DOE/PC/79892--T19

Technical Progress Report

for the Fifteenth Quarter

(October 1, 1991 - December 31, 1991)

DOE/PC/79892--T19

DE92 013353

DEVELOPMENT OF THE CHEMICAL AND ELECTROCHEMICAL COAL CLEANING PROCESS

by

Cesar I. Basilio and Roe-Hoan Yoon

Department of Mining and Minerals Engineering
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061

<u>Contract Number</u>:
DE-AC22-87PC79892

<u>Project Manager</u>

Richard Read
U.S. Department of Energy
Pittsburgh Energy Technology Center
P.O. Box 10940
Pittsburgh, Pennsylvania 15236

U.S. DOE patent clearance <u>not</u> required prior to publication of this document.

ABSTRACT

The continuous testing of the CECC bench-scale unit (Task 6) was completed successfully in this quarter using Middle Wyodak and Elkhorn No. 3 coal samples. The CECC unit was run under the optimum conditions established for these coal samples in Task 4. For the Middle Wyodak coal, the ash content was reduced from 6.96% to as low 1.61%, corresponding to an ash rejection (by weight) of about 83%. The ash and sulfur contents of the Elkhorn No. 3 coal were reduced to as low as 1.8% and 0.9%. The average ash and sulfur rejections were calculated to be around 84% and 47%. The CECC continuous unit was used to treat -325 mesh Elkhorn No. 3 coal samples and gave ash and sulfur rejection values of as high as 77% and 66%. In these tests, the clean -325 mesh coal particles were separated from the liberated mineral matter through microbubble column flotation, instead of wet-screening.

PROJECT OBJECTIVES

The objectives of this work are to: (a) determine the mechanisms by which the CECC process removes ash and pyritic sulfur from coal, (b) learn more about the operating parameters of the process, (c) collect engineering information for the scale-up of the process, and (d) test the CECC process as a bench-scale continuous operation.

PROJECT TASKS

Task 6 - Continuous Unit Operation

Subtask 6.2 - Continuous Test Work

The testing of the CECC bench-scale continuous unit was completed in this quarter. The continuous unit was run at a rate of 2 lb/hr with a corresponding reactor retention time of about 6.3 hrs. Table I shows the conditions used for the continuous testing of the Middle Wyodak and Elkhorn No. 3 coal samples. These conditions were determined to be optimum for processing these coal samples in Task 4. The tests were conducted on dry-screened 65 x 325 mesh Middle Wyodak and Elkhorn No. 3 coal samples. The feed samples used were dry-screened because the screw feeder in the continuous unit could not handle moist samples. The option of wet-screening the feed and drying afterwards was not considered since this would result in the oxidation of the feed, which is detrimental to the CECC process. For the continuous test work on the fine by-zero coal, dry-screened -325 mesh samples were used. After the CECC treatment, the clean fine by-zero coal was separated from the liberated mineral matter by microbubble column flotation, instead of wet-screening. The continuous tests on the fine coal were limited to the Elkhorn No. 3 coal sample since the subbituminous Middle Wyodak coal does not respond well to flotation.

a. Continuous Testing of Middle Wyodak Coal

Table II shows the results obtained for the continuous testing of the 65 x 325 mesh Middle Wyodak coal, which had a feed ash and sulfur content of 6.96% and 0.52%. On the

TABLE I

Conditions Used for the Continuous Testing on Middle Wyodak Coal and Elkhorn No. 3 Coal

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

TABLE II

Results of the Continuous Testing on Middle Wyodak Coal (65 x 325 mesh)

