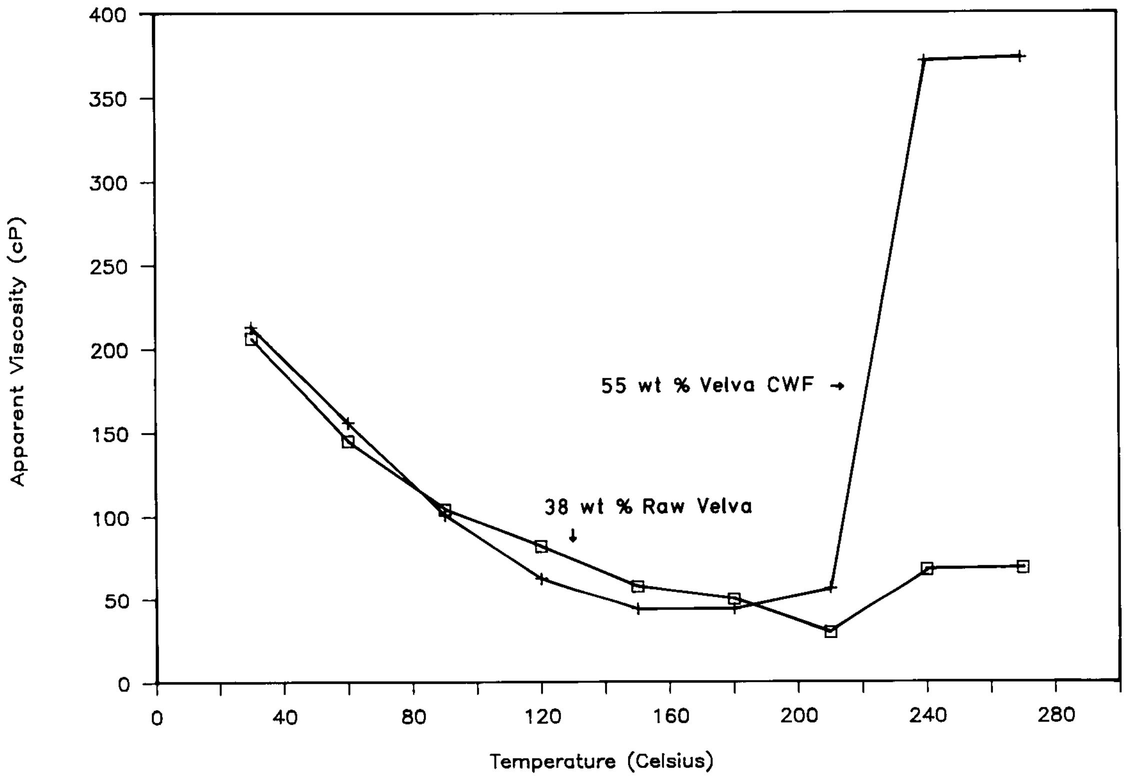

Figure 19. High temperatuare/high pressure for raw Velva lignite and HWD 330°C Velva

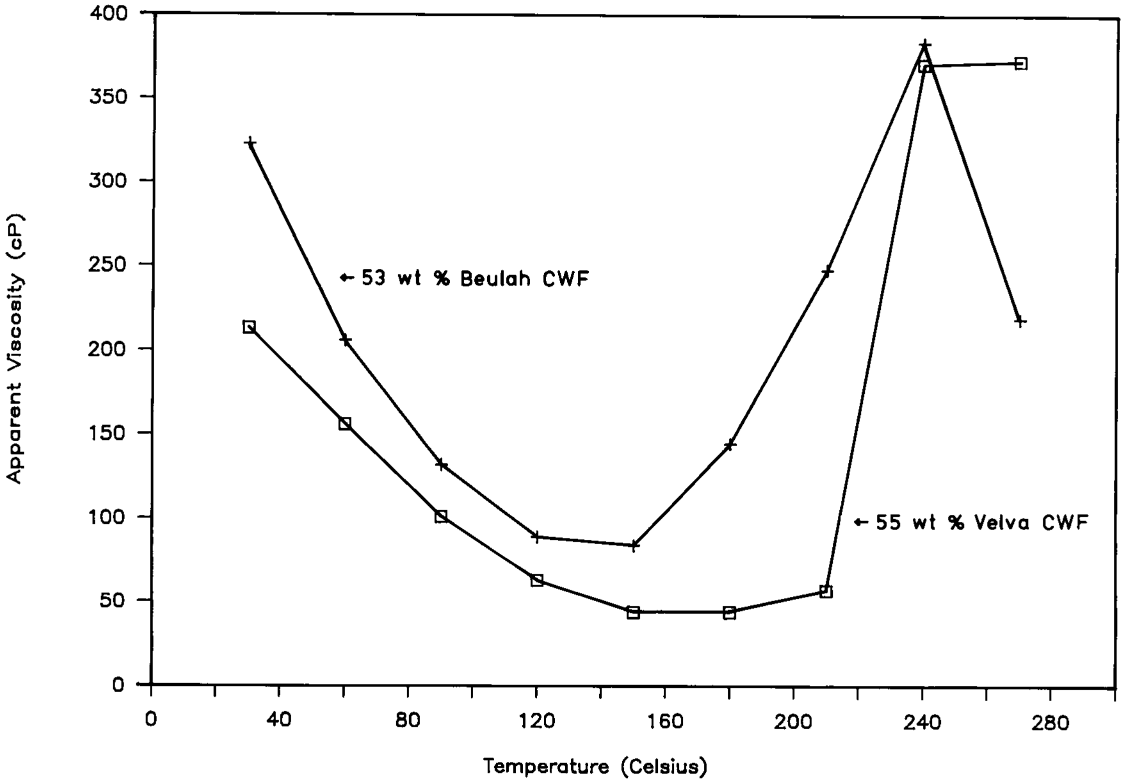

Figure 20. High temperature/high pressure for HWD 330°C Velva lignite and HWD 330°C Beulah lignite

3.10 Freeze-Thaw Study

Testing was recently completed at UNDEMRC on Jacobs Ranch CWF to investigate its resiliency to freeze-thaw effects concerning rheology and stability. Shear stress versus shear rate relationships were used to identify the before-and-after flow behavior characteristics of the fuel.

Five coal/water mixtures were prepared using raw, chemically cleaned, and hot-water-dried samples of Jacobs Ranch coal. In addition, various stabilizers and additives, used to improve the overall fuel performance, were added according to weight percentage of the total weight of the mixture. The coal/water mixtures were frozen for 72 hours at -5°C at approximately atmospheric pressure. The CWFs were then thawed at 25°C for 48 hours and remixed. Rheological testing was completed on the mixtures. Table 31 is a complete summary of the freeze-thaw testing on Jacobs Ranch samples at an apparent viscosity of 100 sec^{-1}.

TABLE 31

JACOBS RANCH COAL/WATER FUELS, BEFORE-AND-AFTER FREEZE-THAW

Mixture	BEFORE Solids (%wt)	Visc. (cp)	AFTER Solids (%wt)	Visc. (cP)
1. Raw	44.82	385	45.50	406
2. Clean, HWD	58.72	584	59.23	666
3. Clean, HWD, 80:20 Mix	59.27	614	59.15	752
4. Clean, HWD, 80:20 Mix, 1% F108, 0.1% Form.	60.86	397	60.67	594
5. Clean, HWD, 80:20 Mix, 1% F108, 0.2% Xanthan Gum, 0.1% Formaldehyde	60.38	438	60.70	457

Results from the freeze-thaw testing show slight increases in solid percentages coupled with an increasing viscosity ranging from 5% to 20% of the original sample. These increases can mainly be attributed to evaporation during the testing process. The low solids and viscosity increases indicate that the Jacobs Ranch mixtures were relatively unaffected by the process.

The CWFs were also quite stable before and after freezing. However, some observations are worth noting. Rheological data on the HWD sample exhibited a noticeable difference in flow behavior. The sample was pseudoplastic before freezing, but exhibited yield pseudoplastic characteristics after freezing. Another distinct flow behavior difference occurred in the 80:20 mix where a slight increase in pseudoplasticity was noticed. It is not readily apparent why these slight changes occurred. Both raw samples indicated yield pseudoplastic behavior, while no flow behavior changes were noticed in the complete additive package of F-108 and xanthan gum. Therefore, coal/water mixtures containing additives and stabilizers can be frozen, thawed, and remixed without any major stability or viscosity changes occurring to the fuel.

3.11 Fuel Economics

Using physical data determined by pilot-scale preparation at UNDEMRC, cost estimations were completed on Jacobs Ranch and Velva coals based on the rheological performance of the fuel. Estimations of cost per million Btu (MMBtu) and per ton of CWF were based on revision of an October 15, 1986, clean, low-rank CWF feasibility study by Dana Maas and Frank Smit (18).

Table 32 consists of operating costs for various production schemes for a combustion ground, low-rank coal fuel plant producing 650,000 tons per year. Elements varied in production included physical cleaning, chemical cleaning, hot-water drying, and an additive package of BASF F-108 dispersant and xanthan gum. Micronizing the fuel would result in a $0.25 - $0.35/MMBtu increase in fuel costs due to the additional processing and reduced rheological performance (18). Operating cost estimations for Jacobs Ranch CWF ranged from $1.90/MMBtu to $4.10/MMBtu, while Velva estimations varied from $2.22/MMBtu to $4.50/MMBtu, depending on which production scheme was implemented.

TABLE 32

OPERATING COSTS FOR VARIOUS SCHEMATIC PLANS
FOR A 650,000 TON/YEAR CWF PLANT

Specific Cost	Jacobs Ranch		Velva	
	$/MMBtu	$/ton CWF	$/MMBtu	$/ton CWF
Raw Coal	0.33	4.8	0.50	6.8
Physical Cleaning	0.28	4.1	0.28	3.9
Chemical Cleaning	1.17	17.4	1.22	16.6
Hot-Water-Drying	1.90	28.3	2.22	30.2
Additives[a]	0.75	11.1	0.78	10.4
Phys. Cleaning and Hot-Water-Drying	2.18	32.4	2.50	34.1
Phys. Cleaning, Hot-Water-Drying, with Additives	2.93	43.5	3.28	44.5
Physical Cleaning, Chemical Cleaning, Hot-Water-Drying, with Additives	4.10	60.9	4.50	61.1

[a] Additives: BASF F-108 and Xanthan Gum

Because of the high cost for surfactant BASF F-108, additional dispersants were screened. The addition of ammonium ligno-sulfonate increased the quality of the fuel at a reduced cost of $0.30/lb. Table 33 consists of operating estimations using ALS as a fuel dispersant. Jacobs Ranch CWF ranged from $1.90/MMBtu to $3.78/MMBtu and Velva CWF estimations were adjusted from $2.22/MMBtu to $4.18/MMBtu. Additional production refinements currently being researched at UNDEMRC on the HWD technique may also adjust the cost estimations and improve the economic scenario for low-rank coal fuel production.

Included in the operating cost estimations were coal at the mine and physical cleaning costs, labor cost, utilities expense, general maintenance cost, fix charges on capital investment, and reagent costs.

TABLE 33

OPERATING COSTS FOR VARIOUS SCHEMATIC PLANS FOR A 650,000 TON/YEAR CWF PLANT

	Jacobs Ranch		Velva	
Processing Scheme	$/MMBtu	$/ton CWF	$/MMBtu	$/ton CWF
Raw Coal	0.33	4.8	0.50	6.8
Physical Cleaning	0.28	4.1	0.28	3.9
Chemical Cleaning	1.17	17.4	1.22	16.6
Hot-Water-Drying	1.90	28.3	2.22	30.2
Additives[a]	0.30	4.4	0.31	4.4
Phys. Cleaning and Hot-Water-Drying	2.18	32.4	2.50	34.1
Phys. Cleaning, Hot-Water-Drying, with Additives	2.48	36.8	2.81	38.3
Physical Cleaning, Chemical Cleaning, Hot-Water-Drying, with Additives	3.78	56.2	4.18	56.9

[a] Additives: Ammonium ligno-sulfunate and Xanthan Gum

3.11.1 Coal at Mine and Physical Cleaning

Coal at Mine rates were determined to be \$8/ton and \$12/ton for Wyoming and North Dakota mines, respectively. The physical coal cleaning costs include magnetite separation of the coal.

3.11.2 Labor

Labor requirements for the coal/water fuel plant were based upon Wyoming wage estimations.

3.11.3 Utilities

Refinements to the AMAX report to lower projected electricity costs include replacing stirred-ball mill grinders with a 2000 hp Attritor wet grinder and replacing Dowtherm Heaters with a continuous fluidized bed reactor capable of generating power from the coal.

3.11.4 Reagents

Reagent costs were evaluated using 100% basis, per ton of fuel.

	Amount	Price	Source
1. Magnetite	(3.4 lb)	(\$120/ton)	from Amax report
2. Dispersant	(15 lb)	(\$0.85/lb)	BASF Corp. (M.J.)
3. Dispersant	(15 lb)	(\$0.30/lb)	Reed-Lignin Co.
4. Formaldehyde	(1.4 lb)	(\$0.25/lb)	Chem. Mark. Rep.
5. Nitric Acid	(250 lb)	(\$195/ton)	Chem. Mark. Rep.
6. Xanthan Gum	(4 lb)	(\$0.20/lb)	Pfizer Corp.(R.K.)
7. Ammonia	(2.8 lb)	(\$210/ton)	from Amax report

3.11.5 General Maintenance and Materials

Maintenance estimates were based on a fixed rate of 3% of the total capital investment. The materials section includes grinding media and various filter aids that are needed for processing the coal.

3.11.6 Fixed Charges

Charges included an estimation for capital amortization at 12% for a 20-year plant based on the total capital.

3.12 Coal/Water Fuel Wastewater Treatment

3.12.1 Introduction

The production of coal/water fuel (CWF) by the hot-water coal drying process results in the generation of process wastewater. Due to the hydrothermal coal dewatering process, a portion of the sodium and other water-soluble inorganic constituents are removed from the coal particles to the aqueous medium. Additionally, water-soluble organic contaminants are extracted from the fine coal particles into the water. Mechanical concentration of the processed coal results in the CWF product and a contaminated wastewater by-product which contains coal fines.

The contaminated process wastewater stream must be treated prior to reuse or discharge to the environment. Treatment of the wastewater for process reuse is generally considered to be the option of choice, as the majority of the United States' coal reserves which would be amenable to commercial-scale slurry pipelining are situated in semi-arid to arid climates. However, discharge of the treated effluent to a receiving body may be preferred in a few special cases.

The centrate from mechanical concentration (continuous centrifugation) collected after hydrothermal processing of Jacobs Ranch subbituminous coal was used for the treatability studies.

3.12.2 Objectives

The objectives of the CWF wastewater treatment studies were to:

1. Test physical and/or chemical methods of reducing the concentration of total suspended solids and evaluate the potential for solids recovery,
2. Determine the constituent(s) which contribute to unaccounted chemical oxygen demand (COD) and total organic carbon (TOC),
3. Utilize bench-scale activated sludge systems to obtain process performance data and develop kinetic parameters obtained during steady-state operation at four mean cell residence times (MCRT), and
4. Evaluate alternative methods available for treatment of this type of wastewater.

3.12.3 Results

3.12.3.1 Suspended Solids Removal

Partial chemical characterization was performed on raw Jacobs Ranch CWF centrate. Results of the characterization analyses are shown in Table 34. Total suspended solids in the CWF centrate are high (35,970 mg/l) with respect to wastewater treatment.

Any successful treatment process must address the reduction of suspended solids prior to subsequent treatment processes. Two methods of suspended solids removal were investigated for CWF product recovery and pretreatment for subsequent wastewater treatment processes. The first method was chemical coagulation/precipitation using standard jar testing procedures. The second method investigated was ultrafiltration of the CWF centrate.

