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Final Report: Coal Desulfurization by Low-Temperature Chlorinolysis, Phase III

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ABSTRACT

The Coal Desulfurization by Low Temperature Chlorinolysis Project was conducted by the Jet Propulsion Laboratory, California Institute of Technology, under DOE Interagency Agreement No. DE-AI01-77ET12547 with NASA for the period March 1, 1980 through March 1, 1981.

Laboratory-scale, bench scale batch reactor and mini-pilot plant tests were conducted on 22 bituminous, sub-bituminous and lignite coals. Chemical pretreatment and post-treatment of coals relative to the chlorination were tried as a means of enhancing desulfurization by the chlorinolysis process. Elevated-temperature (500-700°C) hydrogen treatment of chlorinolysis-processed coal at atmospheric pressure was found to substantially increase coal desulfurization up to 90%. Sulfur forms, proximate and ultimate analyses of the processed coal are included.

Mini-pilot plant operation indicates that the continuous flow reactor provides coal desulfurization results comparable to those that obtained in the batch reactor. Seven runs were conducted at coal feed rates of 1.5-8.8 kg per hour using water and methylchloroform solvents, gaseous chlorine feed of 3-31.4 SCFH at 21-70°C, and atmospheric pressure for retention times of 20-120 minutes.

PREFACE

The work described in this report was performed by the Control and Energy Conversion Division of the Jet Propulsion Laboratory.

ACKNOWLEDGMENT

The support to the Coal Desulfurization by Chlorinolysis Project includes the Caltech research of Professor William Corcoran and his graduate students, who conducted related research studies to the chlorinolysis process; Professor George Gavalas and Dr. Mitsuo Oka, who conducted a study of the "Distribution of Chlorine in Dechlorinated Coals;" Dr. William Mueller of JPL, who conducted supporting research in electrolysis, supercritical CO_2 and solvent swelling related to chlorinolysis. In addition, the operating and technician support in the laboratory, batch reactor system, and mini-pilot plant provided by Mr. Larry Ford, Mr. Ralph Morrow, Mr. Dan Granett, Mr. Jason Kovatch and Mr. Ronald Russing is acknowledged and apppreciated.

The work was supported by the Coal Preparation Division, Pittsburgh Mining Technology, U.S. Department of Energy, with Dr. Scott Taylor as Technical Project Officer. The work was conducted by the Jet Propulsion Laboratory under DOE Interagency Agreement No. DE- AI01-77ET12547 with NASA.

FOREWORD

This is the final report for Phase III of the Coal Desulfurization by Low Temperature Chlorinolysis program conducted by the Jet Propulsion Laboratory under DOE interagency Agreement No. DE-AI01-77ET12547 with NASA for the period March 1, 1980 through March 1, 1981. The reported work covers laboratory tests at 100 grams of coal, batch reactor tests at 2 kilograms of coal and continuous flow mini-pilot plant tests at 2 kilograms of coal per hour. Tests were conducted on 22 bituminous, sub-bituminous and lignite, high sulfur (>1%) and low sulfur (<1%), coals obtained from the East, Midwest, Southeast, and West. The test program was designed and operated to investigate the chlorinolysis process with pretreatment and post-treatment of the coal in order to achieve enhanced coal desulfurization. This included chemical treatment of the coals before and after the chlorination process as well as modifying the dechlorination stage with oxidizing and reducing agents at elevated temperatures. The mini-pilot plant operation was designed to test the chlorinolysis process under conditions of continuous flow operation.

The work described in this report involves the inventions pertaining to coal processing methods and apparatus contained in U.S. Patent 4,146,367 which was made in the performance of Prime Contract NAS7-100 between the National Aeronautics and Space Administration and California Institute of Technology.

CONTENTS

CONTENTS (Cont'd)

CONTENTS (cont'd)

CONTENTS (cont'd)

CONTENTS (cont'd)

LIST OF FIGURES

List of Figures (Cont'd)

LIST OF TABLES

Page

APPENDICES

INTRODUCTION

JPL initiated the development of the chlorinolysis process for coal desulfurization in 1976 under the JPL Director's Discretionary fund. The preliminary results of coal desulfurization by chlorinolysis attracted Bureau of Mines funding for a four month laboratory screening study of twelve bituminous, sub-bituminous and lignite coals obtained from the East, Midwest and West (Ref. 1). The DOE then funded a Phase II follow-on program for a bench-scale, batch reactor test program at two kilograms of coal per batch and a parallel program of design and construction of a continuous flow mini-pilot plant for operation at 2 kilograms of coal per hour (Ref. 2). The Phase II batch reactor test program was based on five bituminous coals obtained from Ohio, Illinois, and Kentucky. Maximum total sulfur removals obtained for the five coals was 45-66% with pyritic sulfur removals of 71-95% and organic sulfur removals of 0 to 24% with water coal slurries. A higher organic sulfur removal of 46-89% was found with methylchloroform coal slurries. However, this higher organic sulfur removal was found on later testing and analyses to be an artifact of the pyritic sulfur determination in the presence of an organic solvent in which "iron" is used to determine the residual pyritic sulfur.

As a result of the Phase II program tests and accomplishments, the current Phase III program was designed to investigate means of enhancing the level of total coal desulfurization above the previous Phase II maximum of 45-66% to achieve the requirement of 90% sulfur removal for high sulfur (>1%) coals and 70% sulfur removal for low sulfur (<1%) coal. In addition, a parallel program requirement was to establish the operating conditions and test results for the continuous flow mini-pilot plant that includes a chlorinator, horizontal belt vacuum filter-spray wash and dechlorinator.

This report covers the laboratory tests, batch reactor tests and mini-pilot plant tests that were conducted as a part of the Phase III program from March 1, 1980 through March 1, 1981.

SUMMARY

This is the final report for Coal Desulfurization by Low Temperature Chlorinolysis - Phase III, conducted by the Jet Propulsion Laboratory, California Institute of Technology at Pasadena, California under DOE Interagency Agreement No. DE-AI01-77ET12547 with NASA for the period March 1, 1980 through March 1, 1981.

PHASE III TASKS

The Phase III activity consisted of: (1) laboratory-scale and bench-scale batch reactor testing of twenty-two bituminous sub-bituminous and lignite coals by the chlorinolysis process that included chlorination, filtration-wash and dechlorination; (2) laboratory-scale and bench-scale batch reactor testing of chemical pretreatment and post-treatment of coal relative to the chlorination process in order to achieve enhancement of coal desulfurization; (3) operation of the continuous flow mini-pilot plant that included: chlorination, horizontal-belt vacuum filtration-spray washing, and dechlorination.

LAB SCALE AND BENCH-SCALE BATCH REACTOR TESTS

Laboratory-scale and bench-scale batch reactor tests of the 22 chlorinolysis-processed coals showed up to 60% desulfurization for the high sulfur coals (>1% sulfur) with an accompanying 90+% pyritic sulfur reduction and up to 30-40% organic sulfur removal. The low sulfur coals (<1% sulfur) showed more limited desulfurization of up to 20-50% total sulfur reduction.