Sampling Period	Ash Content (% wt)		Ash Rejection (% wt)	Sulfur Content (% wt)		Yield (% wt)
	Product	Reject		Product	Reject	
Day 1	4.38	5.49	-	0.85	1.11	-
Day 2	2.48	5.52	-	0.65	1.06	-
Day 3 (avg)	1.88	5.20	80.38	0.75	1.48	81.30
10:30 AM	1.95	5.53	79.94	0.73	1.57	83.10
2:30 PM	1.86	5.00	80.67	0.76	1.52	80.36
5:30 PM	1.83	5.07	80.52	0.75	1.35	80.43
Day 4 (avg)	1.84	5.63	80.54	0.76	1.20	81.35
11:00 AM	1.76	5.58	81.68	0.76	1.41	80.46
2:00 PM	1.61	5.28	83.30	0.85	1.20	80.24
4:00 PM	1.73	5.63	81.88	0.72	1.00	80.80
5:00 PM	2.17	5.49	77.16	0.75	0.97	81.07
7:00 PM	1.96	6.16	78.66	0.76	1.43	84.19
Day 5	2.18	5.58	77.32	0.64	0.99	80.47

Feed: 6.96% ash
0.52% sulfur

first day, the ash content of the Middle Wyodak coal after treatment was 3.38%. The average ash content of the product obtained was reduced to 2.48% on Day 2. The improvement may be attributed to the different parameters of the continuous unit reaching steady state level, particularly the reactor temperature and pulp density. The product obtained on Day 3 gave an average ash content of 1.88%, while the reject had an average ash content of 5.2%. The ash rejection by %weight was calculated in this work according to the following:

$$Ash\ Rejection\ (by\ \%wt) = \frac{Wt\ of\ ash\ in\ Feed\ -\ Wt\ of\ ash\ in\ Product}{Wt\ of\ ash\ in\ Feed} \times 100. \quad [1]$$

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

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

The yield in the continuous testing was lower than that obtained in the parametric batch tests (Task 4). Also, the ash contents of the reject were relatively low, as shown in Table II.

These problems may be attributed to the fact that the feed for the continuous testing was prepared by dry-screening. As a result, the feed coal contained considerable amounts of fine coal that passed through the 325 mesh screen and reported to the reject. Wet-screening would have eliminated this problem, but it was difficult to feed the wet coal at the slow feed rate (2 lb/hr) employed in the present work.

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

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

b. Continuous Testing of Elkhorn No. 3 Coal

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

Table III shows the results obtained for the continuous testing of the 65 x 325 mesh sample. The feed coal had ash and sulfur contents of 9.43% and 1.57%. Samples were not taken during the first two days of operation since the continuous unit did not attain steady state until after about 36 hours due to clogging of some of the lines. On Day 3, the average ash contents of the product and reject were 2.00% and 10.31%. The ash rejection, as given by Equation 1, was 85.23% with a yield of about 70.71%. As discussed above for the Middle Wyodak coal, the yield was lower than that obtained in the parametric batch testing (Subtask 4.1), probably due to the fact that the coal used here was dry-screened while that used in the batch testing was wet-screened.

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

The reactor temperature was lowered to about 50°C for Day 5, and the results show a slight decrease in the amount of mineral matter removed. The average product ash content was

TABLE III

Results of the Continuous Testing on Elkhorn No. 3 Coal (65 x 325 mesh)

a. Ash Rejection

Sampling Period	Ash Content (% wt)			Ash Rejection (% wt)			Yield (% wt)
	Feed	Product	Reject	Total	Liberated	Dissolved	
Day 1	9.43	-	-	-	-	-	-
Day 2	9.43	-	-	-	-	-	-
Day 3	9.43	2.00	10.31	85.23	62.99	37.01	71.62
Day 4 (avg)	9.43	2.10	8.58	83.68	71.62	28.38	73.77
8:00 AM	9.43	1.79	8.11	86.13	74.60	25.40	74.17
10:00 AM	9.43	2.29	9.01	82.37	69.95	30.05	73.70
12:00 PM	9.43	2.24	8.39	82.99	69.64	30.36	71.69
2:00 PM	9.43	2.01	8.83	84.20	71.24	28.76	74.14
4:00 PM	9.43	2.17	8.58	82.71	72.66	27.37	75.14
Day 5	9.43	2.27	10.04	82.97	66.26	33.74	72.90

b. Sulfur Rejection

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

2.27%, while the ash rejection was calculated to be around 83% with a yield of 72.9%. The ash rejection and yield were slightly lower than those obtained at a higher temperature, but the decrease was not significant enough to indicate any temperature dependence.