TABLE 34

RESULTS OF PARTIAL CHARACTERIZATION OF JACOBS RANCH CWF CENTRATE

Parameter/Constituent	Value[a]
pH	6.9
Alkalinity (as $CaCO_3$)	740
Ammonia	40
Chemical Oxygen Demand (COD)	4800
Biochemical Oxygen Demand (BOD)	780
Total Carbon	1860
Total Inorganic Carbon	740
Total Organic Carbon (TOC)	1120
Cyanide	0.15
Acetate	28
Formate	93
Propionate	58
Phenol	5
O-Cresol	<5
P,M-Cresol	<5
Methanol	49
Acetone	14
Total Dissolved Solids	4390
Total Suspended Solids	35970
Arsenic	<0.01
Barium	18
Boron	3.4
Cadmium	<0.04
Calcium	390
Chromium	0.5
Iron	92
Lead	<0.6
Magnesium	110
Mercury	<0.04
Phosphorus	27
Potassium	36
Selenium	<0.02
Silicon	84
Silver	<0.5
Sodium	340

[a] All values expressed in mg/l, except pH.

3.12.3.2 Coagulation/Precipitation

Aluminum sulfate and ferric sulfate were two coagulants tested without producing favorable results. Initial jar tests with acidification of the raw CWF centrate resulted in solids separation of 200 ml solids per liter of wastewater at a dosage of one ml/l of concentrated sulfuric acid. However, these results could not be duplicated with wastewater samples that had been stored for a period of approximately two months. The characteristics of the wastewater had apparently changed during storage. Subsequent tests designed to optimize the volume of acid required to induce separation on the stored wastewater samples, and to determine the most economical type of acid to be used, produced only a 900 ml/l solids separation, even at high acid doses (6 ml/l). Batch, high-speed centrifugation of acidified samples produced excellent solid-liquid separation. However centrifugation of 18 liters of acidified wastewater through the PDU continuous centrifuge resulted in very poor, if any, solids separation.

Due to the encouraging initial jar testing results on fresh wastewater samples, additional efforts should be directed at coagulation/precipitation for the separation of colloidal suspended solids from fresh CWF centrate.

3.12.3.3 Ultrafiltration

Ultrafiltration is a membrane process for the separation of solids and high molecular weight dissolved materials from liquids. Low molecular weight species, such as salts, pass through the membrane and are removed in the permeate. Suspended solids and colloids are rejected by the membrane and are concentrated. Process fluids flow past the membrane surface at high velocity, as opposed to the characteristic perpendicular flow of conventional filtration. The cross-flow pattern prevents cake buildup on the membrane surface, resulting in higher filtration rates and extended filter runs.

3.12.3.3.1 Equipment and Procedures

Figure 21 is a schematic diagram of the ultrafiltration system used during the study. The system consisted of a stainless steel storage vessel with an approximate volume of 225 liters, a pneumatic diaphragm pump, a pressure surge dampening chamber, a micromotion flowmeter capable of reading both instantaneous and cumulative flows, two ultrafilter membranes, and pressure gauges. Further operations and procedure descriptions have been made elsewhere (12).

3.12.3.3.2 Results of Ultrafiltration

The ultrafiltration system was tested initially with CWF centrate produced from an acid-cleaned coal for shakedown purposes. Only one of the two membranes was used to ensure that, if irreversible fouling of the membrane occurred, one good membrane would still be available for the Jacobs Ranch wastewater testing. The ultrafilter was tested until the flux rate remained stable over a period of several days.

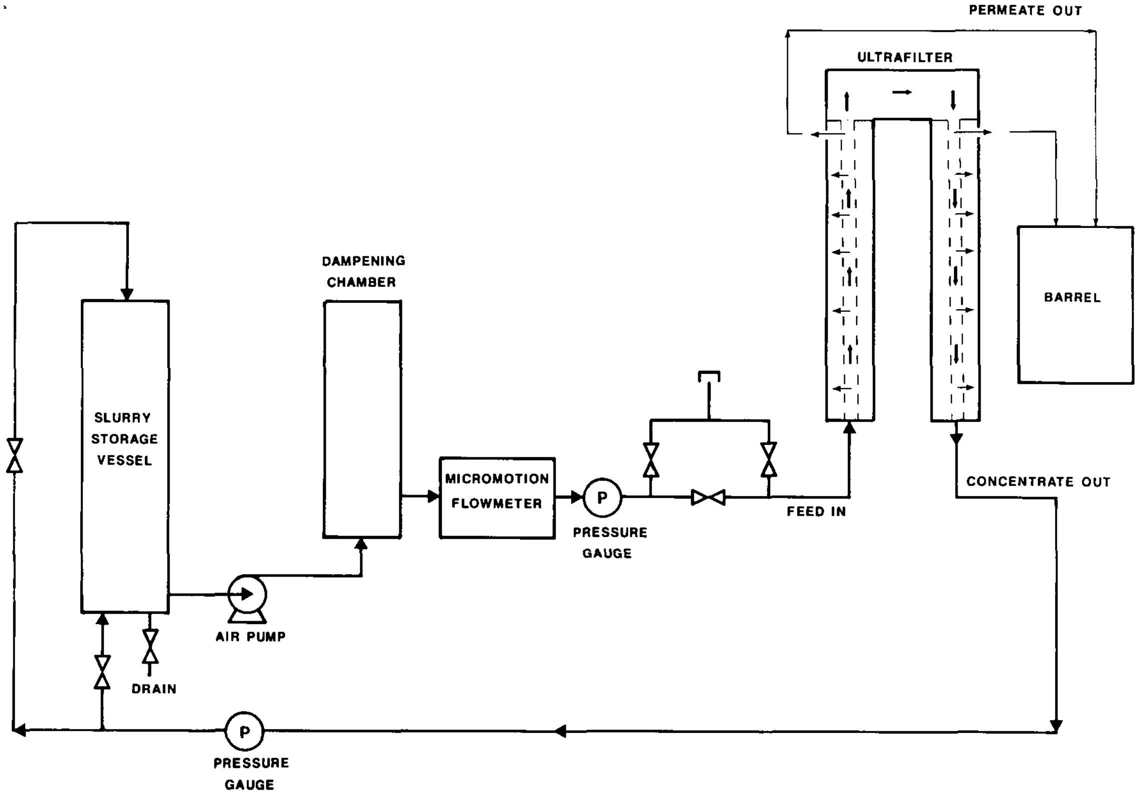

Figure 21. Schematic of ultrafiltration test system

A matrix of tests was designed using temperature and concentration as the independent variables and flux as the dependent variable. The temperatures were varied from 22° to 49°C. The lower temperature was used since it is about the lowest practical temperature to which the centrate could be cooled in a commercial plant. The higher temperature was chosen because it is the upper limit recommended for the PVC pipe housing for the ultrafilter membrane. A concentration range from 5 to 25 wt% was used. If the ultrafilter was to be operated for the purpose of mixing ultrafilter concentrate with the centrifuge cake to produce CWF, the ultrafilter concentrate would need to contain between 5 and 25 wt% solids, depending upon the type of coal used. In the case of the Jacobs Ranch CWF, for every 62.5 lbs of 70 wt% centrifuge cake produced, 37.5 lbs of 3.3 wt% centrate would be produced. If the centrate was concentrated to 9.8 wt% and mixed with the 70 wt% filter cake, the desired 60 wt% CWF would be produced. However, different coal types produce different solids percentages for both the centrifuge cake and the centrate. Both of the ultrafilter membrane types were used since the previous testing had indicated that the centrate would not irreversibly foul the membranes. A 2 x 2 matrix with replicated midpoints, shown in Table 35, was designed and tested. In all cases, the flux remained relatively stable during the four hours of readings. It should be noted that only six data points were used, but that each data point actually contains two responses (one response for each membrane).

TABLE 35

ULTRAFILTER FLUX RATE TESTING TEMPERATURE AND CONCENTRATION STUDY PERFORMED ON JACOBS RANCH CENTRATE

Test Sequence	Temperature (°C)	Concentration (wt%)
1	35	15
2	49	5
3	21	5
4	35	15
5	49	25
6	21	25

A computer model was formulated to predict the flux through the ultrafilter membranes based on seven separate effects. The seven effects included in the model were concentration, temperature, membrane type, a cross product between concentration and temperature, a cross product between concentration and type, a cross product between temperature and type, and, finally, a term indicating curvature. The twelve observations from the six tests were then used to predict the average flux and the contribution to the flux from each of the seven effects. The observed flux rates were also used to indicate which of the effects were significant at the 0.10 significance level, using forward, backward, and maximum R-Square procedures. The forward procedure consecutively adds the most significant term to the intercept until the last term added is not significant at the 0.10 significance level. The backward procedure starts with the full model and eliminates effects until all of the terms left are significant at the 0.10 significance level. Finally, the maximum R-Square procedure calculates which effects would be consecutively added to the model to indicate the maximum R-Square. All three of the methods indicated that a model using all of the above effects, with the exception of a cross product between temperature and membrane type, and curvature was the most appropriate model. Table 36 shows the variables, parameter estimates, standard errors, sum of squares, F-ratio, and probability of being significant for each of the effects. The effects are listed in order of significance. Curvature of the model was not indicated at the 0.10 significance level, suggesting that a linear model is sufficient. An R-square of 0.97 indicates a reasonably good model for the flux determination. A plot of the measured flux versus the predicted flux by the model can be seen in Figure 22. The 45-degree line indicates where a perfect fit between the model and the data would lie.

TABLE 36

STATISTICS ON ULTRAFILTRATION FLUX OF JACOBS RANCH CWF CENTRATE

R-square = 0.97

	DF	Sum of Squares	Mean Square	F	Prob > F
Regression	5	14190	2840	36.1	0.0002
Error	6	471	78.5		
Total	11	14660			

Variable	Parameter Estimate	Standard Error	Type II Sum of Squares	F	Prob > F
Intercept	60.4	2.6	43800	558	0.0001
Concentration	-36.5	3.1	10650	136	0.0001
Temperature	15.5	3.1	1930	25	0.0026
Type	8.1	2.6	790	10	0.0192
Conc X Temp	-8	3.1	516	6.6	0.0426
Conc X Type	-6.1	3.1	301	3.8	0.098

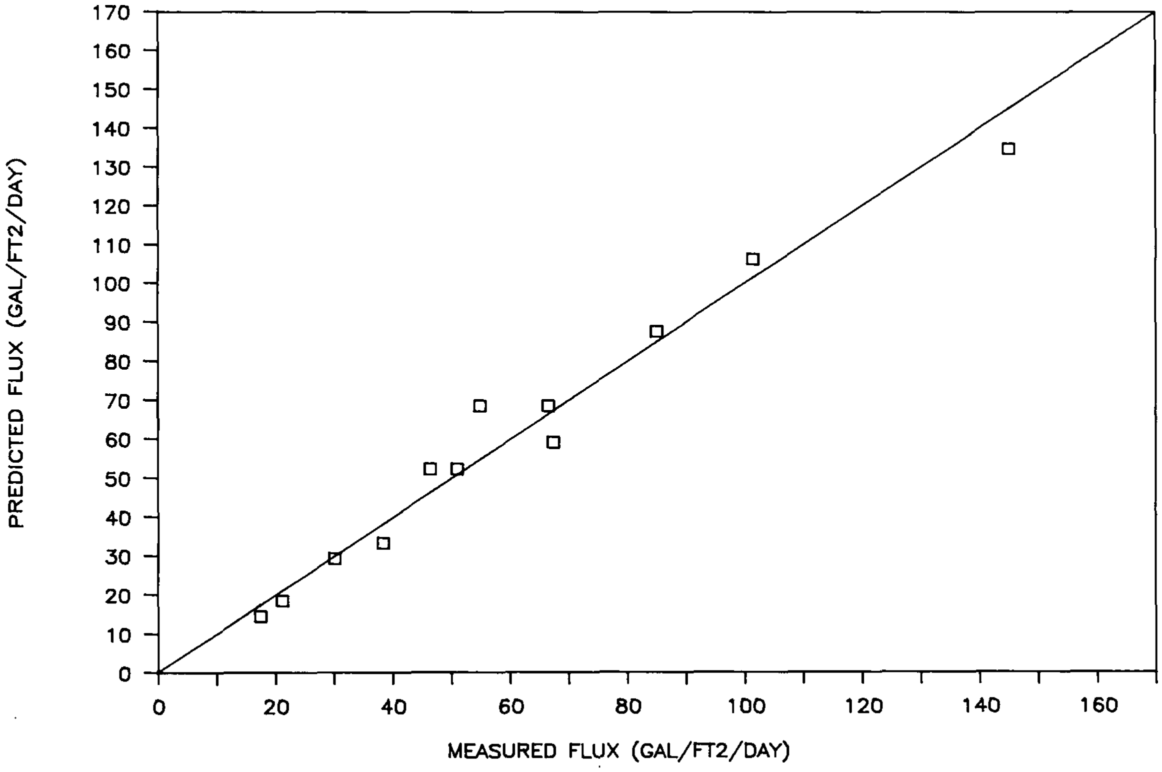

Figure 22. Measured vs. predicted flux for ultrafiltration of CWF

The model equation for determining the flux would be:

$$\text{Flux} = 60.4 - 36.5*X1 + 15.5*X2 + 8.1*X3 - 8.0*X1*X2 - 6.1*X1*X3 \quad [5]$$

where

Flux = $\text{gal}/(\text{ft}^2/\text{day})$
X1 = (wt%-15)/10
X2 = (temp-95)/25
X3 = -1 for the negatively charged 35,000 M.W. membrane
1 for the neutral 15,000 M.W. membrane

An initial screening of the COD from the two ultrafilters indicated that the permeate from the 35,000 M.W. membrane had a lower COD than the permeate from the 15,000 M.W. membrane. This was considered to be an anomaly since the 15,000 M.W. membrane should have filtered out more of the organic contaminants from the wastewater due to the smaller pore size. Three samples from each membrane were taken at 30-minute intervals. The samples were then analyzed for COD. Table 37 shows the results of COD analyses from each of the samples. The average COD for the 35,000 M.W. membrane was 1520 mg/L. The average COD for the 15,000 M.W. membrane was determined to be 1900 mg/L. A pooled standard deviation for these samples was calculated to be 35 mg/L. Using a student's T test with 4 degrees of freedom to estimate the probability of this difference being random, there is better than a 99% chance that the COD from the 15,000 M.W. ultrafilter with the neutral charge is higher than from the 35,000 M.W. ultrafilter with the negative surface charge.

TABLE 37

RESULTS OF COD ANALYSIS FROM JACOBS RANCH CWF ULTRAFILTER PERMEATE

Time (minutes)	COD from 35,000 M.W. Membrane (mg/l)		COD from 15,000 M.W. Membrane (mg/l)
0	1700		1900
30	1460		1940
60	1400		1870
Average	1520		1900
Std. Deviation	157		35
Pooled Std. Dev.		114	
T-Distribution		4.1	
Deg. of Freedom		4	

A major concern with any filtration system, but especially with a membrane-based filtration system, is the length of time that the unit can be run between cleanings without significant loss in filtration rates. A two week run using 15 wt% Jacobs Ranch centrate was performed. The system was operated without temperature control and a steady-state temperature of around 35°C was reached. A plot of flux versus time can be seen in Figure 23.