COAL PRETREATMENT AND POST-TREATMENT FOR CHLORINOLYSIS PROCESS

Laboratory-scale and bench-scale batch reactor tests of coal pretreatment and post-treatment relative to the coal chlorination showed no significant improvement in desulfurization. The pretreatment included: 9% NaOH at 93-230°C for 60 minutes; methanol and 50% methanol - 50% carbon-tetrachloride at 58-65°C for 60 minutes; 9-12% HNO_3 at 70-100°C for 30-60 minutes; 1-10% Na_2CO_3 added to the chlorination and 9% NaOH added to the chlorination. The more severe coal pretreatment with 10% NaOH and 9-12% HNO_3 showed desulfurization comparable to that obtained in the chlorinolysis, i.e., 50-60% desulfurization. However, the ensuing chlorinations were not able to achieve any significant increase in desulfurization as a result of the pretreatments. The pretreatment with solvents methanol and methanol-carbontetrachloride mixture showed no effect on the chlorination. The addition of Na_2CO_3 and NaOH to the chlorination did not have any positive effect on desulfurization.

Post-treatment with 6.5-10% NaOH at 65-290°C for 60 minutes did not increase desulfurization. Post-treatment with 10% H_2SO_4 and 10-40% HNO_3 at 95°C for 60 minutes produced no improvement on desulfurization. Post-treatment with 10% Na_2CO_3 at 230°C for 60 minutes provided no improvement. Organically bound sulfur, resistant to the chlorination process, also resisted the action of even extremely strong oxidizing and leaching agents.

DECHLORINATION STAGE FOR ADDED DESULFURIZATION

An investigation of the dechlorination stage for improving desulfurization by means of elevating the dechlorination temperature from 400°C to 700°C with nitrogen showed some additional increase in desulfurization, but not much above that normally found at 400°C. The addition of oxidizing agents to the nitrogen such as 1% NO_2, 1% SO_2, 5-21% O_2 in the dechlorination stage showed no improvement in desulfurization.

A major achievement was obtained in increased desulfurization by introducing hydrogen in lieu of nitrogen and increasing the temperature from 400 to 500-700°C for 60 minutes, at atmospheric pressure. Coal desulfurization was increased from 60% for chlorinolysis processed coal up to 90% desulfurization. Raw coal with hydrogen treatment at 700°C also showed substantial desulfurization but not to the same extent as chlorinolysis processed coal.

MINI-PILOT PLANT

Six mini-pilot plant runs were conducted to demonstrate continuous flow operation of the chlorinator, horizontal belt vacuum filter-spray wash and dechlorinator. Operating conditions of the chlorination were: 1.5-8.8 kg coal feed (-200 mesh); solvents-water and methylchloroform at solvent/coal-2/1; 20-120 minutes retention time; 21-70°C; atmospheric pressure; gaseous chlorine feed of 3-31.4 SCFH. The horizontal belt vacuum filter-spray wash was operated at 2 kg per hour, water/coal-3/1, 20°C. The dechlorinator was operated at 2 kg coal per hour, 400°C, 55 minutes, atmospheric pressure, nitrogen feed of 5 SCFH. Duration of the runs after achieving steady state was from 1 to 2-1/2 hours. The results of the mini-pilot plant runs indicated that desulfurization achieved for PSOC 282 and 276 coals were up to 50-60%, comparable to bench-scale batch reactor results.

There were some discrepancies in the results of the grab samples, relative to the bulk coal samples from the runs. The grab samples in some cases showed abnormally low desulfurization values. Also, pyritic sulfur removals appeared to be low for PSOC 282 coal with organic sulfur removals being relatively high. Also, the washing step for the samples appeared to be poor in the mini-pilot plant with a high residual of sulfate sulfur which is normally readily removed by washing in the bench-scale batch reactor tests.

With PSOC 276 coal, methylchloroform gave better desulfurization than water, which corresponds to the Phase II test results.

PROXIMATE-ULTIMATE ANALYSES

Proximate and ultimate analyses were conducted for product coals PSOC 276 and 282 obtained from the chlorinolysis process in the bench-scale batch reactor, mini-pilot plant and from hydrogen treatment of raw and chlorinolysis processed coal. Volatile matter and hydrogen were reduced substantially, respectively 50% and 30%, in chlorinolysis processed coal with dechlorination at 500°C. Dechlorination at 500°C showed a more substantial reduction in volatiles than dechlorination at 400°C. Treatment of chlorinolysis processed coal and raw coal with hydrogen at 700°C showed increased volatiles and hydrogen reduction as well as a substantial oxygen reduction. Ash levels were also increased - to a greater extent for the raw coal relative to the chlorinolysis processed coal by treatment at 700°C.

COAL MATERIAL BALANCES

Coal Material balances for the bench-scale batch reactor showed a good accounting — 95-100% across the chlorination filtration-wash. Accountings across the batch dechlorination were generally less than 90%. Mini-pilot plant coal accountings were generally inferior to the batch reactor across the chlorination filtration-wash and much better across the dechlorinator. It is not known whether this reflects some intrinsic differences between the batch reactor and continuous flow reactor operation or just differences in mass balance measurements.

CONCLUSIONS AND RECOMMENDATIONS

The introduction of a high temperature hydrogen treatment of chlorinolysis-processed coal provides a dramatic increase in coal desulfurization. Although some added reductions in volatiles and hydrogen accompany this increase in desulfurization, it is expected that the overall process of chlorinolysis and hydrogen treatment can be optimized to meet NSPS for sulfur emissions and achieve an acceptable quality of coal for utilities and industrial boilers.

SELECTED COALS FOR PHASE III TESTS

A total of 22 bituminous, sub-bituminous and lignite coals were tested in the current Phase III program. They were selected by JPL in concert with the Department of Energy.

The coals have been analyzed for sulfur forms, proximate and ultimate analyses, as shown in Table 1. Pyritic and organic sulfur forms were analyzed by the ASTM procedure and also by an "alternate procedure." The "alternate procedure" determines pyritic sulfur by analyses of the attendant sulfur as a barium sulfate precipitate in lieu of an "iron" determination.

The coals are grouped as: three high sulfur bituminous coals; twelve low sulfur bituminous, sub-bituminous and lignite coals; one Kentucky coal supplied by TVA; five bituminous coals supplied by DOE; and one Texas lignite coal supplied by Dow Chemical. The coals represent twelve eastern, midwestern and western states.

HIGH SULFUR BITUMINOUS COALS

Three bituminous coals, PSOC 276, 219, and 282, are coals that were tested as part of the previous Phase II program and represent coals on which there is extensive laboratory-scale and bench-scale experimental data. Five tons of PSOC 276, and PSOC 282 coals were obtained from the mine site as part of the Phase II program. PSOC 276 and PSOC 282 coals were the coals primarily used in the pretreatment and post-treatment experiments relative to the chlorinolysis process. These two coals were used also for the mini-pilot plant operation. Total sulfur in the three coals is 1.54, 2.16 and 3.87 wt.%. for PSOC 282, 219 and 276, respectively.