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

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

Continuous test work was also conducted on -325 mesh Elkhorn No. 3 coal. The continuous unit was run under the same conditions used for the 65 x 325 mesh samples. The CECC-treated samples were collected, rinsed with water and filtered to remove any acid solution present in the moist sample. The clean coal was then separated from the liberated mineral matter by microbubble column flotation. The flotation tests were conducted on a 3-inch diameter by 6-ft long column. The sample was fed as 5% solids (by weight) slurry at a rate of either 150 ml/min or 300 ml/min. Frother additions of 0.5 lb/ton of Dowfroth 250 were employed in all the tests.

Table IV shows the continuous test results on -325 mesh Elkhorn No. 3 coal samples. Also shown for comparison are the flotation test results obtained with the coal that was not treated by the CECC process. There was no collector added in this set of flotation tests. For the untreated sample that was floated at a feed rate of 150 ml/min (Test No. 1), the ash content was reduced from 5.46% to 2.91%. There were no significant changes in the removal of mineral matter when the feed rate was increased to 300 ml/min (Test No. 2). However, the sulfur rejection was lower with that obtained at a higher feed rate. For the CECC-treated samples (Test Nos. 3 and 4), the ash rejections were much higher than those for the untreated samples. The amount of mineral matter rejected by the CECC process was as high as 76.9%, while the sample floated directly gave an ash rejection of only 49%. This is to be expected since the CECC process liberates the mineral matter. However, the yield was lower for the CECC-treated sample than for the untreated sample. The lower yield may be attributed to the decrease in the floatability of the sample that was brought about by the oxidation of the coal during the CECC process.

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

The mass balance indicates that liberation is playing a major role in the removal of mineral matter by the CECC process. As much as 70% of the mineral matter removed is due

TABLE IV

Results of the Continuous Testing on Elkhorn No. 3 Coal (-325 mesh)

a. Ash Rejection

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

b. Sulfur Rejection

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

* Flotation feed rate = 150 ml/min
** Flotation feed rate = 300 ml/min

to liberation. On the other hand, the average amount of sulfur rejection due to liberation is only about 32%. This is opposite to what was observed for the 65 x 325 mesh sample. However, total sulfur removal in the CECC treatment of the -325 mesh sample was better probably because pyrite liberation and dissolution increased with the decrease in particle size.

To increase the yield, another set of tests was carried out on -325 mesh coal samples using 1 to 3 lb/ton of kerosene as a collector during the flotation stage. The feed rate was set at 300 ml/min, while the rest of the test conditions were similar to those employed for tests conducted without collector addition. Table V shows the results obtained for untreated and CECC-treated Elkhorn No. 3 coal samples. Using 1 lb/ton of kerosene, the ash content of the untreated sample was reduced from 5.27% to 2.75%, representing an ash rejection of 51.4%. When the coal was CECC-treated and floated using 1 lb/ton of kerosene (Test No. 2), the ash content was reduced from 6.66% to 2.35%. In this case, the ash rejection was determined to be 72.4% with a yield of about 78.25%. At a higher kerosene addition of 3 lbs/ton (Test No. 3), the yield increased to 86.2% with only a slight decrease in the ash and sulfur rejection. It can be seen that the addition of kerosene in the flotation stage can help improve the recovery significantly without any noticeable decrease in ash and sulfur rejection. According to the mass balance analysis, the amount of mineral matter rejection due to liberation was about 83.7%, which was higher than that obtained without collector addition.