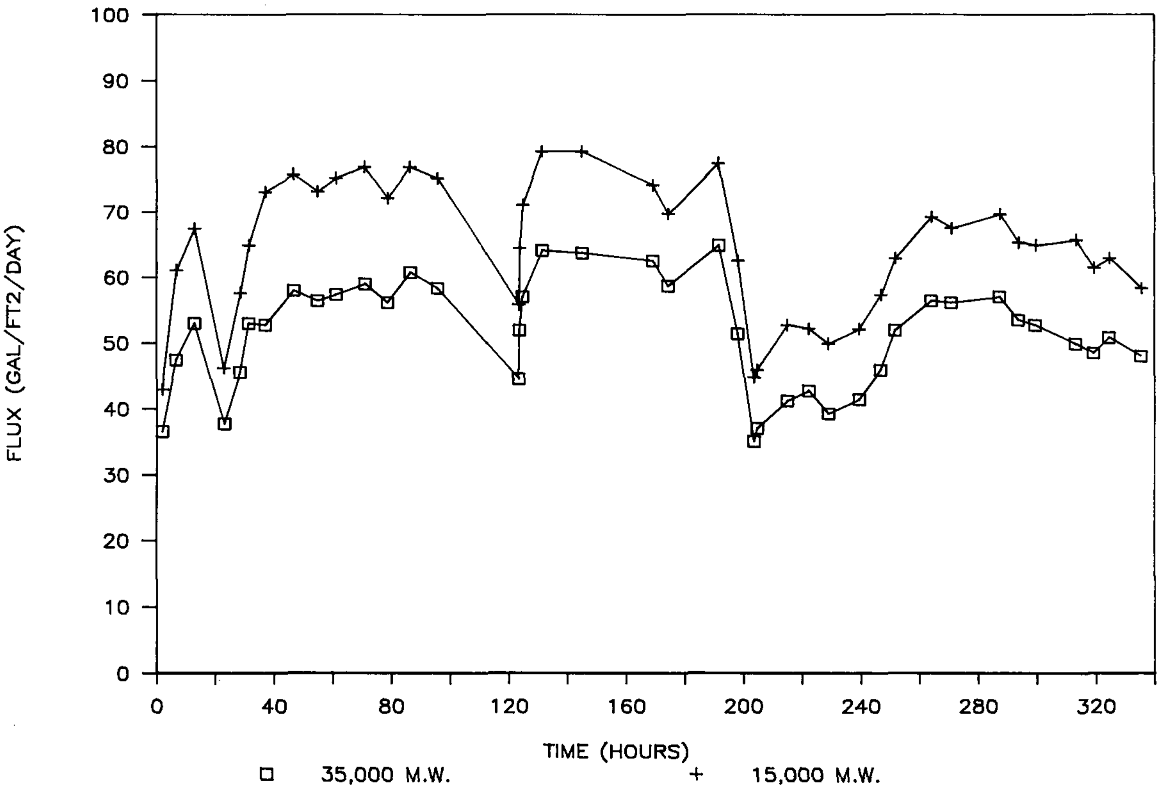

Figure 23. Flux over extended run using Jacobs Ranch CWF centrate

The initial increase in flux over the first 15 hours can be attributed to the increase in temperature from the mechanical energy of the pump. As can be seen, the flux exhibited several sharp decreases at approximately 20 hours, 120 hours, and 195 hours. All three of these sudden decreases were the result of either pump or piping problems.

3.12.3.4 Investigation of Unaccounted COD and TOC

Efforts were also directed at determining the COD and TOC component(s) which are not evident from the results of the partial wastewater characterization. Initially, it was believed that a majority of the unaccounted TOC was caused by ultrafine coal particles in the centrate. However, this was discounted following ultrafilter treatment as particulate matter will not pass through the ultrafilter membrane.

Observation of the ultrafilter permeate revealed that, with time, the initially light amber water developed a deep chestnut color. An extensive study was performed at UNDEMRC (24) to characterize the constituents present in the coal gasification condensate from the Great Plains Gasification Plant. Results of the study revealed that catechol polymers (aromatic diols) may account for 20% to 70% of the unidentified organic carbon in coal conversion wastewaters. Acidification of the colored ultrafilter permeate produced a dark precipitate. GC/MS analysis of the precipitate indicated that the color-causing compound was composed primarily of humic acid-type material, and probably was the result of the polymerization of catechol.

Jar testing results of acidification, and basification followed by aeration and acidification, have shown that the COD of the centrate can be reduced from 4800 mg/l to levels on the order of 1500 mg/l. Chemical pretreatment of centrate prior to ultrafiltration was tested in order to verify the results of initial jar tests. One barrel (50 gallons) of Jacobs Ranch centrate was pH adjusted to 10.0 using a sodium hydroxide solution. The basified centrate was then aerated and stirred for a period of 48 hours. Following aeration and mixing, the centrate was pH adjusted to 3.0 with concentrated sulfuric acid. The acidified centrate was then run through the PDU ultrafiltration system. Three grab samples of ultrafilter permeate were taken from each ultrafilter at regular intervals throughout the five-hour test run. Analysis of the permeate samples showed that the COD was reduced to an average of 790 mg/l from the 35,000 M.W. ultrafilter, and 785 mg/l from the 15,000 M.W. ultrafilter. The permeate samples from the basified/acidified centrate exhibited very little color. This suggests that the color-causing polymer was not present, to a significant extent, in the ultrafilter permeate.

3.12.3.5 Bench-scale Biological Treatment

Two bench-scale activated sludge systems, designated CWF I and CWF II, were operated at four mean cell residence times for the determination of organic removal efficiencies, and the development of activated sludge kinetic coefficients. Both activated sludge reactors were fed ultrafilter permeate composited from both the 15,000 and 35,000 molecular weight cutoff ultrafilters. The permeate collected was completely mixed in an 800-liter vessel to assure uniformity of wastewater quality during bench-scale activated sludge treatability studies. A sample of the composited ultrafilter permeate was submitted to the UNDEMRC Waste Analysis Laboratory for partial chemical characterization. Table 38 lists the results of characterization analyses.

3.12.3.5.1 Equipment and Procedures

A schematic diagram of the activated sludge systems used for bench-scale treatability testing is shown in Figure 24. Further description and procedures have been discussed elsewhere (12). During the period of ultrafilter permeate collection for biological treatment, an activated sludge reactor was established for the acclimation of an active bacterial population. Four liters of mixed liquor from the acclimation activated sludge system was transferred to each of the six-liter activated sludge systems to be used for treatability testing. Effluent from the acclimation system was used to fill each of the six-liter reactors to the given operating volumes.

TABLE 38

RESULTS OF PARTIAL CHARACTERIZATION OF JACOBS RANCH CWF ULTRAFILTER PERMEATE

Parameter/Constituent	Value[a]
pH	7.7
Alkalinity (as $CaCO_3$)	692
Ammonia	12
Nitrite	4.0
Nitrate	1.1
Total Kjeldahl Nitrogen (NH_3 as N)	2.6
Chemical Oxygen Demand	2500
Biochemical Oxygen Demand	550
Total Carbon	980
Total Inorganic Carbon	445
Total Organic Carbon	535
Cyanide	<2
Thiocyanate	3
Sulfate	38
Thiosulfate	13
Acetate	<10
Propionate	<10
Butyrate	<10
Iso-butyrate	<10
Phenol	5
O-Cresol	<5
P,M-Cresol	<5
Methanol	<5
Acetone	<5
Acetonitrile	<5
Total Solids	2252
Total Volatile Solids	632
Total Dissolved Solids	2067
Total Volatile Dissolved Solids	851
Total Suspended Solids	18
Aluminum	<1
Barium	0.2
Calcium	46
Copper	<0.05
Iron	<0.2
Magnesium	23
Phosphorus	0.65
Potassium	20
Silicon	58
Sodium	410
Zinc	0.06

[a] All values expressed in mg/l, except pH.

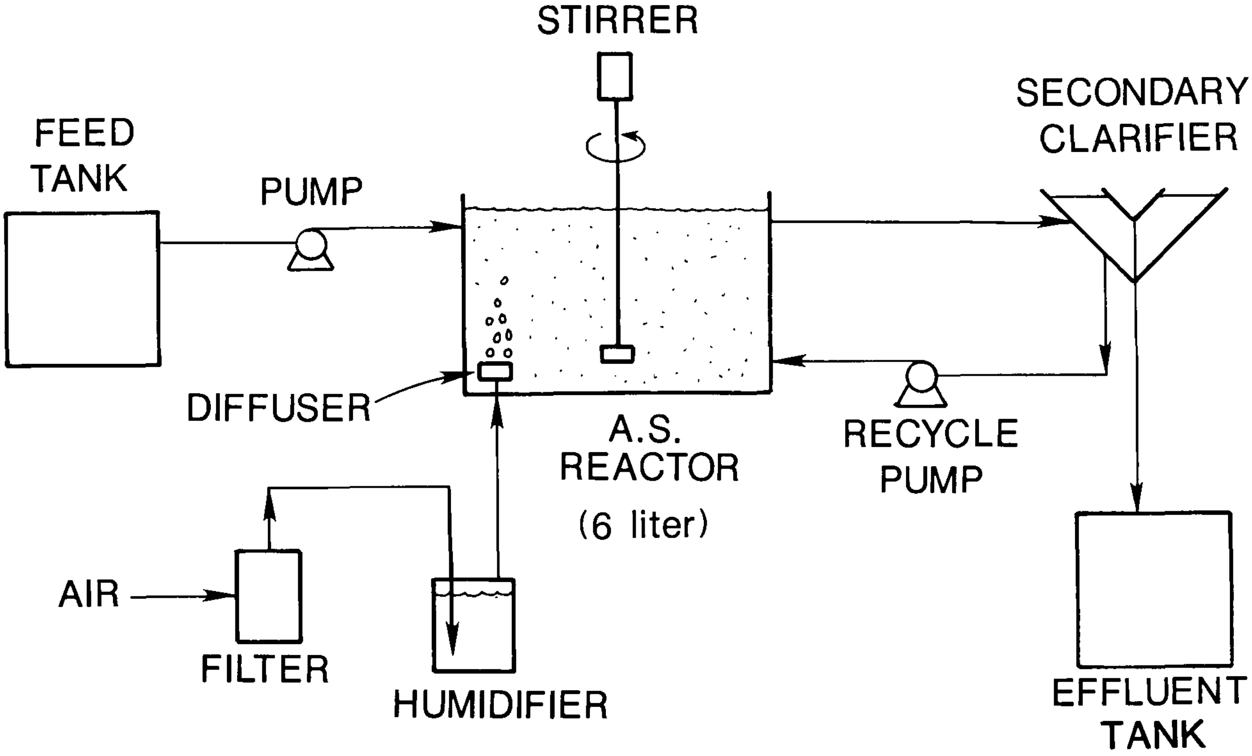

Figure 24. Schematic of bench-scale activated sludge system

Major operating parameters which were used to control the operation of the activated sludge systems at the desired conditions were the hydraulic retention time (HRT), the mean cell residence time (MCRT), and the concentration of biomass within the reactor. The HRT was regulated by the influent feed rate, measured in conjunction with the operating volume of the aeration basin. The MCRT was controlled through volumetric wasting of mixed liquor directly from the aeration basin in relation to the mass of mixed liquor volatile suspended solids (MLVSS) and the mass volatile suspended solids lost to the effluent each day.

The 6-liter activated sludge systems were initially operated at a relatively long HRT during a six-week period of acclimation to the new feed. The ultrafilter permeate was diluted with tap water at decreasing ratios during the acclimation period, until undiluted ultrafilter permeate was being fed to both systems. The feed rate was then gradually increased until an HRT of 1.5 days was obtained. A 1.5-day HRT was maintained in both systems throughout the remainder of the testing period.

Nitrogen and phosphorus are principal nutrients that are required for the growth of microorganisms in the metabolism of organic matter. Ultrafilter permeate is deficient in both nitrogen and phosphorus, with respect to biological growth factors. Therefore, a solution of ammonium phosphate was added to the feed at a BOD:N:P ratio of 100:5:1 to provide adequate nutrients for favorable growth conditions.

3.12.3.5.2 Results

Figure 25 shows a summary diagram for the Jacobs Ranch bench-scale activated sludge treatability study. Each activated sludge system was operated for acclimation at a nominal mean cell residence time for a period of at least three times the given MCRT. Following the acclimation period, a steady-state operating period was initiated in an effort to characterize reactor performance and obtain data for the development of kinetic parameters.

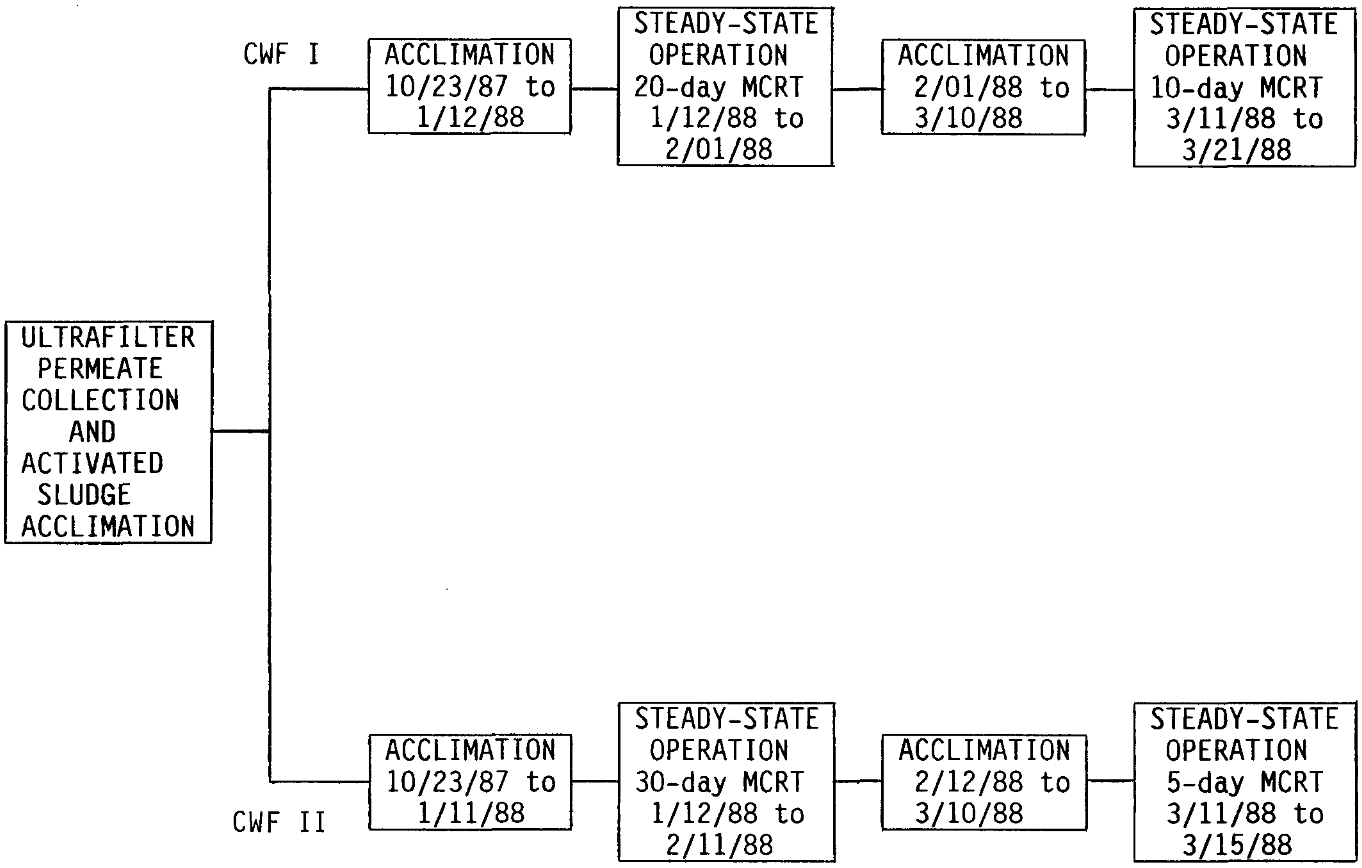

Figure 25. Summary diagram of Jacobs Ranch CWF activated sludge treatability study

Table 39 lists average steady-state operating and performance characteristics as a function of the mean cell residence time. Steady-state influent and effluent concentrations of BOD_5, COD, and TOC for each system, along with percent removals, are shown in Table 40.