LOW SULFUR BITUMINOUS, SUB-BITUMINOUS AND LIGNITE COALS

A total of 11 low sulfur coals, 0.47 to 1.3 wt.% total sulfur, and one lignite coal, 2.39 wt.% total sulfur were selected for evaluation of the chlorinolysis process on low sulfur coals. Previous testing in Phases I and II had been carried out on high sulfur coals greater than 1 wt.%. A need existed to demonstrate the chlorinolysis process on low sulfur coals with total sulfur values less than 1 wt.%.

TVA BITUMINOUS TEST COAL

For comparative evaluation purposes of various chemical coal-cleaning processes by DOE and TVA, a West Kentucky No. 11 (washed) coal was received by JPL and treated by the chlorinolysis process. Comparative analyses are to be conducted of this chlorinolysis-processed coal with coal treated by other chemical coal-cleaning processes. Total sulfur content is 3.32 wt.%.

DOE HIGH SULFUR BITUMINOUS COALS

Five coals that were under test evaluation in the "oxydesulfurization" process, and "Ames" caustic oxidation-leaching process were tested at DOE request by the chlorinolysis process to provide a comparison with other chemical coal-cleaning processes.

Table 1. Selected Coals and Attendant Analyses

PSOC No.	Seam, County, State (Mine)	Rank	Mesh Size	ASTM SULFUR (wt.%)[a]				ALTERNATE[e] SULFUR(wt.%)[a]		PROXIMATE ANALYSIS (wt.%)[a]					ULTIMATE ANALYSIS (wt.%)[a]						
				Org.	Pyr.	Sulf.	Total	Org.	Pyr.	Vol. Mat.	Fixed Carbon	Ash	Heat Val. (Btu/lb)[b]	Moisture[c]	C	H	S	N	Cl	O	ASH
HIGH SULFUR BITUMINOUS COALS																					
276	Ohio No.8, Harrison, OH. (Georgetown No. 24	Bit. HVA	100-200	1.17	263	0.06	3.87	-	-	37.2	51.3	11.5	12,755	1.89	71.6	5.[illegible]7	3.91	1.28	0.16	5.87	11.5
			-325[d]	1.19	1.68	0.49	3.36	1.19	1.68	35.5	52.6	11.9	12,274	1.89	70.0	4.94	3.36	1.25	0.10	8.4	11.9
219	Ky. No.4, Hopkins, KY.	Bit. HVA	100-200	0.82	0.73	0.60	2.15	-	-	35.5	58.1	6.42	12,966	3.74	73.8	5.32	2.16	1.76	0.12	10.46	6.42
			-200	-	-	-	2.62	0.78	0.89	-	-	-	-	4.61	-	-	2.62	-	0.07	-	6.70
282	ILL. No.6, Jefferson, ILL, (Orient No. 6 Mine, Washed[f])	Bit. HVA	100-200	0.75	0.43	0.36	1.54	0.70	0.50	33.8	59.5	6.70	13,092	3.10	74.8	4.82	1.60	1.69	0.47	9.92	6.70
			-325[d]	-	-	-	1.54	0.89	0.45	-	-	-	-	2.12	-	-	1.54	-	0.45	-	-
LOW SULFUR BITUMINOUS, SUBBITUMINOUS AND LIGNITE COALS																					
-	Mary Lee, Jefferson ALA. (Chetopa)	Bit. HVA	-325	0.33	0.41	<0.05	0.74	0.33	0.41	18.7	34.0	47.3	7,559	0.73	43.7	2.93	0.74	0.97	<0.05	4.3	47.3
274A	Sewell, Nicholas, W.VA (Quinwood No.7)	Bit. HVA	-325	0.40	0.18	<0.05	0.58	0.58	<0.05	22.1	54.1	23.8	11,499	0.87	66.6	4.19	0.58	1.29	0.10	3.45	23.8
371	Imboden, Letcher, KY. (Scotia)	Bit. HVA	-325	0.47	0.49	<0.05	0.96	0.60	0.36	23.8	41.5	34.7	9,602	0.97	55.4	3.97	0.96	0.99	<0.05	3.91	34.7
126	Lower Kittanning, Cambria, PA. (Cambria Slope #33)	Bit. LV	100-200	0.43	0.60	<0.05	1.03	0.52	0.51	17.3	62.5	20.2	12,309	0.55	72.0	3.82	1.03	1.07	0.06	1.82	20.2
126	Lower Kittanning, Cambria, PA. (Cambria Slope #33, Washed)	Bit. LV	100-200	0.53	0.15	<0.05	0.68	0.61	0.07	18.9	75.8	5.26	14,883	0.48	86.6	4.60	0.68	1.38	0.10	1.36	5.26
230	Rosebud Colstrip Field, Rosebud, MT.	Subbit.	100-200	0.52	0.35	<0.05	0.87	0.36	0.51	38.9	52.1	9.03	11,892	7.26	69.6	4.40	0.87	1.06	<0.05	14.9	9.03
241	Monarch & Dietz No.3, Sheridan, WYO. (Big Horn)	Subbit.-B	-325	0.45	0.29	0.11	0.85	0.55	0.19	39.3	50.9	9.78	11,535	17.8	67.9	4.36	0.85	1.19	<0.05	15.9	9.78

Table 1. (cont'd)