Figure 1 shows the combustible recovery versus ash rejection curves for the tests conducted on the -325 mesh Elkhorn No. 3 coal. The curve for the CECC-treated samples was shifted to the right of that for the untreated samples suggesting that the combination of CECC process and flotation gives better ash rejection than flotation only. A similar trend is shown in

TABLE V

Results of the Continuous Testing on Elkhorn No. 3 Coal (-325 mesh)

a. Ash Rejection

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

b. Sulfur Rejection

Test No	Process	Sulfur Content (% wt)			Sulfur Rejection (% wt)		
		Feed	Product	Reject	Total	Liberated	Dissolved
1*	Flotation	1.91	1.44	3.58	29.79	-	-
2*	CECC & Flotation	2.22	1.26	1.96	55.59	34.55	65.45
3**	CECC & Flotation	2.22	1.29	2.02	49.90	25.14	74.86

* Collector addition = 1 lb/ton kerosene
** Collector addition = 3 lb/ton kerosene

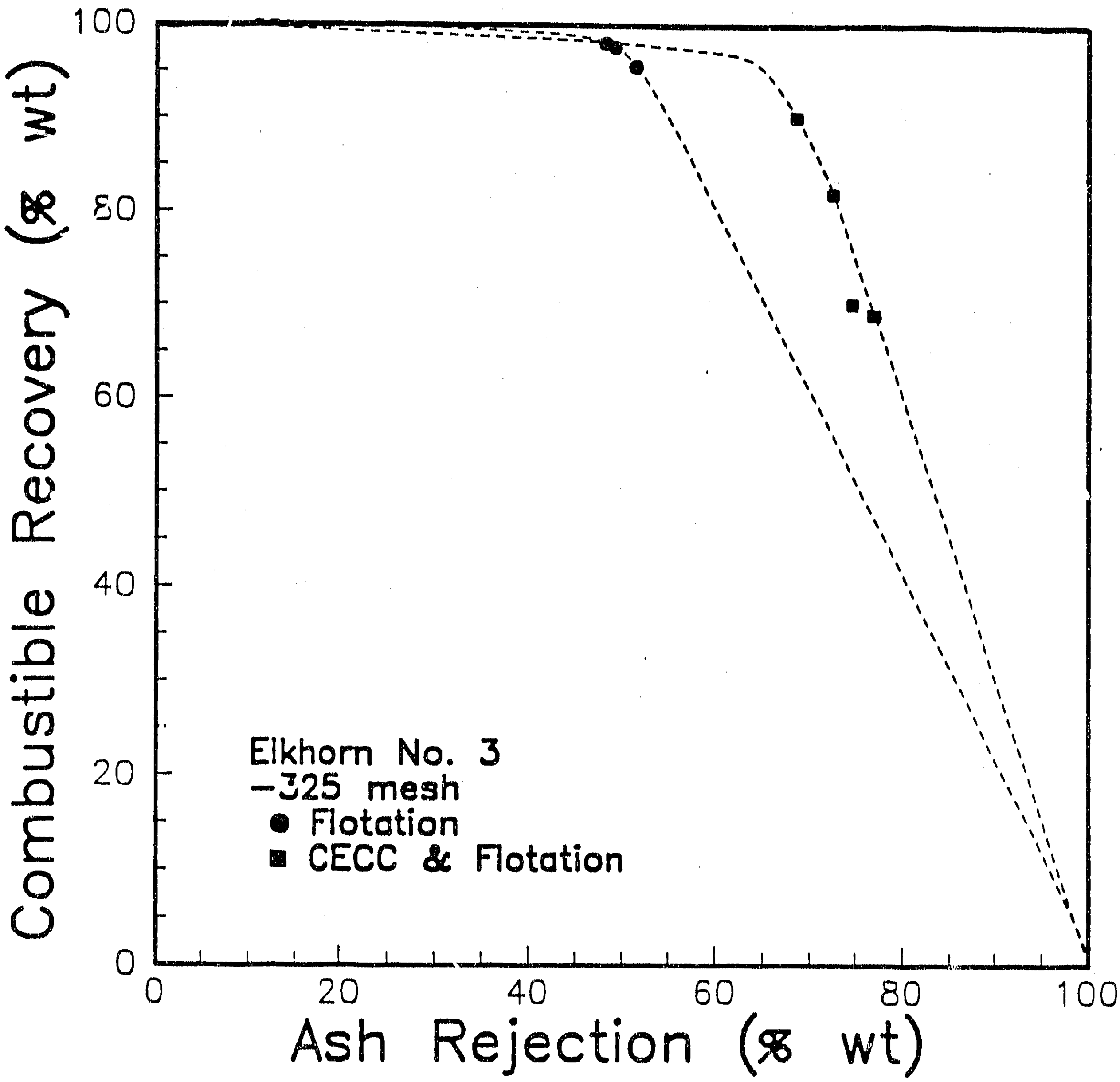

Figure 1. Combustion recovery versus ash rejection curves for the continuous testing of -325 mesh Elkhorn No. 3 coal.