TABLE 39

AVERAGE STEADY-STATE OPERATION CONDITIONS DURING ACTIVATED SLUDGE TREATMENT OF JACOBS RANCH CWF ULTRAFILTER PERMEATE

	Nominal Mean Cell Residence Time			
Parameter/Condition	5-day	10-day	20-day	30-day
HRT (days)	1.53	1.53	1.53	1.53
MLSS (mg/l)	275	557	1708	2297
MLVSS (mg/l)	243	494	1499	2032
ESS (mg/l)	17	36	55	35
EVSS (mg/l)	10	27	44	30
MCRT (days)	5.1	10.1	21.7	33.6
Oxygen Uptake (mg O_2/g MLVSS-hr)	26.5	14.9	6.9	5.9
Settleability (ml/l)	12	37	120	176
SVI (ml MLSS/g)	44	66	70	76

TABLE 40

AVERAGE STEADY-STATE CONSTITUENT CONCENTRATIONS FOR JACOBS RANCH CWF ACTIVATED SLUDGE TREATABILITY STUDY

Nominal MCRT	Constituent	Influent (mg/l)	Effluent (mg/l)	Percent Change
5-day:				
	BOD_5	174	18	89.7
	COD	1910	1510	20.9
	TOC	360	215	40.3
10-day:				
	BOD_5	173	13	92.5
	COD	1920	1480	22.9
	TOC	360	210	41.7
20-day:				
	BOD_5	226	17	92.5
	COD	2000	1320	34.0
	TOC	435	190	56.3
30-day:				
	BOD_5	254	12	95.3
	COD	2070	1280	38.2
	TOC	375	150	60.0

Influent and effluent BOD_5 concentrations over the period of the treatability study for the CWF I activated sludge system are shown in Figure 26. BOD_5 removal rates averaged 92.5% during steady-state operation at both the 20-day and the 10-day mean cell residence times. Figure 27 shows influent and effluent BOD_5 concentrations versus time for the CWF II system. BOD_5 removals averaged 95.3% during steady-state operation at the 30-day MCRT and 89.7% at the 5-day steady-state operating period. It should be noted that the influent BOD_5 concentration exhibited a general decline during the treatability study. This suggests that biological degradation was occurring within the bulk feed storage tank, even though care was taken to minimize air contact with the stored wastewater. A check of BOD_5 concentrations through the CWF I system for the seven weeks prior to the 20-day MCRT steady-state operating period revealed an average BOD_5 removal rate of 95.7%, comparable to steady-state operation. Variability in influent quality, especially in terms of BOD, will have an impact on the derivation of kinetic constants.

Influent and effluent COD concentrations for the CWF I and CWF II activated sludge systems are presented in Figures 28 and 29, respectively. Data collected during steady-state operation at the various mean cell residence times indicated increasing COD removal efficiency with increasing MCRTs. COD removals averaged 38.2%, 34.0%, 22.9%, and 20.9% during steady-state operation at the 30-day, 20-day, 10-day, and 5-day MCRTs, respectively. Since influent COD concentrations remained relatively stable over the course of the study, it is assumed that COD-based kinetic derivations may produce more realistic results.

The concentration of total organic carbon exhibited the same general decreasing trend as BOD_5. However, the magnitude of the change in TOC concentration over time is much less than that exhibited by BOD_5. Therefore, as with COD, kinetic coefficient derivations based on TOC should produce more accurate predictions than those of BOD_5. Steady-state TOC removals averaged 60.0%, 56.3%, 41.7%, and 40.3% during steady-state operation at the 30-day, 20-day, 10-day, and 5-day mean cell residence times, respectively. Figure 30 shows influent and effluent TOC concentrations for the CWF I activated sludge system during the treatability testing period. Influent and effluent TOC concentrations for the CWF II system during the same period are shown in Figure 31.

Mixed liquor suspended solids and effluent suspended solids for the CWF I activated sludge system are shown in Figures 32 and 33, respectively. During steady-state operation at the 20-day MCRT (Days 99 through 103), mixed liquor total suspended solids (MLSS) averaged 1708 mg/l, while mixed liquor volatile suspended solids (MLVSS) averaged 1499 mg/l. During the same operating period, effluent total suspended solids (ESS) averaged 55 mg/l and effluent volatile suspended solids (EVSS) averaged 44 mg/l. Following steady-state sampling and analysis at the 20-day MCRT, mixed liquor suspended solids decreased in response to the rate of mixed liquor wasting performed to attain a 10-day MCRT. During steady-state operation at the 10-day MCRT (Days 141 through 145), MLSS averaged 557 mg/l, while MLVSS averaged 494 mg/l. Correspondingly, ESS averaged 36 mg/l, and EVSS averaged 27 mg/l.

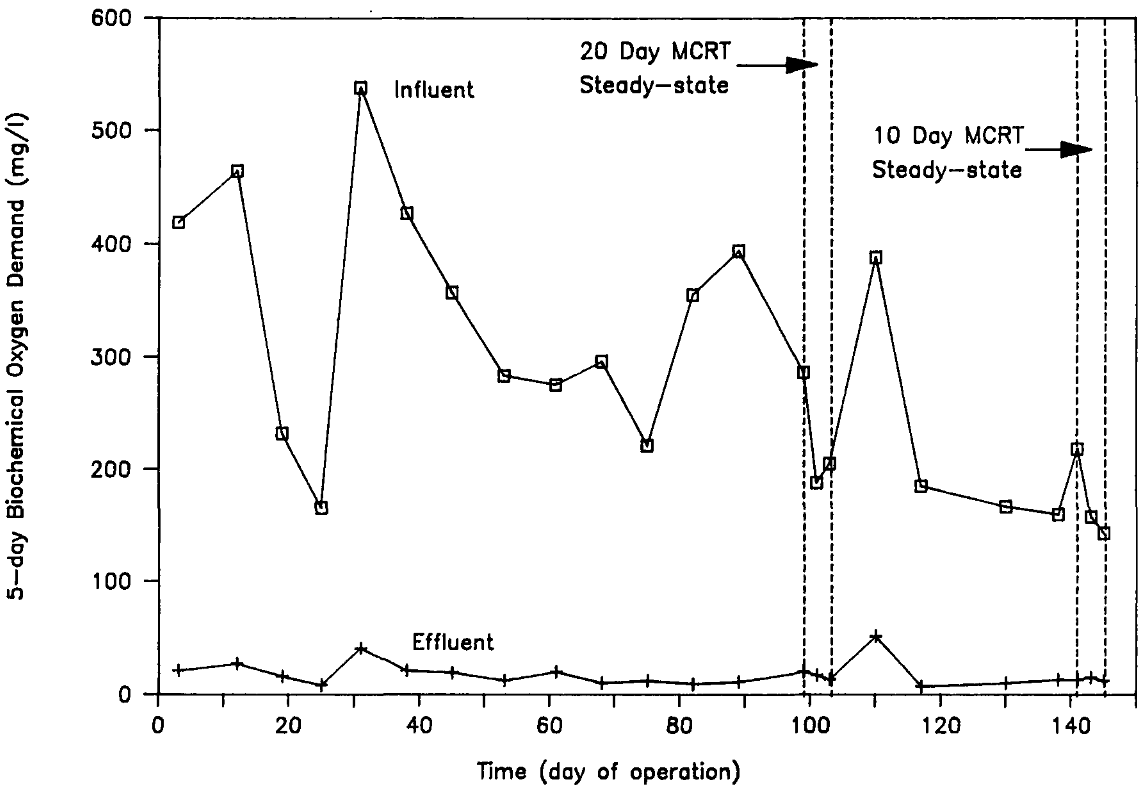

Figure 26. BOD_5 vs. time for the CWF I activated sludge system on Jacobs Ranch CWF ultrafilter permeate

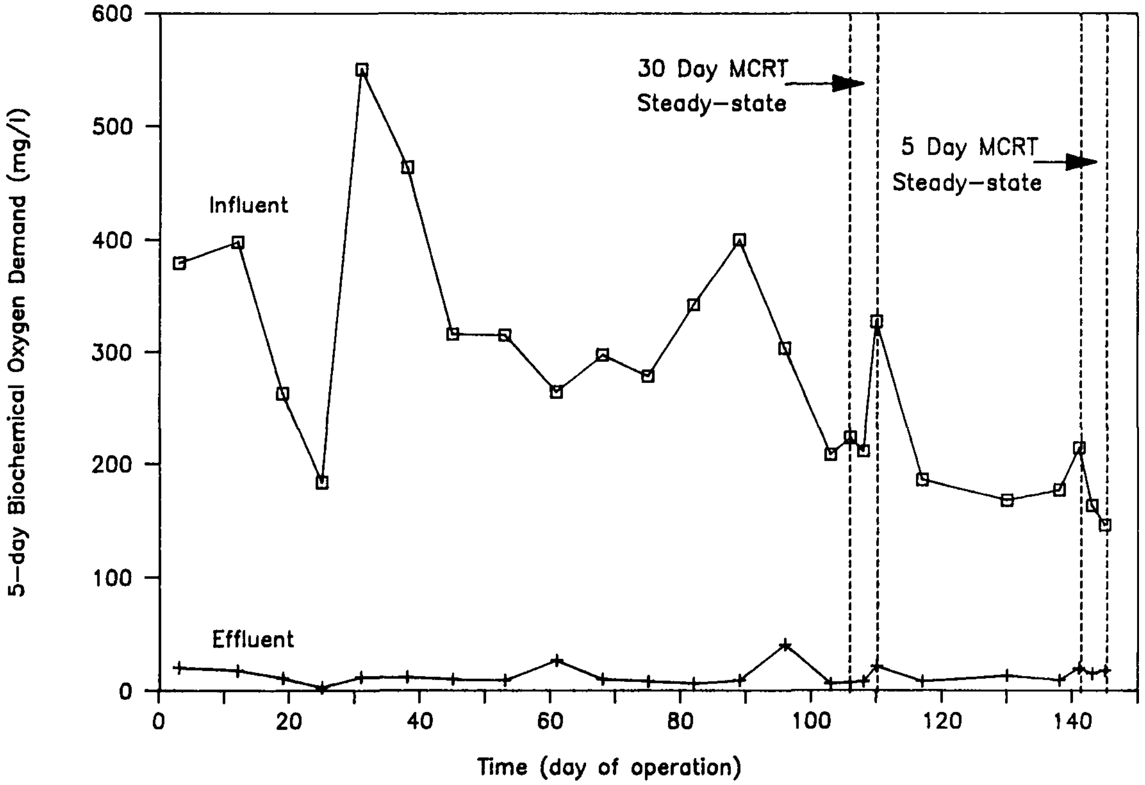

Figure 27. BOD_5 vs. time for the CWF II activated sludge system on Jacobs Ranch CWF ultrafilter permeate

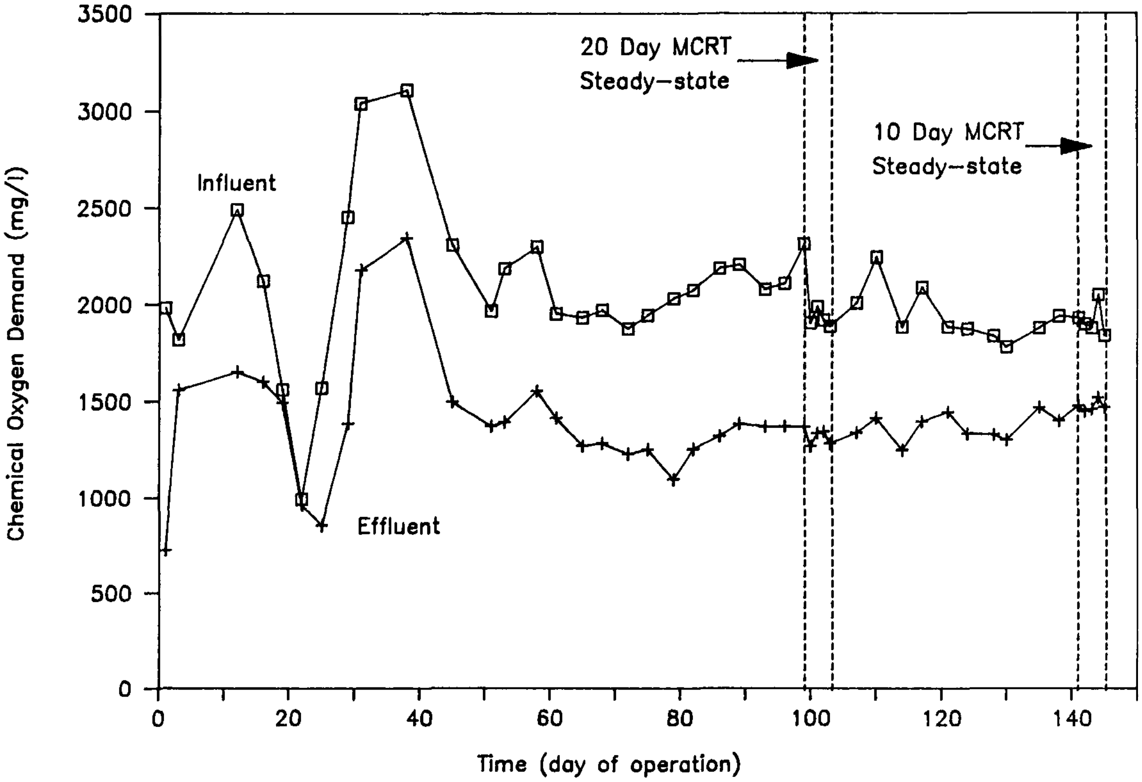

Figure 28. COD vs. time for the CWF I activated sludge system on Jacobs Ranch CWF ultrafilter permeate

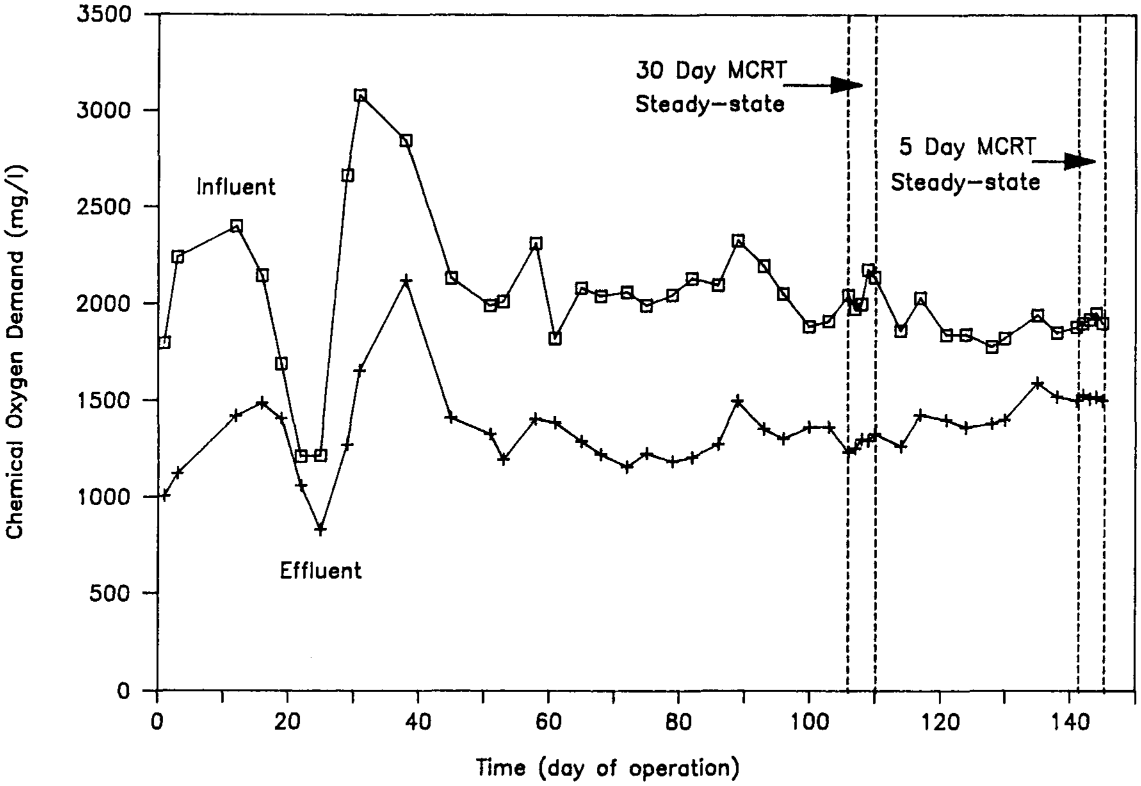

Figure 29. COD vs. time for the CWF II activated sludge system on Jacobs Ranch CWF ultrafilter permeate