PSOC No.	Seam, County, State (Mine)	Rank	Mesh Size	ASTM SULFUR (wt.%)^a				ALTERNATE SULFUR(wt.%)^a		PROXIMATE ANALYSIS (wt.%)^a					ULTIMATE ANALYSIS (wt.%)^a						
				Org.	Pyr.	Sulf.	Total	Org.	Pyr.	Vol. Mat.	Fixed Carbon	Ash	Heat Val (Btu/lb)^b	Moisture^c	C	H	S	N	Cl	O	ASH
-	Rosebud-McKay & Robinson, Big Horn, MT. (Absaloka)	Subbit.	-325	0.45	0.30	<0.05	0.75	0.58	0.17	34.6	47.6	17.7	10,452	14.2	63.3	3.82	0.75	0.72	<0.05	13.7	17.7
090	Gust, Richland, MT. (Savage)	Lignite	100-200	0.38	0.09 -	<0.05	0.47	0.47	<0.05	38.8 --	50.6 -	10.56 -	10,539 -	10.2	66.8	3.87	0.47	1.01	0.05	17.2	10.56
074	Beulah-Zap, Mercer, N.D. (Beulah)	Lignite	100-200	0.58	0.29	<0.05	0.87	0.51	0.36	53.1	37.6	9.30	10,719	24.6	65.5	4.01	0.87	0.89	<0.05	19.4	9.30
-	No.2 Lehigh Bed, Stark, N.D.	Lignite	-325	0.75	1.44	0.20	2.39	0.71	1.48	40.8	45.4	13.9	10,285	18.9	62.5	4.10	2.39	0.72	<0.05	16.4	13.9
-	Black Mesa, Ariz.	-	100-200	0.56	<0.05	<0.05	0.56	0.56	<0.05	--	-	-	-	9.02	-	-	0.56	-	<0.05	-	-
TENNESSEE VALLEY AUTHORITY BITUMINOUS TEST COAL																					
-	West Kentucky No. 11, KY. (Washed)	-	-325	2.07	1.25	<0.05	3.32	1.98	1.34	38.5	53.0	8.50	12,957	4.95	72.8	5.22	3.32	1.40	<0.05	8.74	8.50
DOE TEST HIGH SULFUR BITUMINOUS COALS																					
-	Western Kentucky No. 9 Bed, Union, KY. (Hamilton Mine No. 1)	Bit.	-200	1.22	2.24	0.22	3.68	1.25	2.21	33.0	42.9	24.1	10,860	5.46	60.6	4.00	3.68	1.17	0.29	6.16	24.1
-	Lower Kittanning Bed, Armstrong, PA. (C.H. Snyder Mine)	Bit.	-200	0.74	4.27	0.10	5.11	0.98	4.03	34.7	51.6	13.7	12,960	1.22	71.4	4.96	5.11	1.16	0.27	3.40	13.7
-	Pittsburgh Bed, Harrison, OH. (Franklin Mine)	Bit.	-200	0.84	1.37	<0.05	2.21	0.90	1.31	36.9	55.2	7.85	13,564	3.34	76.2	5.11	2.21	1.23	0.20	7.20	7.85
-	Illinois No. 6 bed, St. Clair, ILL. (River King Mine, Washed)	Bit.	-200	2.16	1.19	0.14	3.49	1.86	1.49	39.6	48.7	11.6	12,469	8.63	64.2	4.31	3.49	1.15	0.12	15.1	11.6
-	Lucas Co. No. 5 Bed, Monroe, Iowa (Lovilia No.4 Mine)	Bit.	-200	0.69	1.32	0.12	2.13	0.70	1.31	42.7	49.9	7.44	13,249	13.1	74.2	5.03	2.13	1.39	0.09	9.7	7.44
DOW CHEMICAL TEXAS LIGNITE COAL																					
	Texas Lignite, TX.	Lignite	30x100	0.78	0.31	0.14	1.23	0.82	0.27	38.6	41.0	20.4	9,767	29.1	57.9	3.81	1.23	1.24	0.07	15.3	20.4

(a) Dry basis.
(b) High heating value, dry wt. basis.
(c) As determined basis.
(d) Air classified.
(e) Direct determination of pyritic sulfur by $BaSO_4$ precipitation in lieu of the iron determination.
(f) Unwashed coal has 2.2 wt.% sulfur.

A lignite coal sample from Texas was obtained from Dow Chemical for desulfurization by the chlorinolysis process. Total sulfur content is 1.23 wt.%.

Coals tested were initially ground and sieved to provide 100 x 200 mesh coal particles. However, particle sizes of -200 and -325 mesh were found to give improved desulfurization results over 100 x 200 mesh coal particles. As a result, a large number of test runs were made with -200 and -325 mesh coal particles. Particle size is noted under the operating conditions of each test run.

Coal in large quantities, greater than 100 pound lots, was ground and classifed by the Corosil Corporation, Corona, CA.

Laboratory-scale quantities of coal were ground with a SH-Bantam Micro Pulverizer, Pulverizing Machinery Company, New Jersey. Coal sieving was accomplished with a Sweco Vibro-Energy Separator, capacity of 800 pounds per hour, (dry, 100 x 200 mesh), equipped with 100, 200 and 325 mesh stainless steel screens.

PART I - LABORATORY-SCALE EXPERIMENTAL TESTS

EQUIPMENT AND OPERATING PROCEDURE

The laboratory-scale experimental test operation was set up in a laboratory trailer especially equipped for conducting coal research studies in support of the batch-reactor and mini-pilot plant operations.

CHLORINATION

The apparatus for conducting tests on 100 gram samples of coal consists of a 500 ml round bottom flask equipped with a turbine style impeller, with gaseous chlorine injection through a fritted glass diffuser, reflux condenser, oil and tar trap and caustic scrubber, Figure 1. A water bath was used for controlling chlorination temperatures, generally at 70°C. A detailed operating procedure is included, Appendix A.

FILTRATION-WASH

Coal slurries from the chlorination were filtered in a Buchner funnel using Whatman No. 1 filter paper. Filter cake was reslurried with 2 parts of water to one part of coal and refiltered. The washing procedure in the laboratory was redone until the filtrate was clear. Added operating procedure details are included, Appendix A.

PRETREATMENT/POST-TREATMENT

Tests were conducted with 150 gram samples in the 500 ml round bottom flask used for chlorination. Operating temperatures were up to 100°C at atmospheric pressure.

Tests with 10% NaOH in water at elevated temperatures and pressures were conducted in a 2-liter autoclave equipped with electric heaters, stirrer, and cooling coil. The autoclave is designed for operation up to 350°C and 1400 psig, Figure 2.

DECHLORINATION

Dechlorinations were carried out with 2 to 5 gram samples in a 1-inch diameter, 40-inch long quartz tube, inserted in a split tube muffle furnace, equipped with a rotary chain drive for rotation at 2 rpm and with a nitrogen purge, Figure 3. Added details of the operating procedure are included, Appendix A.

HYDRODESULFURIZATION

Laboratory treatment of raw and chlorinolysis-processed coal samples of 2 to 5 gram size were carried out in the dechlorination apparatus, Figure 3, with substitution of hydrogen for the nitrogen purge gas. Investigations with other oxidizing and reducing gases were also tried by addition of these