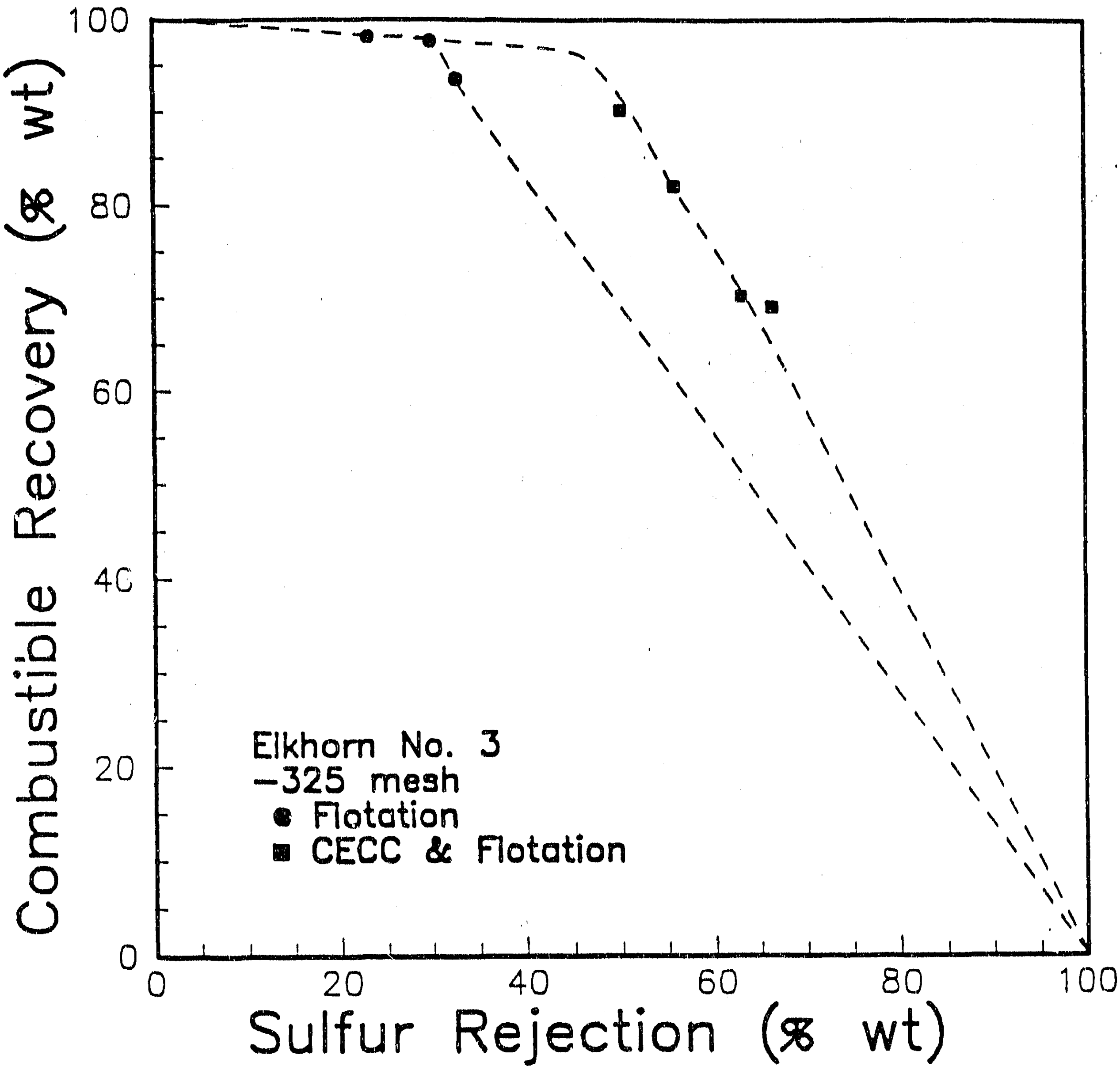

Figure 2. Combustion recovery versus sulfur rejection curves for the continuous testing of -325 mesh Elkhorn No. 3 coal.

the combustible recovery versus sulfur rejection curves (Figure 2). This suggests that sulfur rejection improves with the use of the CECC process. Additional data points are being collected to verify this conclusion.

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

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

SUMMARY AND CONCLUSIONS

Continuous testing of the bench-scale CECC process was conducted on the Middle Wyodak and Elkhorn No. 3 coal samples at a throughput of 2 lb/hr. The feed sample used in all the tests was dry-screened since the screw feeder could not handle moist samples at the low feed rate employed in these tests. The continuous testing was conducted at the optimum conditions established in Task 4 for these coal samples.

The ash content of the 65 x 325 mesh Middle Wyodak coal was reduced from 6.96% to as low as 1.61% in the continuous tests. The average ash rejection obtained for this coal was about 80% (by weight) with an average yield of 81% (by weight). The mineral matter removal observed here was higher than that observed in the parametric batch tests (Subtask 4.1) or that predicted in the optimization and validation tests (Subtask 4.2). However, the yield was lower, which may be attributed to the fact that the coal used in the continuous tests was dry-screened while wet-screened coal was used in the batch tests. Presumably, the feed coal used for the continuous tests still contained some -325 mesh coal particles, which reported to the reject during the wet-screening stage of the CECC process. With the Middle Wyodak coal, the sulfur content increased due to the adsorption of sulfate ions on the oxygen-functional groups of this low-rank coal.