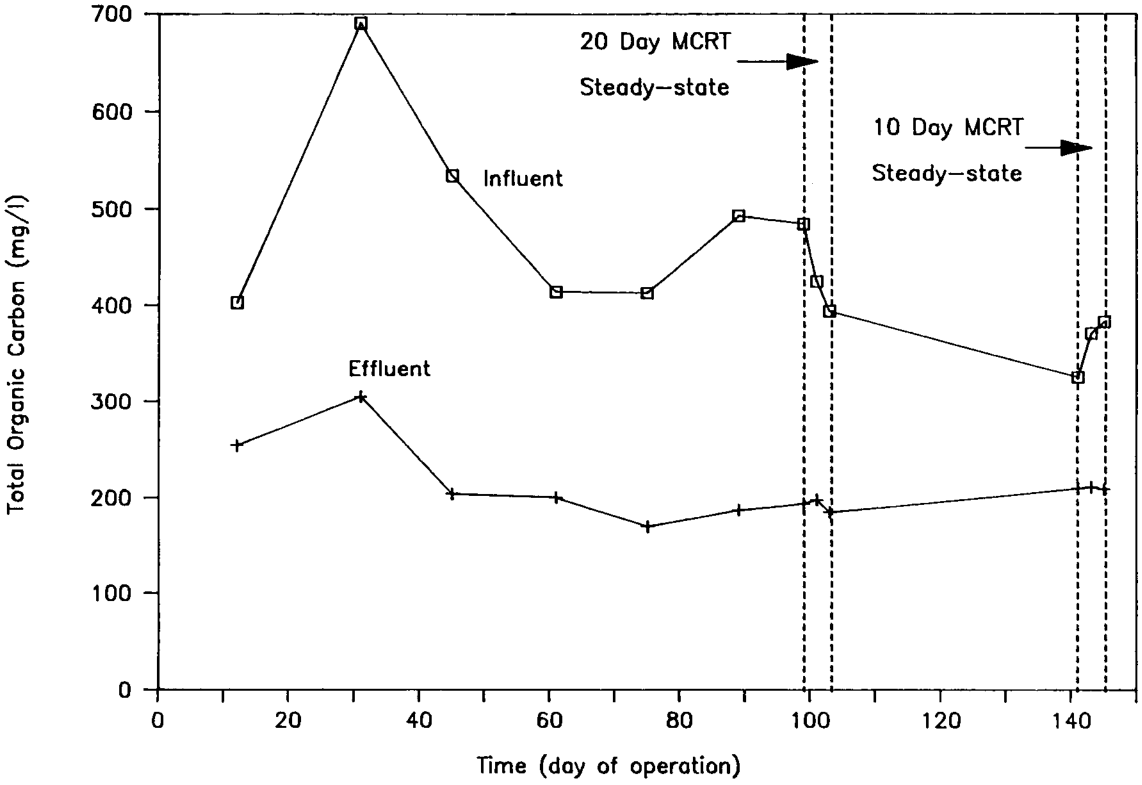

Figure 30. TOC vs. time for the CWF I activated sludge system on Jacobs Ranch CWF ultrafilter permeate

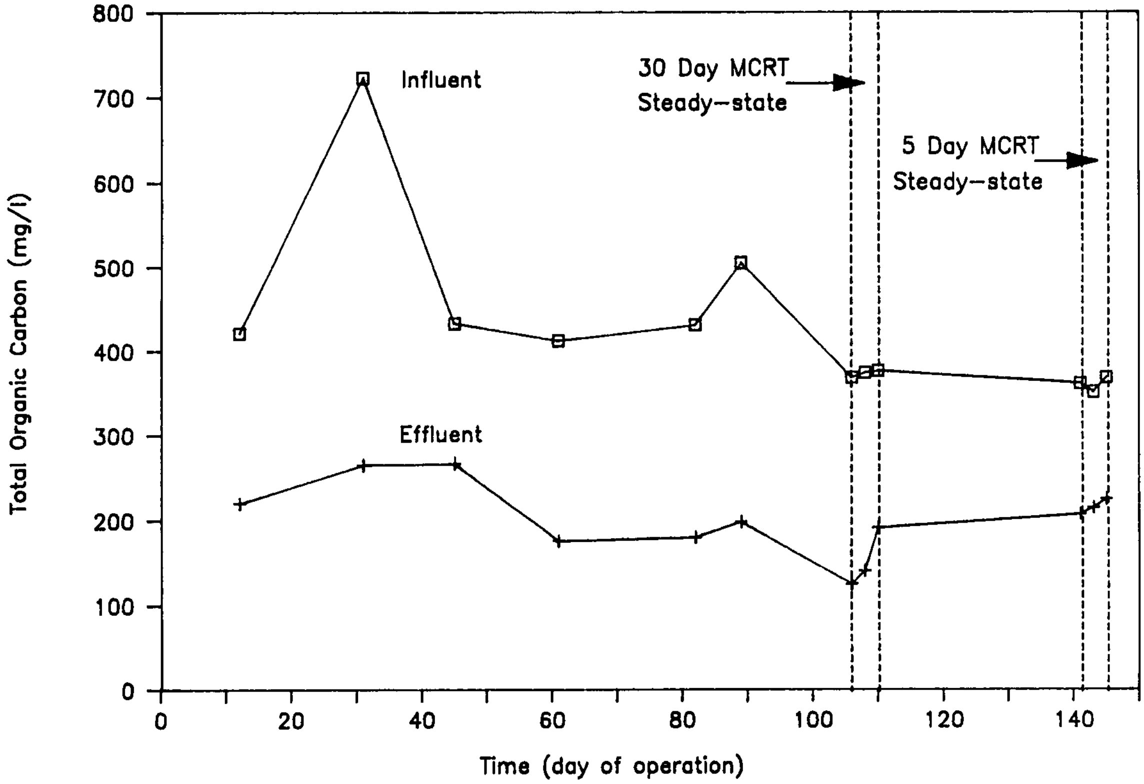

Figure 31. TOC vs. time for the CWF II activated sludge system on Jacobs Ranch CWF ultrafilter permeate

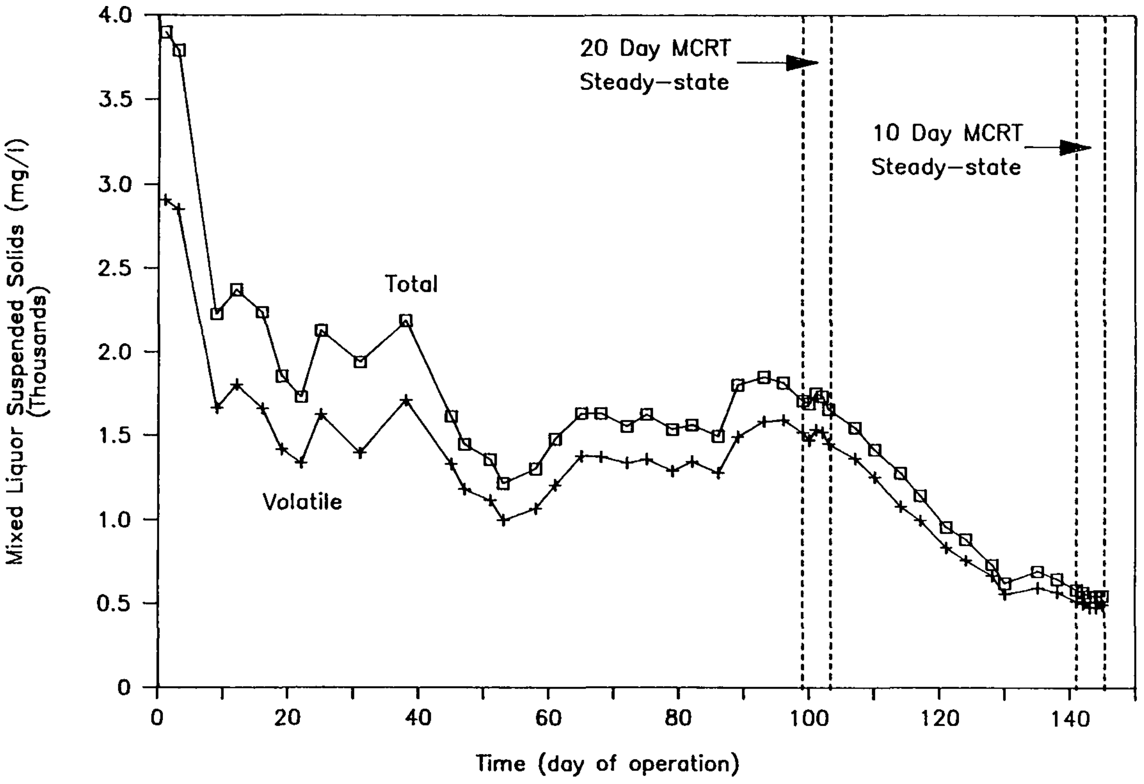

Figure 32. Mixed liquor suspended solids vs. time for the CWF I activated sludge system

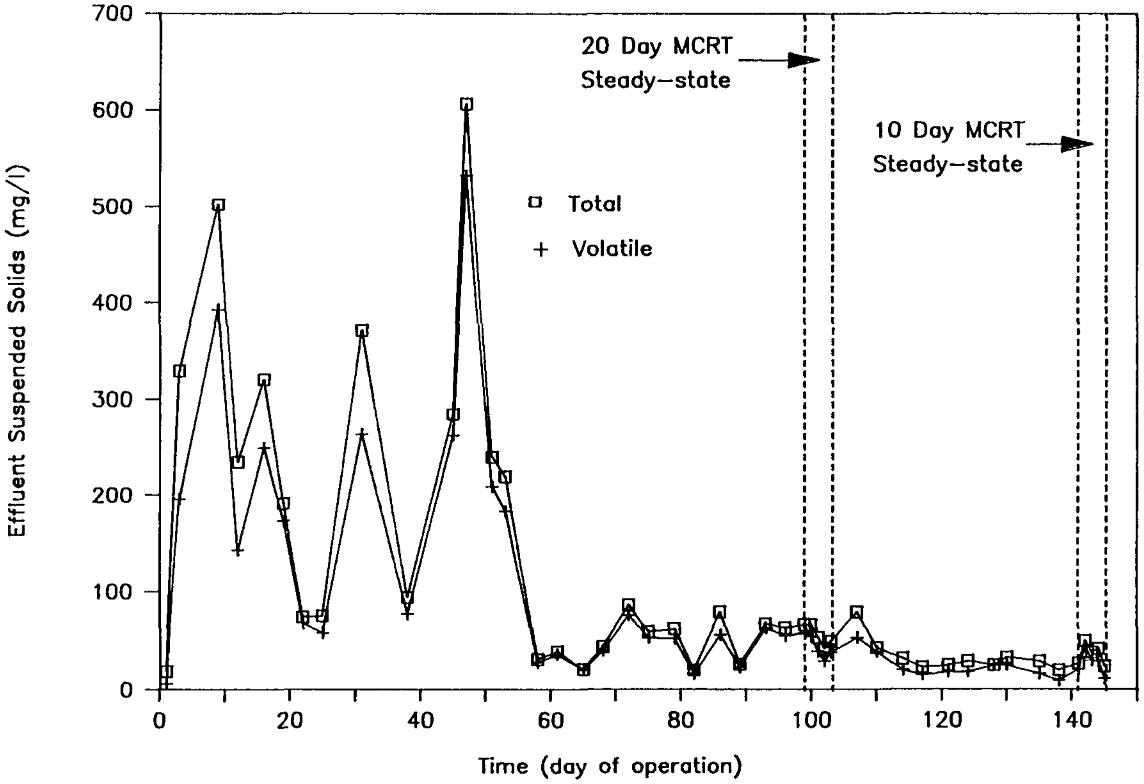

Figure 33. Effluent suspended solids vs. time for the CWF I activated sludge system.

Mixed liquor and effluent suspended solids for the CWF II activated sludge system are shown in Figures 34 and 35, respectively. Steady-state operation at the 30-day MCRT occurred on Days 106 through 110 of operation. During that period, MLSS and MLVSS averaged 2297 mg/l and 2032 mg/l, respectively. ESS averaged 35 mg/l, while EVSS averaged 30 mg/l during the same period of operation. A dramatic decrease in mixed liquor suspended solids occurred in the CWF II system during mixed liquor wasting to attain the 5-day MCRT. Steady-state operation at the 5-day MCRT was initiated on Day 141, and completed on Day 145 of operation. During 5-day MCRT steady-state operation, MLSS averaged 275 mg/l and MLVSS averaged 243 mg/l. ESS and EVSS averaged 17 mg/l and 10 mg/l, respectively, during the 5-day MCRT steady-state operating period.

One of the operational problems encountered during initial stages of the treatability test program was the inadequate solid-liquid separation in the secondary clarifier. This resulted in biological solids spilling over the effluent weir, making it difficult to maintain proper process control. The results of this condition can be seen in the variability of effluent suspended solids on Figures 33 and 35. Following Day 54 of operation, the frequency and duration of solids recycle from the secondary clarifier back to the aeration basin was varied and closer control of system operation was attained. However, the variability in effluent suspended solids resulted in wide fluctuations in mean cell residence times, delaying the development of the first two steady-state operating periods. Due to this condition, the treatability study was delayed for approximately 45 days.

As previously discussed, the polymerization of catechol was believed to be the cause of color formation in the ultrafilter permeate. Color analyses were performed on the influent and effluent of both activated sludge systems during the bench-scale treatability study. Figures 36 and 37 show influent and effluent color (APHA PtCo units) versus time for the CWF I and CWF II systems, respectively. The formation of color appeared to be relatively constant, regardless of treatability test conditions, and is most likely a function of the hydraulic retention time. Throughout the treatability testing period, effluent color increased an average of 1.8 times that of influent color.

The sludge volume index (SVI) is the volume in milliliters occupied by one gram of mixed liquor suspended solids after 30 minutes settling. It is the measure of activated sludge settleability and is used to indicate the onset of operational problems, such as sludge bulking. Generally, an SVI in the range of 50 to 150 ml/g is indicative of a good-settling sludge. Figures 39 and 40 show mixed liquor solids settleability and sludge volume index versus time for the CWF I and CWF II bench-scale activated sludge systems, respectively. Settleability varied in direct proportion to the concentration of mixed liquor suspended solids at the various mean cell residence times. The SVI averaged 76, 70, 66, and 44 ml MLSS/gram during operation at the 30-day, 20-day, 10-day, and 5-day mean cell residence times, respectively.