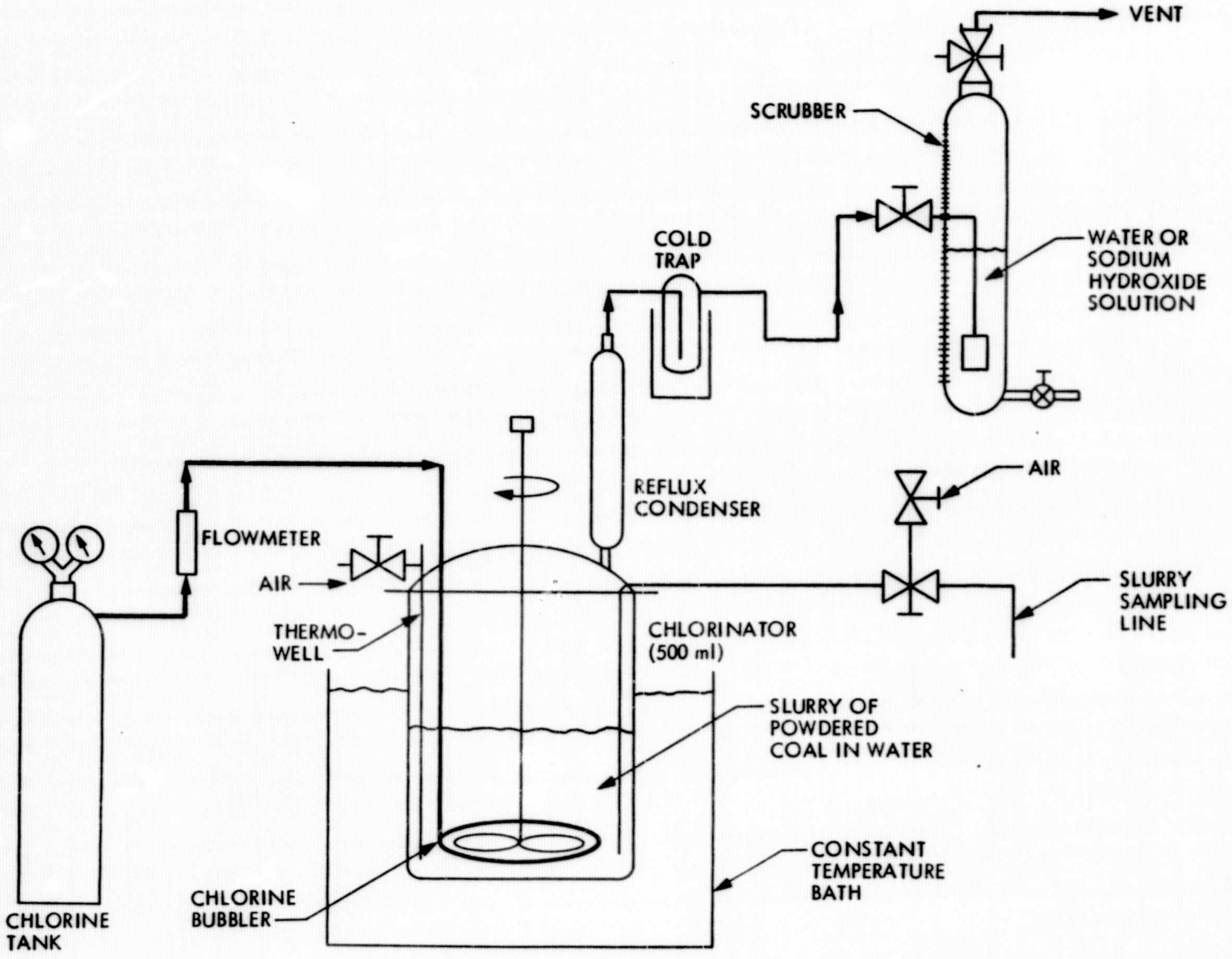


Figure 1. Laboratory Glassware Apparatus for Chlorination of Coal

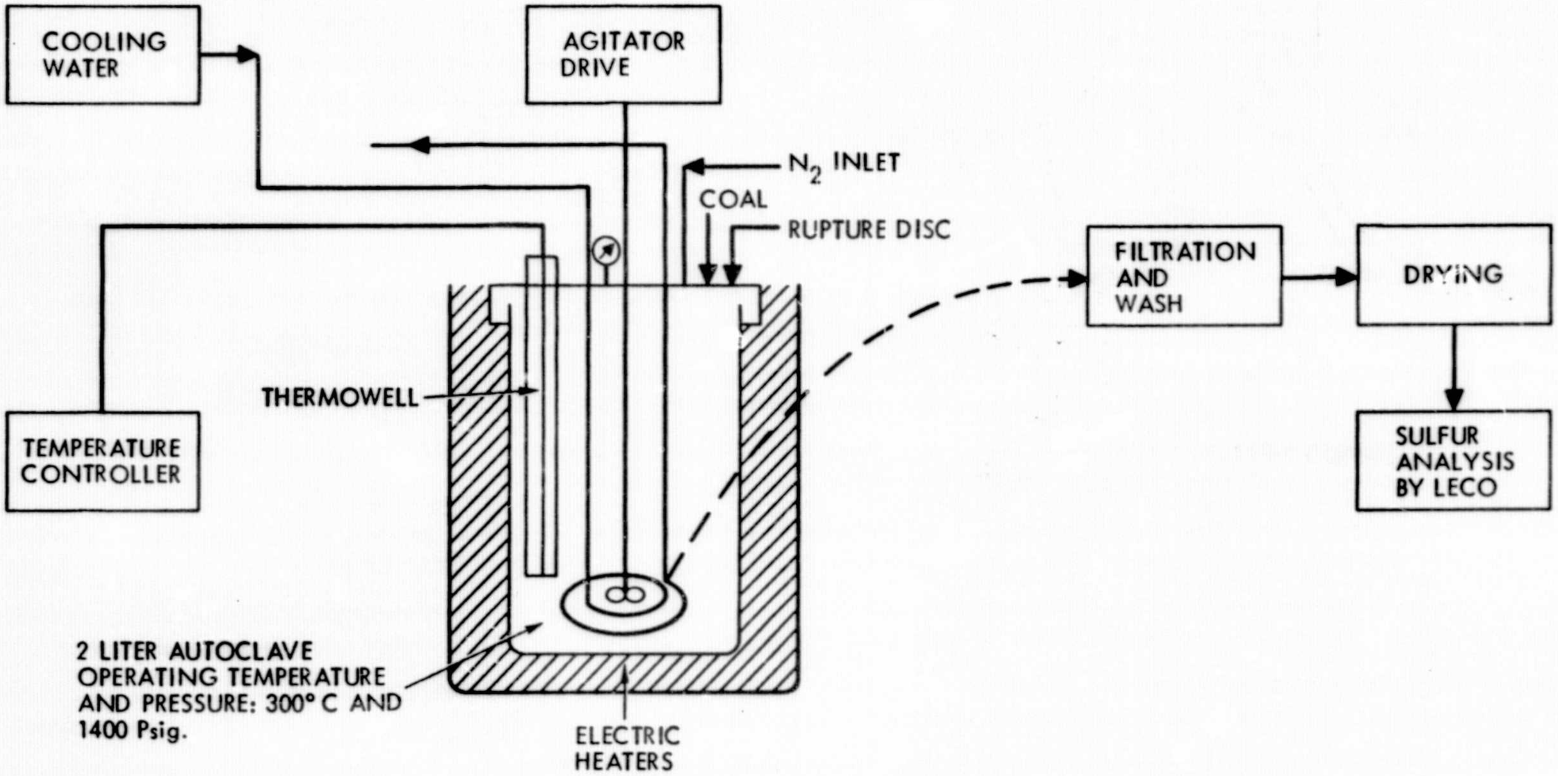


Figure 2. Two Liter Autoclave for High Temperature High Pressure Operation

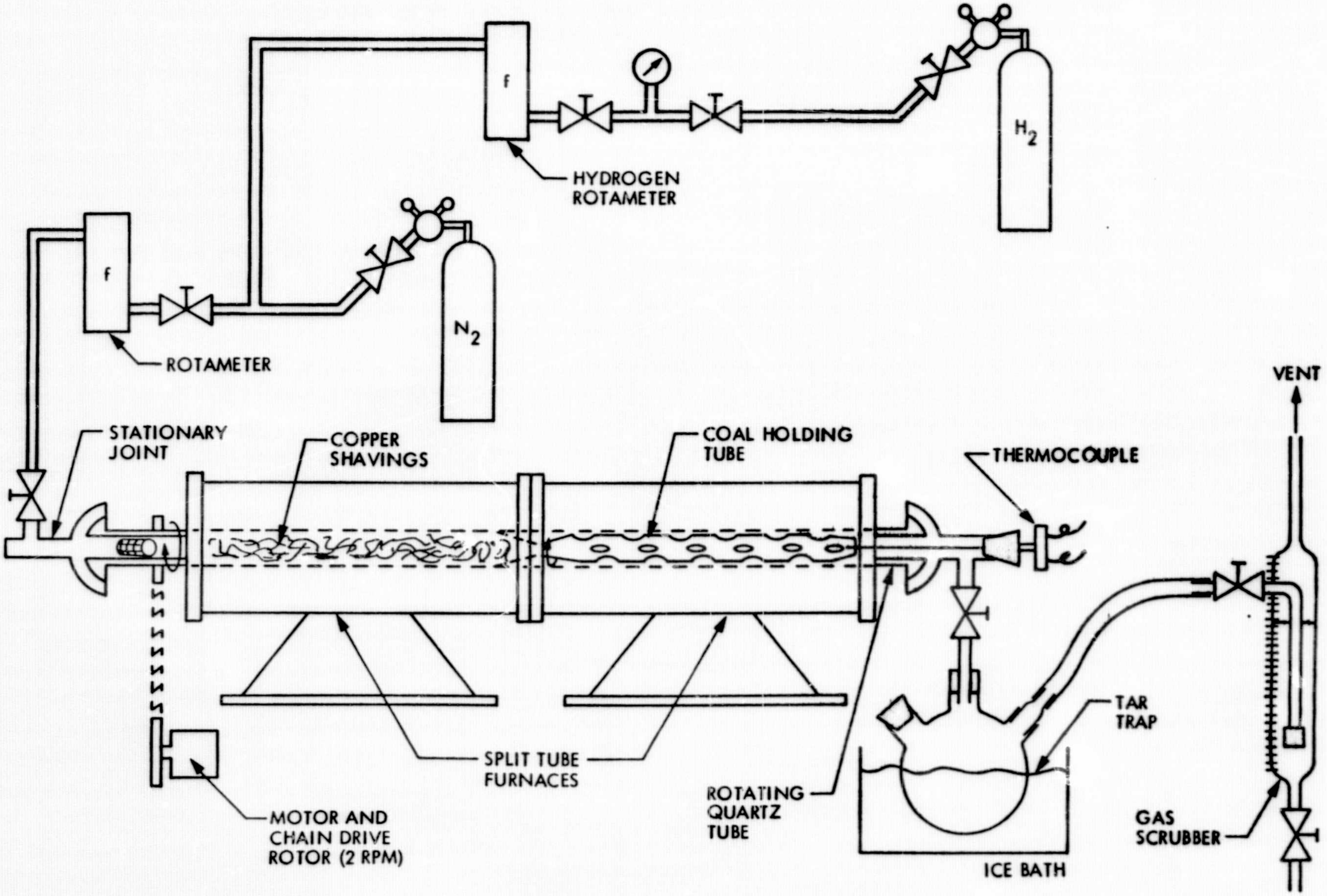


Figure 3. Laboratory Scale Apparatus for Coal Dechlorination and Hydrodesulfurization

gases along with the nitrogen purge gas. Gas flows were monitored by a Linde flowmeter. Normal operating procedure called for purging the quartz tube containing the coal sample with nitrogen and allowing the sample to reach temperature before substituting hydrogen gas flow for the nitrogen. After completion of the test run at the prescribed temperature, hydrogen was replaced with nitrogen flow before the tube was removed and cooled. After cooling of the tube to approximately 150°C, the coal sample is emptied into a half-ounce vial for storage before undergoing analyses. Gas flows were normally at 90 $Scm^3/min.$ with operating temperatures in the range of 400 to 700°C. Added operating details are included in Appendix A.

LABORATORY SCALE EXPERIMENTAL DATA

Laboratory scale experimental data (14 test runs) were obtained with coal pretreatment and post-treatment to the chlorination as well as chemical/solvent additions to the chlorination in order to enhance coal desulfurization (Table 2). The majority of tests were conducted with PSOC 282 coal. A Black Mesa coal was treated under standard chlorinolysis conditions using water. Additionally PSOC 276 coal was treated under chlorinolysis conditions using a 1/1 solvent mixture of methanol and carbon-tetrachloride.

PRETREATMENT/POST-TREATMENT PSOC 282 COAL

The objective of pretreatment was to provide possible changes in coal surface characteristics such as opening up pores and/or surface activation of the coal that would contribute to enhanced coal desulfurization.