The continuous CECC tests conducted on the 65 x 325 mesh Elkhorn No. 3 coal gave encouraging results. The ash content was reduced from 9.43% to as low as 1.79%, while the sulfur was reduced from 1.57% to 0.9%. The ash and sulfur rejections obtained in these tests averaged about 84% and 47.3%, respectively, with an average yield of around 72.5%. The results obtained here were better than those obtained in Task 4, but produced lower yield because the feed coal was prepared by dry-screening.

Continuous CECC tests were conducted on -325 mesh Elkhorn No. 3 coal, with the product being treated by microbubble column flotation to separate the clean coal from the liberated mineral matter. The use of flotation was necessary because the screening technique cannot be used for the by-zero coal. The tests were conducted at the same operating conditions employed for the 65 x 325 mesh sample. After CECC treatment, the coal was subjected to flotation using a 3-inch diameter by 6-ft long column. The ash and sulfur contents were reduced to as low as 2.35% and 1.25%, respectively. When no collector was used for flotation, the ash rejection obtained was 76.9% with a yield of 65.7%. The relatively low yield obtained here may be attributed to the decrease in the hydrophobicity of the sample resulting from the oxidation of the coal in the CECC process. When 1 to 3 lbs/ton of collector was used for flotation, the yield increased to 86.2% while the product ash increased to only 2.4%. The ash and sulfur rejections by the combination of CECC treatment and flotation were significantly higher than those obtained by flotation only.

According to the mass balance, the liberation of mineral matter by the CECC process is found to play a major role in the removal of mineral matter from the Elkhorn No. 3 coal sample. This was not the case, however, with the Middle Wyodak coal; much of the ash rejection was due to the dissolution of carbonates in this low-rank coal.

END

DATE FILMED

6/15/92