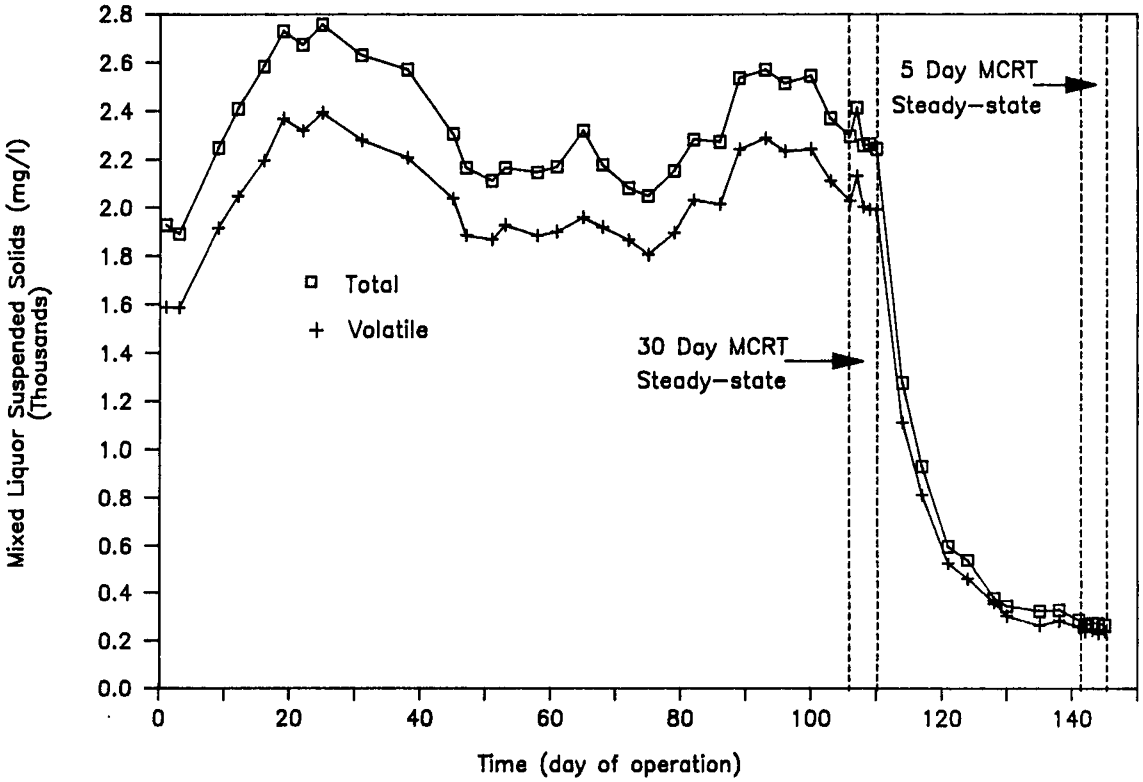

Figure 34. Mixed liquor suspended solids vs. time for the CWF II activated sludge system

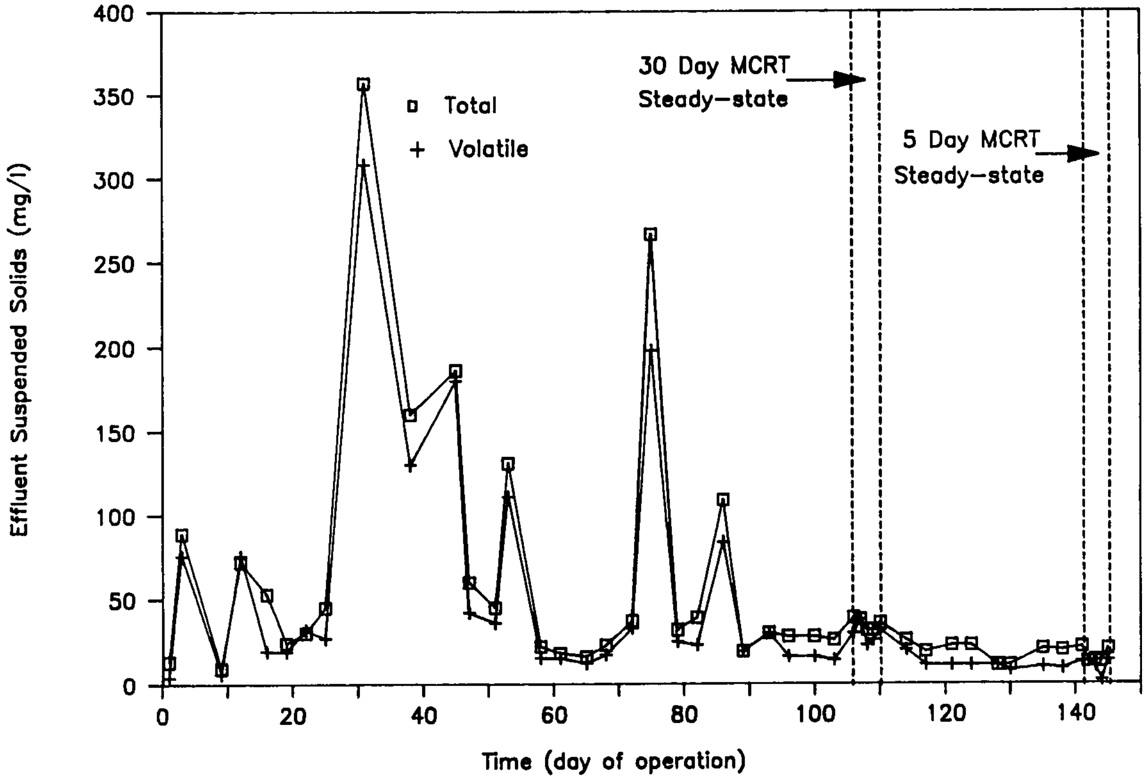

Figure 35. Effluent suspended solids vs. time for the CWF II activated sludge system

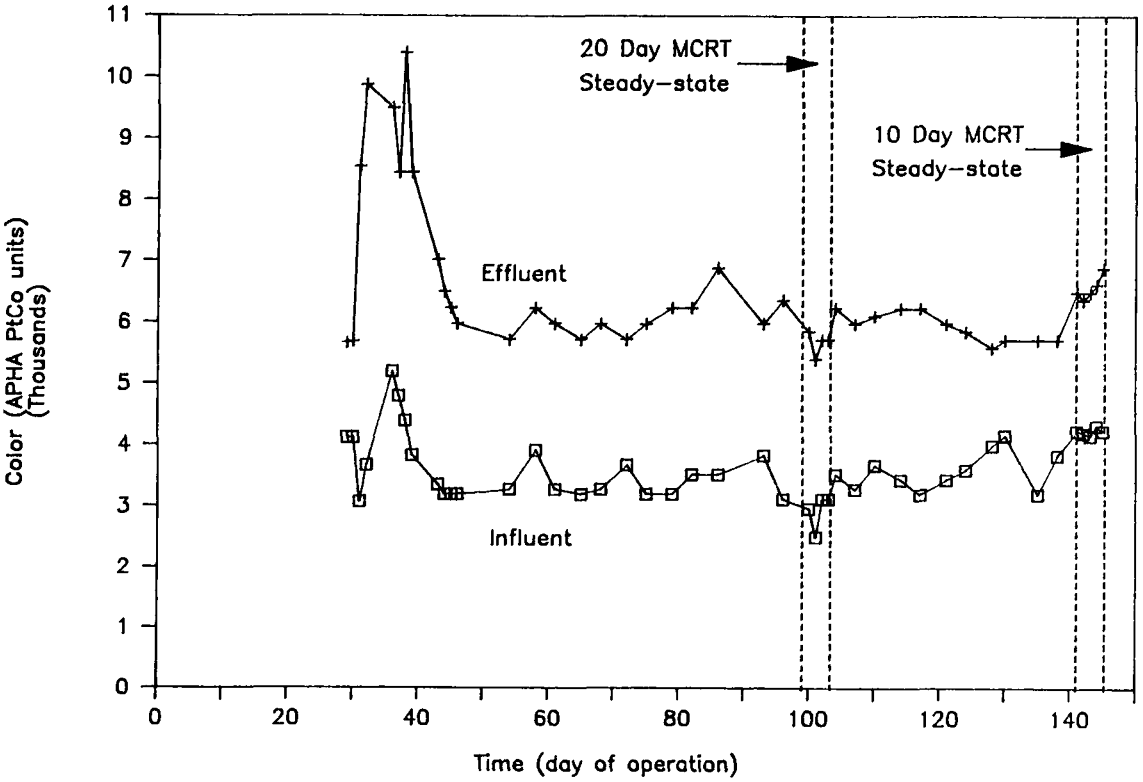

Figure 36. APHA PtCo color units vs. time for the CWF I activated sludge system

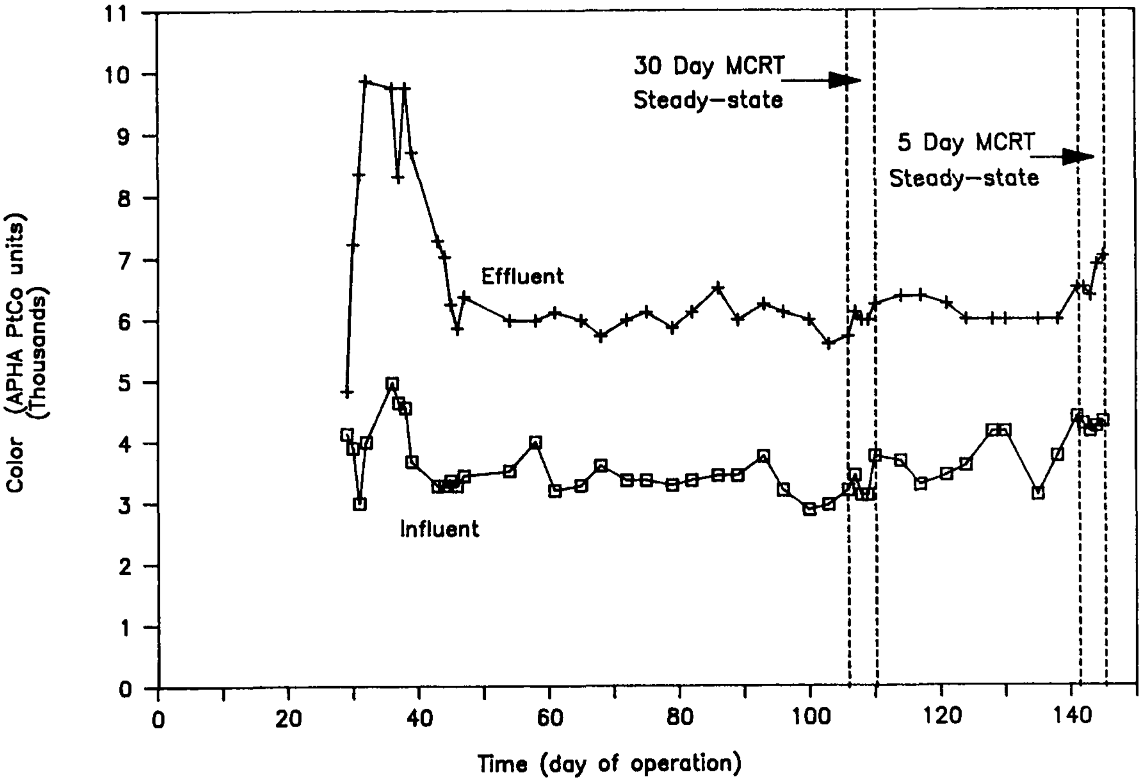

Figure 37. APHA PtCo color units vs. time for the CWF II activated sludge system

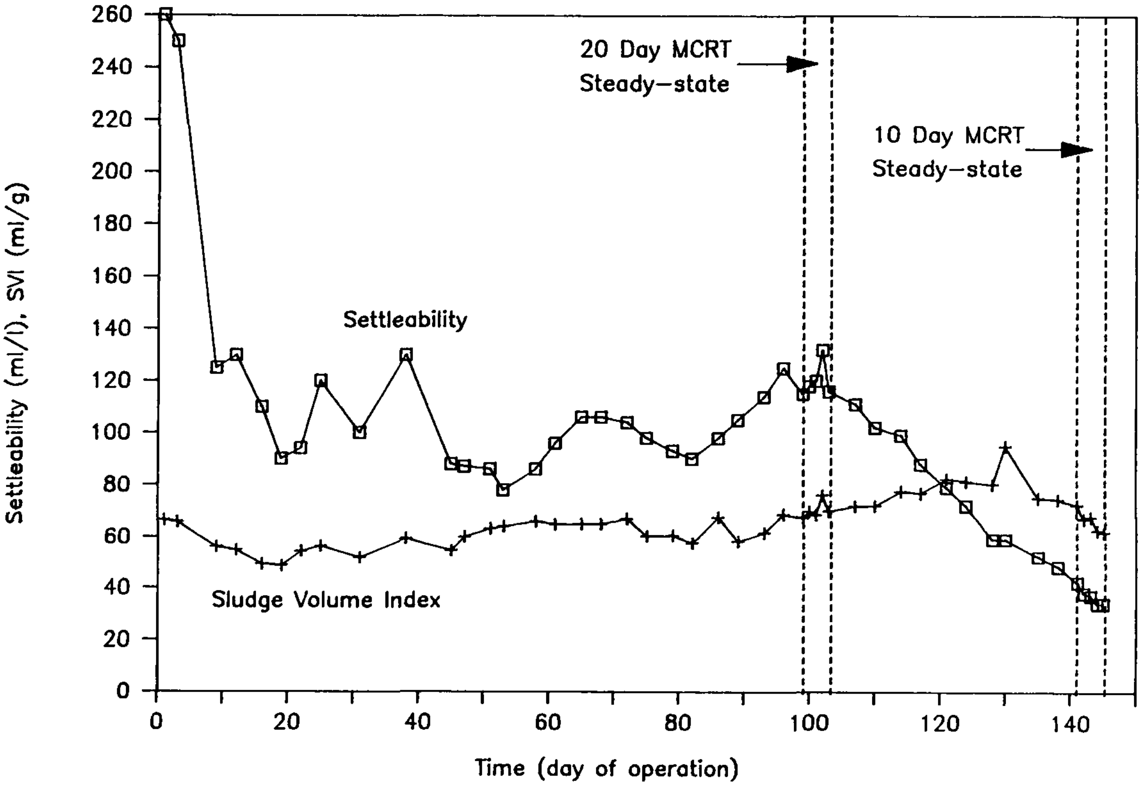

Figure 38. Mixed liquor solids settleability and sludge volume index vs. time for the CWF I activated sludge system

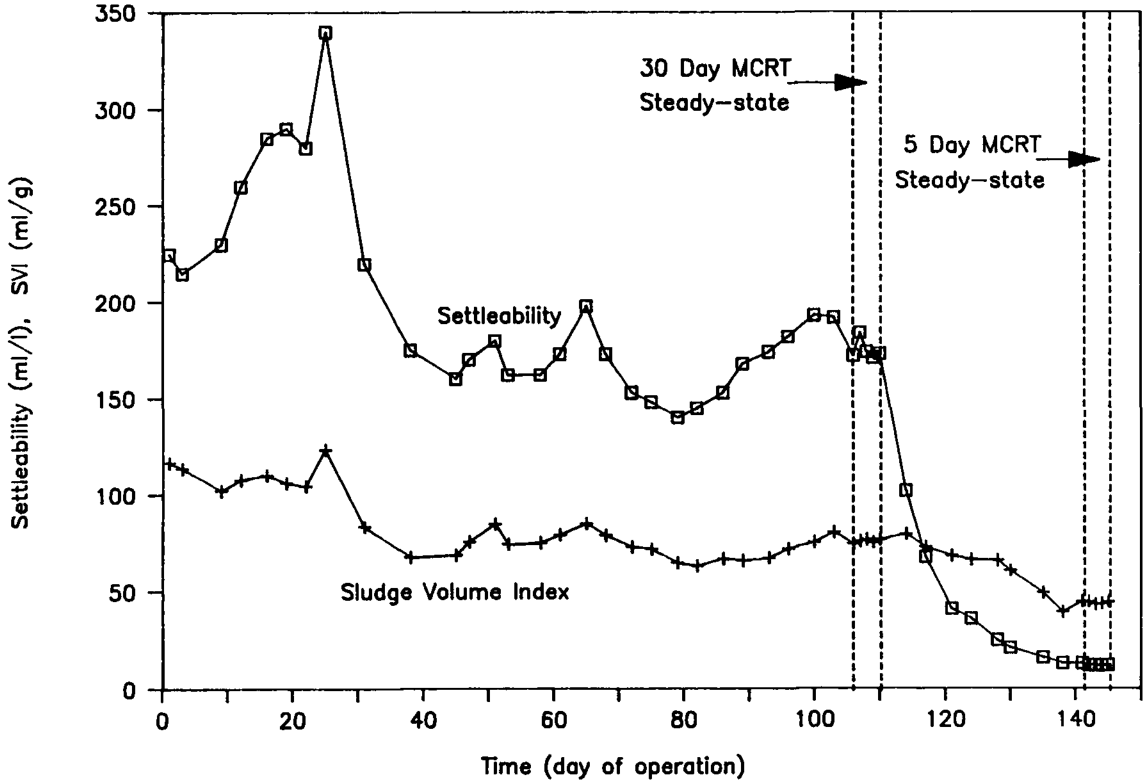

Figure 39. Mixed liquor solids settleability and sludge volume index vs. time for the CWF II activated sludge system

A partial chemical characterization was performed on a composite effluent sample taken during steady-state operation at the 30-day mean cell residence time, and the results are presented in Table 41. COD and TOC were reduced to 1250 mg/l and 124 mg/l, respectively, while BOD_5 was reduced to 5 mg/l. This indicates that a large fraction of the oxidizable matter in the wastewater effluent is nonbiodegradable (biorefractory). The high effluent COD:TOC ratio may be attributable to oxygen demand contributed by organically bound elements, such as nitrogen and hydrogen, and inorganic compounds. Experience with coal gasification wastewaters has shown that ozone treatment is effective at converting a majority of the biorefractory organic constituents to biodegradable forms. Activated carbon adsorption is another method of removing biorefractory organics. However, tertiary treatment of activated sludge-treated effluents will be governed by the sensitivity of subsequent wastewater polishing operations, such as reverse osmosis and/or ion exchange prior to process reuse, effluent discharge permit regulations, and economics.