Sodium Hydroxide Treatment

Treatment of raw PSOC 282 coal, 100 x 200 mesh, with 9% NaOH at 93°C for 60 minutes produced a 14-30% desulfurization. Chlorination of the coal in water at 93°C for 45 minutes with subsequent dechlorination increased the desulfurization to 36%. Dechlorination of pretreated coal without chlorination did not improve the desulfurization of the pretreated coal. The addition of 9% NaOH to the chlorination gave a 40% desulfurization after dechlorination, which was approximately the same as with water.

The post-treatment of this pretreated, chlorinated coal with 6.5-9% NaOH at 93°C for 60 minutes gave results in run 2-6/5/80 that were considerably lower desulfurization values, 13-16%. This may have been due to the interference of residual NaOH in the treated coal with the Leco acid-base analysis for total sulfur. With run 3-6/18/80, desulfurization was increased from 36 to 43-51% with the 6.5% NaOH post-treatment. Desulfurization levels of 50% have been achieved by the chlorinolysis process with PSOC 282 coal without benefit of this pretreatment or post-treatment. Therefore, the conclusion was that this added post-treatment with 6.5-9% NaOH solution does not assist desulfurization.

Table 2. Laboratory Scale Experimental Data

Conditions: Equipment-500 ml, round bottom flask, reflux condenser, agitator, water bath, chlorine diffuser; chlorination-100 grams coal, 100 x 200 mesh (except runs 8-64 grams, 21-150 grams, 34-300 grams), chlorine 0.1 s.l/min. (except runs 29-0.24, 34-0.73); dechlorination-1-inch diam. quartz tube, muffle furnace, 2 RPM, 2 grams coal, 20 scm^3/min. N_2, 60 Min., atm. pressure; analyses-Leco acid-base for total sulfur and chlorine. Note: a-coal from batch run 20, 0.88 wt.% sulfur, 43% sulfur removal, b-analyses on chlorine, moisture-free basis, c-water added during run.