TABLE 41

RESULTS OF PARTIAL CHARACTERIZATION OF JACOBS RANCH CWF ACTIVATED SLUDGE EFFLUENT AT A 30-DAY MCRT

Constituent	Value[a]
pH	7.8
Alkalinity (as $CaCO_3$)	863
Ammonia	11
Nitrite	<2
Nitrate	41
Total Kjeldahl Nitrogen (NH_3 as N)	17.8
Chemical Oxygen Demand	1250
Biochemical Oxygen Demand	5
Total Carbon	590
Total Inorganic Carbon	466
Total Organic Carbon	124
Cyanide	2.1
Thiocyanate	<1
Sulfate	31
Thiosulfate	<1
Phenol	0.7
Total Solids	1822
Total Volatile Solids	531
Total Dissolved Solids	1775
Total Volatile Dissolved Solids	522
Iron	0.5
Magnesium	23
Phosphorus	14.6
Potassium	30
Silicon	42
Sodium	375

[a] All values expressed in mg/l, except pH.

3.12.3.6 Development of Activated Sludge Kinetic Parameters

Kinetic coefficients allow for design of scaled-up versions of the activated sludge unit or for the prediction of conditions required to meet various effluent criteria when treating the same wastewater. Data collected during the four steady-state sampling and analysis periods were used for the development of activated sludge kinetic coefficients. Kinetics for the bench-scale activated sludge systems were determined on the basis of BOD_5, COD, and TOC. The nonbiodegradable fraction of COD and TOC were determined and corrected for in the determination of kinetic constants.

Figure 40 is a plot of the specific rate of BOD_5 removal versus effluent soluble BOD_5. The slope of the line is equal to the reaction rate constant K. For Jacobs Ranch ultrafilter permeate, K was predicted to be 0.567 l/g MLVSS-hr.

Figure 41 is a plot of the specific rate of total COD removal versus effluent soluble COD. The x-intercept represents the fraction of nonbiodegradable COD, and was determined to be approximately 1200 mg/l. The nonbiodegradable fraction of COD was then subtracted from the data prior to the evaluation of kinetic coefficients. Figure 42 shows a plot of the specific rate of utilization of the biodegradable fraction of COD. The reaction rate constant K, based on biodegradable COD, was estimated to be 0.117 l/g MLVSS-hr.

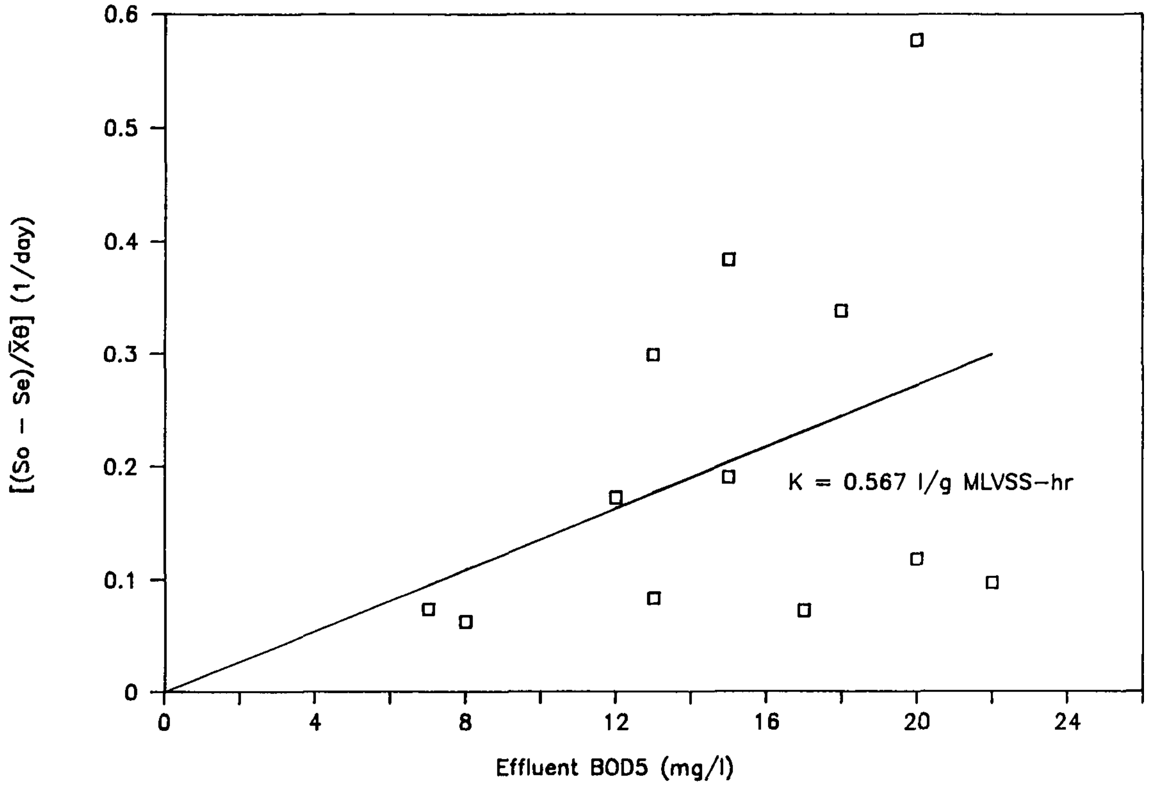

Figure 40. Plot of BOD_5 utilization rate vs. the effluent BOD_5 concentrate for activated sludge treatment of Jacobs Ranch CWF ultrafilter permeate

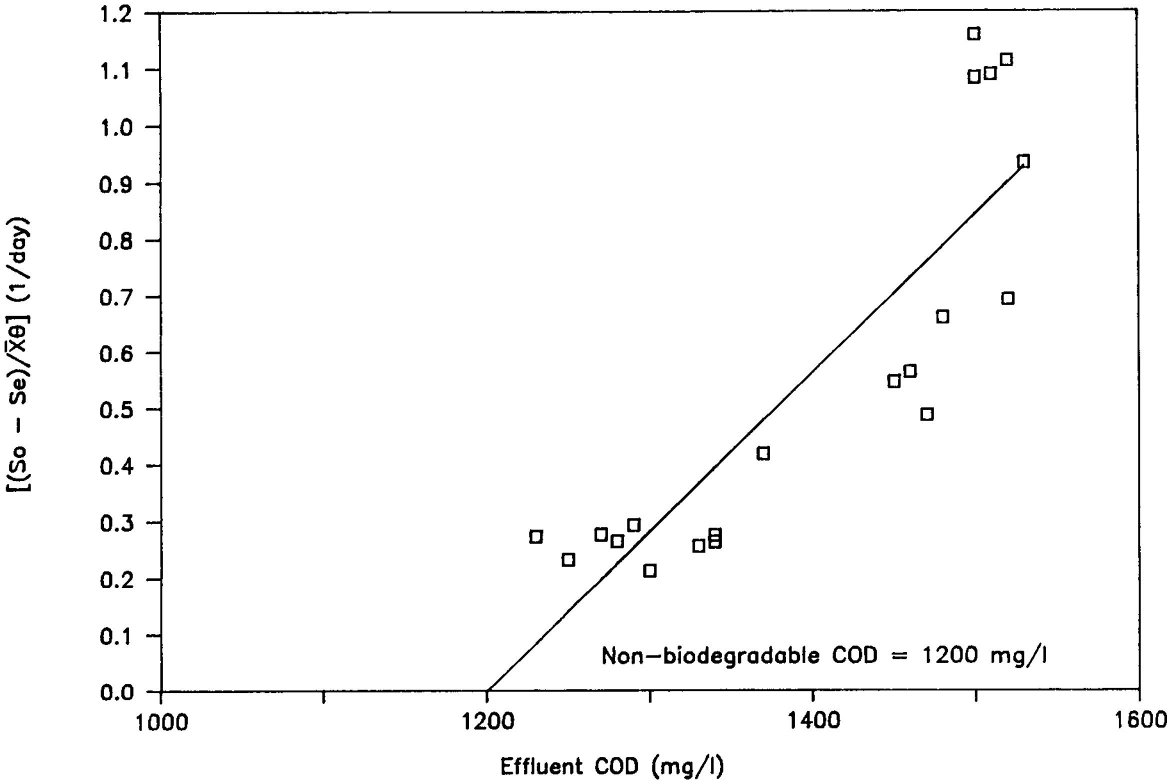

Figure 41. Plot of total COD utilization rate vs. the effluent COD for activated sludge treatment of Jacobs Ranch CWF ultrafilter permeate

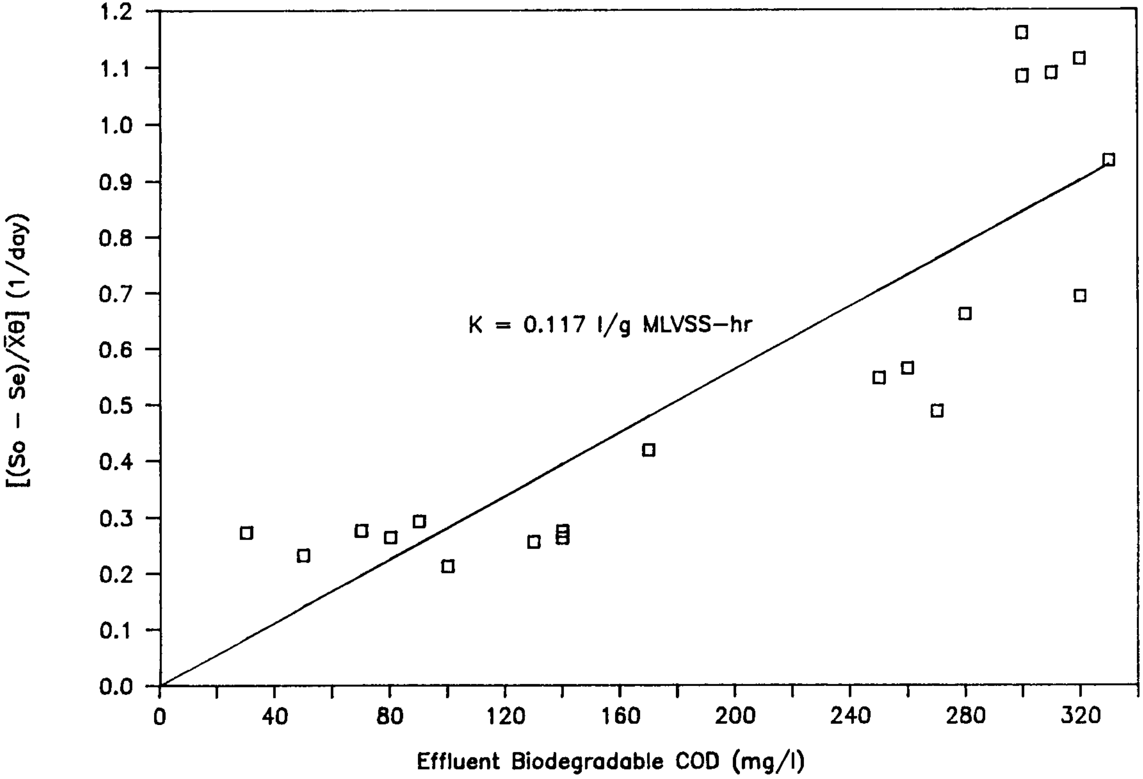

Figure 42. Plot of the biodegradable COD utilization rate vs. effluent biodegradable COD for activated sludge treatment of Jacobs Ranch CWF ultrafilter permeate

The specific yield coefficient, Y, and the endogenous decay constant, ke, are determined by the slope of the line, and the y-axis intercept, respectively, from a plot of the reciprocal of the mean cell residence time versus the specific rate of substrate removal. Such a plot, based on biodegradable COD, is shown in Figure 43. Based on biodegradable COD, the yield coefficient, Y, was estimated to be 0.189 mg MLVSS produced/mg COD removed, with an endogenous decay constant, ke, of 0.012 day^{-1}.

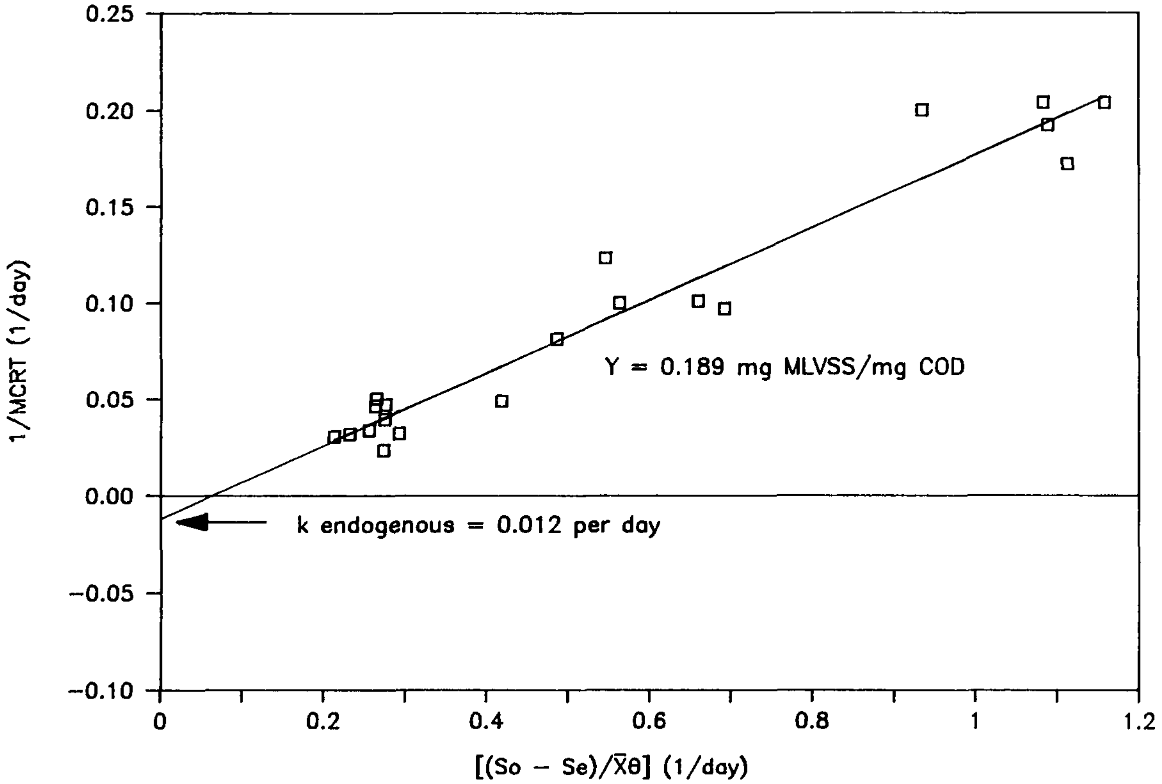

Figure 43. Plot of the reciprocal of the mean cell residence time vs. biodegradable COD utilization rate for activated sludge treatment of Jacobs Ranch CWF ultrafilter permeate

Figure 44 shows a plot of the specific rate of TOC removal versus effluent soluble TOC. The nonbiodegradable fraction (x-intercept) was determined to be 123 mg TOC/l. Figure 45 illustrates a plot of the specific utilization rate of the biodegradable TOC fraction. The reaction rate constant K, based on TOC, was estimated to be 0.117 l/g MLVSS-hr, which is in agreement with that determined for COD utilization.

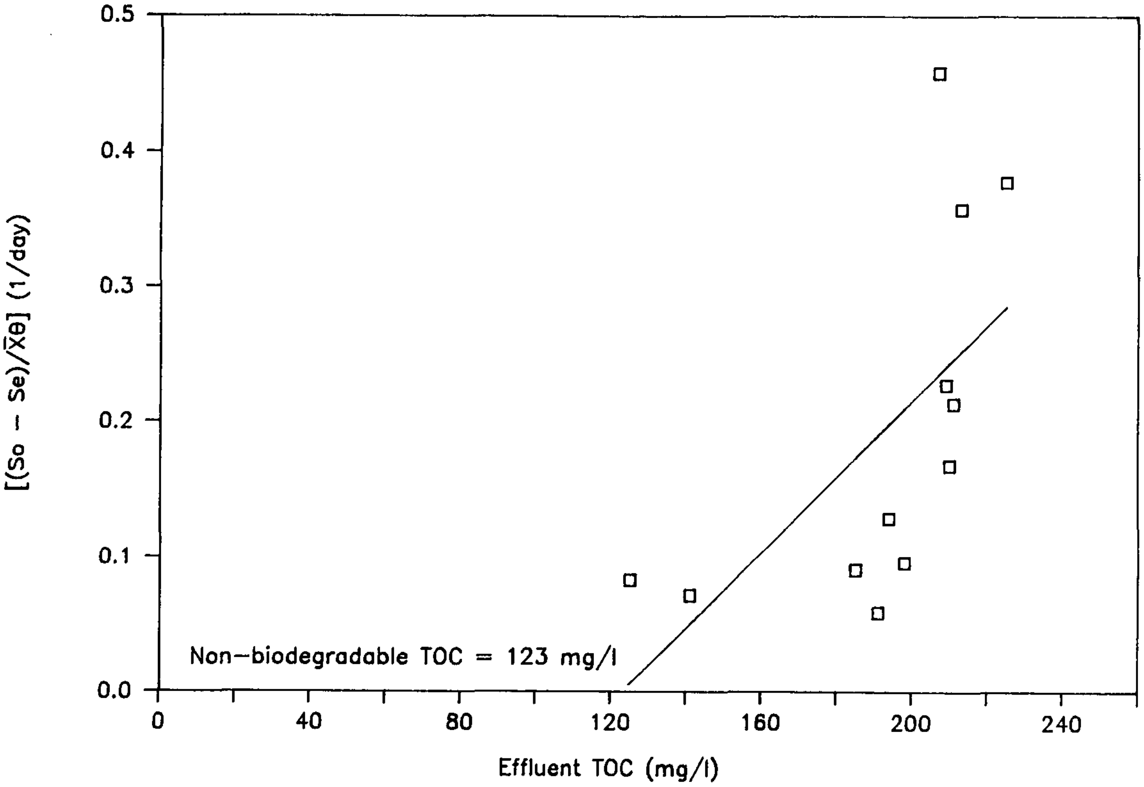

Figure 44. Plot of specific rate of TOC removal vs. effluent TOC for activated sludge treatment of Jacobs Ranch CWF ultrafilter permeate

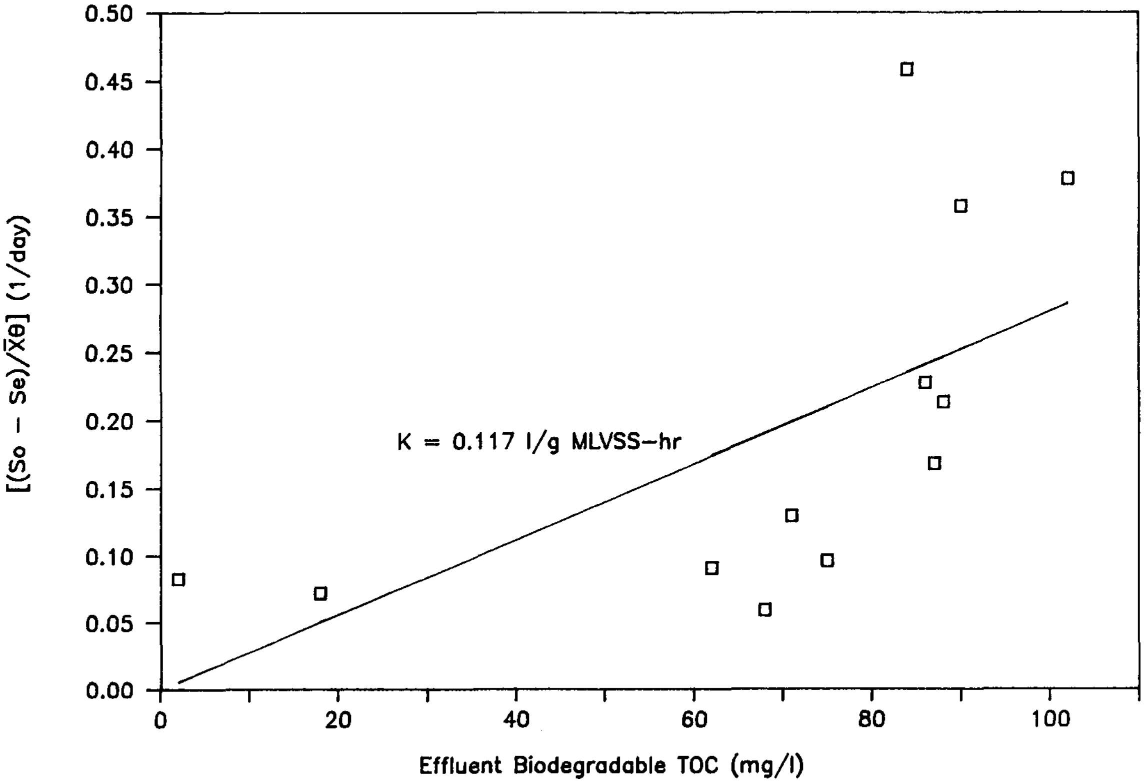

Figure 45. Plot of biodegradable TOC removal rate vs. effluent TOC for activated sludge treatment of Jacobs Ranch CWF ultrafilter permeate

Figure 46 is a plot of specific oxygen uptake versus the specific rate of biodegradable COD utilization. The oxygen coefficient, Y', and the endogenous oxygen coefficient, ke', are determined from the slope of the line and the y-axis intercept, respectively. The oxygen and endogenous oxygen coefficients are used for the estimation and design of aeration equipment associated with the activated sludge process. The oxygen coefficient, Y', was found to be 0.582 mg O_2/mg COD removed. The endogenous oxygen coefficient, ke', was determined to be 0.003 mg O_2/mg MLVSS-day. An approximation of the endogenous oxygen coefficient may be calculated from the endogenous decay coefficient, ke. The endogenous oxygen coefficient theoretically equals 1.42 ke. Based on the endogenous decay coefficient determined from steady-state COD results, ke should theoretically be equal to 0.017 mg O_2/mg MLVSS-day.

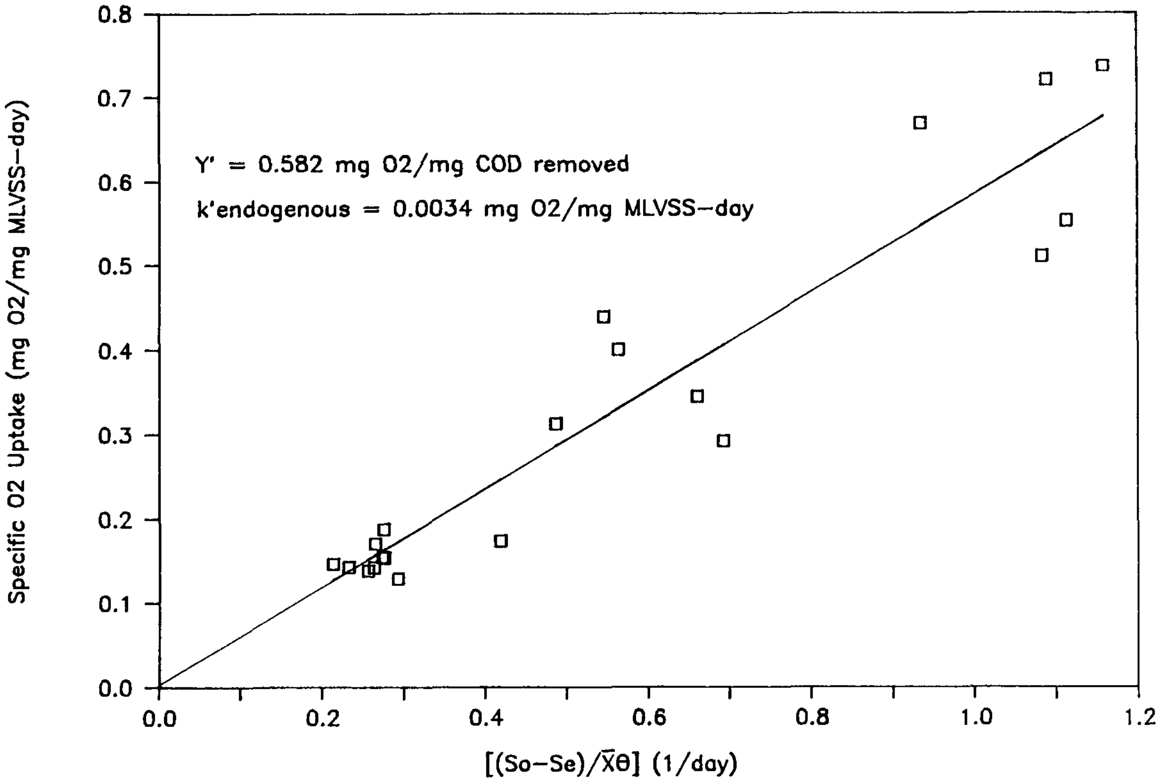

Figure 46. Plot of the specific oxygen uptake vs. the specific rate of biodegradable COD utilization

4.0 CONCLUSIONS

1. ASTM static-float sink method substantially reduced ash concentrations in North Dakota lignite and Alaskan and Wyoming subbituminous coals.

2. Both physical and chemical cleaning of raw coals yielded products with less than 2 wt% ash. However, the HWD products proved to be relatively unstable due to the removal of the majority of ions from the cleaning.

3. Froth flotation is a difficult cleaning technique when applied to low-rank coal and is very reagent specific.

4. Dispersion of clean coal in oil (DCCOT) proved to be less effective in removing ash from low-rank coal then static-float sink and froth flotation.

5. Collodial coal cleaning was effective in reducing ash levels, yet design and operation problems make it an unlikely candidate for scale-up.

6. Optimization of packing effeciency for a coal/water fuel enhances solids concentrations of HWD fuels typically by 5%.

7. An additive package, consisting of xanthan gum and a non-ionic surfactant, was designed to produce a stable, high-solids-loaded coal/water fuel with favorable flow behavior. However, due to the high cost of the non-ionic surfactant, slight dilatancy in flow behavior, and additive degradation at high temperatures, alternatives such as low-cost anionic dispersants may prove to be more effective.

8. Ultrafiltration is a technically viable means for removal and recovery of suspended solids from centrifuge centrates.

9. Activated sludge treatment of the ultrafilter permeate was effective at removing biological oxygen demand (BOD_5).

5.0 RECOMMENDATIONS

1. With combined physical and chemical cleaning methods, pilot-scale production of clean low-rank coal should be implemented.

2. Additional froth flotation testing for investigating potential frothing reagents should be performed.

3. Additive and particle size optimization findings should be tested in combination to produce high-quality CWF in pilot-scale quantities.

4. Identification of effective additives should continue, with emphasis placed on anionic additives combined with other stabilizing additives.

5. The PDU should continue to be used for basic and supportive roles in producing hot-water-dried coal/water fuels.

6. Further efforts should be expended on the development of a process development-scale ultrafiltration loop to treat and recycle coal/water process water.

7. Economic feasibility for the various wastewater treatment process options should be accessed for inclusion with overall economic cost of CWF preparation from low-rank coals.

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3.3 Physical Coal Cleaning

3.3.1 Float-Sink Analysis

3.3.1.1 Background

Float-sink testing is the standard test for determining the washability characteristics of coals. The various specific-gravity components obtained from the float-sink test represent theoretical limits attainable by gravity separation. This method can be performed either statically or centrifugally. Static separation (4) has historically been most often used for coarse-coal size fractions (3/8" (9.5 mm) - 10 mesh), although it could be used for finer-coal size fractions (as low as 100 mesh). A centrifugal separation method (5) is primarily used for fine-coal size fractions (-10 mesh).

3.3.1.2 Experimental Methods

Both static and centrifugal float-sink methods were performed using 1.3, 1.4, 1.5, and 1.6 specific gravity Certigrav solutions. Static float-sink testing involved adding 100-150 grams of coarse coal (1/4" x 10 mesh) to a float-sink flask containing 1600 milliliters of Certigrav solution. The test was completed when the coal separated into two distinct fractions. Centrifugal separation was accomplished by combining 20-30 grams of fine coal and 350 milliliters of solution into each of four centrifugal beakers and centrifuging for 20 minutes at 1500 rpm. After centrifugation and filtration, the samples were separated into float and sink fractions.

3.3.1.3 Results

Float-sink tests using Certigrav solution were completed on samples of Beulah-Zap lignite and Spring Creek, Jacobs Ranch, and Usibelli subbituminous coals. The 1/4" x 10 mesh samples were prepared by crushing the coal to -1/4 inch and then screening out the -10 mesh fraction. The combustion grind samples were prepared by using a pilot-scale pulverizer containing a 200 mesh screen. Micronized samples were made using a jet-mill pulverizer containing a 325 mesh screen. Centrifugal separation was performed only on the combustion grind and micronized samples.

Table 3 summarizes the washability results on Beulah-Zap lignite. The weight recovery for the products was initially greatest at 1.3 sp. gr. for the 1/4" x 10 mesh sample. As the particle size became smaller higher specific gravity was needed to recover 50% of the product. Fifty percent recovery was obtained with the combustion grind sample at the 1.4 sp. gr. level. For the micronized sample, 50% recovery was not obtained until between 1.4 and 1.5 sp. gr.

Table 4 contains the washability results of Spring Creek subbituminous coal. This coal has a raw ash content of approximately 4%. When float-sink analysis was performed, liberation of the ash was at a minimum. The weight recovery of the sample did not fluctuate from one particle size to the next; the main difference in weight recovery occurred at 1.3 sp. gr. for the 1/4" x 10 mesh sample. This coal did not benefit significantly from grinding to smaller particle sizes.