Run/ Date	Pretreatment to Chlorination					Pretreated Coal		Chlorination				Post-Treatment				Post-Treated Coal		Dechlorinated Coal			
						Sulfur										Sulfur				Sulfur(b)	
	Coal (g)	Solvent	Solvent /Coal	Temp (°C)	Time (min)	(Wt.%)	(% Rem)	Solvent	Solvent /Coal	Temp (°C)	Time (Min)	Solvent	Solvent /Coal	Temp (°C)	Time (Min)	(wt.%)	(% Rem)	Temp (°C)	Cl (Wt.%)	(wt.%)	(% Rem)
	PSOC 282, HVB, ILL. NO. 6 JEFFERSON COUNTY, ILL., ORIENT NO. 6 MINE, WASHED 100 x 200 MESH, TOTAL SULFUR 1.54 WT.%																				
2-6/5/80	150	9% NaOH	2.2	93	60	1.08	30	------	------	----	----	------	------	----	----	------	------	400	0.01	1.12	27
	"	"	"	"	"	"	"	9% NaOH	2.2	93	45	------	------	----	----	------	------	410	0.03	0.93	40
	"	"	"	"	"	"	"	"	"	"	"	9% NaOH	3.9	93	66	-	-	300	0.21	1.29	16
	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	-	-	390	0.17	1.28	17
	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	-	-	450	0.20	1.34	13
3-6/18/80	150	9% NaOH	2.2	93	60	1.33	14	------	------	----	----	------	------	----	----	------	------	410	0.00	1.50	3
	"	"	"	"	"	"	"	H_2O	2	93	45	------	------	----	----	------	------	400	0.11	0.98	36
	"	"	"	"	"	"	"	"	"	"	"	6.5% NaOH	2	93	60	-	-	310	0.38	0.88	43
	"	"	"	"	"	"	"	"	"	"	"	"	"	"	"	-	-	410	0.44	0.76	51
	"	"	"	"	"	"	"	"	"	"		"	"	"	"	-	-	450	0.57	0.77	50
7-7/16/80	150	MeOH	2.0	65	60	1.56	0	H_2O	2	70	45	------	------	----	----	------	------	390	0.20	1.07	31
8-7/17/80	95	9% HNO_3	3.0	70	60	0.78	49	H_2O	3	70	45	------	------	----	----	------	------	400	1.12	0.73	53
9-8/6/80	150	1 MeOH/ 1 CCl_4	2.0	58	60	1.47	5	H_2O	2	70	45	------	------	----	----	------	------	400	0.49	0.83	46
10- 8/21/80	150	------	------	----	----	------	------	1% Na_2CO_3	2	70	45	------	------	----	----	------	------	400	0.28	0.85	45
								"	"	"	"	10% NaOH	2.0	90	60	0.95	38	400	0.49	0.85	45
								"	"	"	"	10% H_2SO_4	2.0	90	60	1.43	7	380	0.28	0.89	42
35- 11/21/80	150	------	------	----	----	------	------	10% Na_2CO_3	2.2	70	45	------	------	----	----	------	------	400	0.23	0.93	40
17- 9/26/80	150	------	------	----	----	------	------	H_2O	2	93	45	------	------	----	----	------	------	400	0.33	0.84	45
								H_2O	2-6^c	93	180	------	------	----	----	------	------	400	1.23	0.70	55
31- 11/7/80	15^a							H_2O	2	100	45	10% HNO_3	2.2	100	30	0.72	53	-	-	-	-
32- 11/14/80	40	12% HNO_3	12	100	30	0.75	52	-	-	-	-	40% HNO_3	2.8	95	30	0.63	59	400	0.07	0.64	59
	PSOC 276, HVA, OHIO NO. 8, HARRISON COUNTY, OHIO, GEORGETOWN NO. 24 MINE, -200 MESH, TOTAL SULFUR 3.87 Wt.%																				
29- 11/4/80	100	------	------	------		------	------	1 MeOH/ 1 CCl_4	2	58	45	------	------	----	----	------	------	400	0.99	2.78	28
34- 11/9/80	300	------	------	------		------	------	1 MeOH/ 2 CCl_4	2	57	45	------	------	----	----	------	------	400	0.68	2.65	32
	BLACK MESA COAL, 100 x 200 MESH, TOTAL SULFUR 0.56 WT.%																				
21- 10-7-80	150	------	------	------		------	------	H_2O	2	70	45	------	------	----	----	------	------	400	0.04	0.37	34

Methanol/1 Methanol-1 Carbontetrachloride

Pretreatment with methanol and 1 methanol-1 carbontetrachloride of raw PSOC 282 coal at 58-65°C for 60 minutes gave 0-5% desulfurization. Subsequent chlorination in water of the pretreated coal followed by dechlorination at 400°C gave desulfurization of 31-46%. No marked improvement in desulfurization is noted as a result of the solvent pretreatment.

Nitric Acid (9-12%)

Pretreatment of PSOC 282 coal with 9-12% HNO_3 at 70-100°C for 30-60 minutes gave 49-52% desulfurization. Chlorination of the pretreated coal followed by dechlorination gave a 53% total desulfurization. No marked improvement in desulfurization was observed. A treatment of the 12% HNO_3 treated coal without benefit of chlorination but with 40% HNO_3 at 95°C for 30 minutes increased total desulfurization to 59%. Again, no impressive gain in desulfurization was observed by this severe nitric acid treatment.

Sodium Carbonate (1-10%)

The addition of 1 to 10% Na_2CO_3 in the chlorination gave a desulfurization after dechlorination of 40-45%. Post-treatment of the chlorinated coal with 10% NaOH or 10% H_2SO_4, at 90°C for 60 minutes showed no improvement in desulfurization.

PSOC 276 COAL, 1 METHANOL-1 CARBONTETRACHLORIDE

Use of a 1/1 mixture of methanol and carbontetrachloride as a solvent in the chlorination of PSOC 276 coal at 58°C for 45 minutes gave a disappointing desulfurization of 28-32%. This was especially disappointing because earlier research work at Caltech had shown some promise for dissolution of the coal structure with an apparent high sulfur removal.

BLACK MESA COAL, CHLORINOLYSIS

Chlorinolysis of the Black Mesa Coal gave a desulfurization of 34%. This result can be considered relatively good because the sulfur composition is almost totally organic sulfur.

ADVANCED DECHLORINATION/DESULFURIZATION

Laboratory scale experiments on the dechlorination stage were made with samples of chlorinolysis-processed coal obtained from the batch-reactor experiments. The test data on eight bituminous, sub-bituminous and lignite coals comprising 46 test runs are included with the batch-reactor data.

COAL ANALYSES

A major portion of the coal samples treated on a laboratory scale were analyzed by the Leco Acid-base Analyzer for total sulfur and chlorine. A detailed description of the method is included, Appendix B. A comparative assessment of Leco total sulfur values relative to total sulfur values obtained by Colorado School of Mines Research Institute (CSMRI) using the Eschka method is included, Table B-1. Analyses of the chlorinolysis-processed coals in the bench-scale batch reactor which were than treated in the laboratory scale "dechlorination" apparatus are included as part of the batch reactor data. Sulfur forms data as well as proximate and ultimate analyses are included with batch reactor data. ASTM analytical procedures (Ref. 3) were followed by the CSMRI for chlorine, total sulfur, sulfur forms, ultimate and proximate analyses.

PART II - BENCH-SCALE BATCH REACTOR SYSTEM TESTS

EQUIPMENT

BENCH-SCALE BATCH SYSTEM

The bench-scale batch reactor system is depicted in Figure 4, with Instrumentation and Controls shown in Figure 5. The reactor provides for chlorination of 2 kilograms of coal with a solvent to coal ratio of 2 to 1 at temperatures of 50 to 150°C, and pressures of 0 to 100 psig using gaseous chlorine injected into the coal slurry. Organic solvent recovery after chlorination is provided by steam distillation from the reactor. The coal-water slurry remaining after distillation is drained from the reactor and added to a batch vacuum filtration unit for filtration and spray wash. Dechlorination of the washed coal is provided by an electrically heated Lindberg furnace equipped with a 5-inch diameter by 5-foot long rotary tube with a capacity of 2 kilograms of coal.

REACTOR

The batch reactor is shown in Figure 6, drain assembly in Figure 7, condenser in Figure 8, and gas holding tank in Figure 9. The reactor was made from 18-inch, schedule 40, mild steel pipe lined with 1/4-inch triflex semi-hard rubber membrane and three layers of red-shale type "L" acid proof brick laid with 1/8-inch joints using Pennwalt's asplit CN mortar. The brick and mortar were selected on the basis of immersion tests of brick and mortar samples conducted by JPL with the guidance of Pennwalt Corporation. The reactor cavity dimensions are 7-inches I.D. by 23-inches deep. A bottom drain assembly provides for removal of the coal slurry. The 316 and 304 stainless steel parts of the drain assembly were damaged by corrosion. Successful repairs were made by replacing the metal portion with graphite G-90 parts, Figure 7. The reactor head is carbon steel and coated with 8 mils of teflon for protection, The head is removable and consists of a 150 pound, 18-inch blank pipe flange drilled to accomodate a centrally-mounted agitator unit and port openings for instrumentation and process lines. The agitator is a Chemineer Model No. VLA-2, top entering agitator with 1/4 H.P. electric motor drive controlled by a SCR variable drive unit for shaft speeds of 40 to 565 RPM. The agitator shaft is of Hastelloy B construction, 1-inch diameter by 35-inch long with four, 45 degree pitched turbine blades, 1-inch by 4-1/2 inch diameter. A 316 stainless steel, single tube cooling water reflux condenser provides 1.2 square feet of heat transfer surface. A 1-1/2 inch Kynar lined ball valve is located between the reactor and reflux condenser to provide reactor operation independent of the reflux condenser. Temperature control of the reactor is provided by a cooling water coil and indirect steam injection (through cooling coil). The cooling water coil consists of 9 turns of 1/4-inch 316 stainless teel tubing on a 6-inch diameter circle. An outer cover of graphoil tape was provided to protect the tubing from the highly corrosive environment. Steam injection was provided for the reactor by a Hot Shot Model No. MB-6L steam generator,

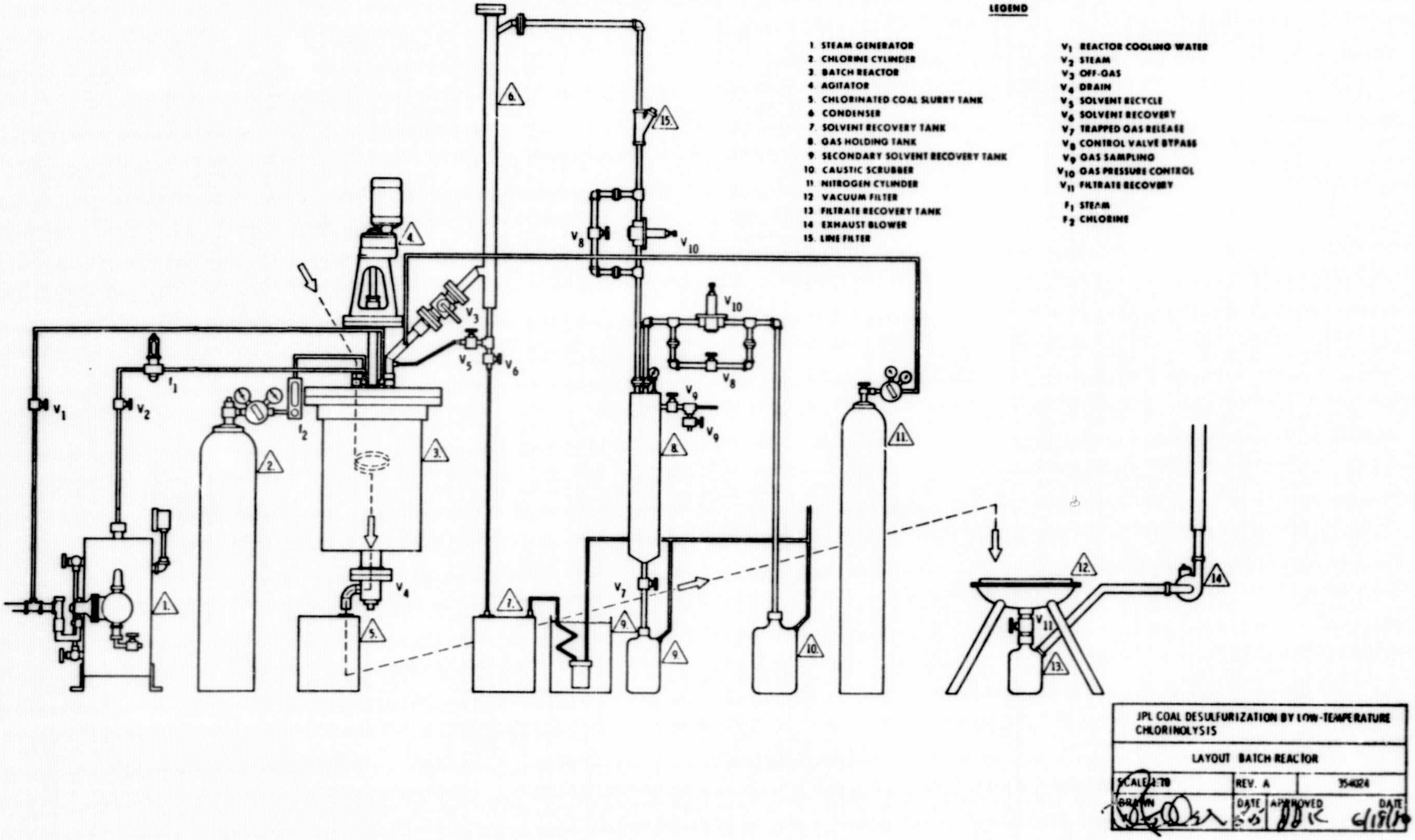


Figure 4. Batch Reactor Equipment System

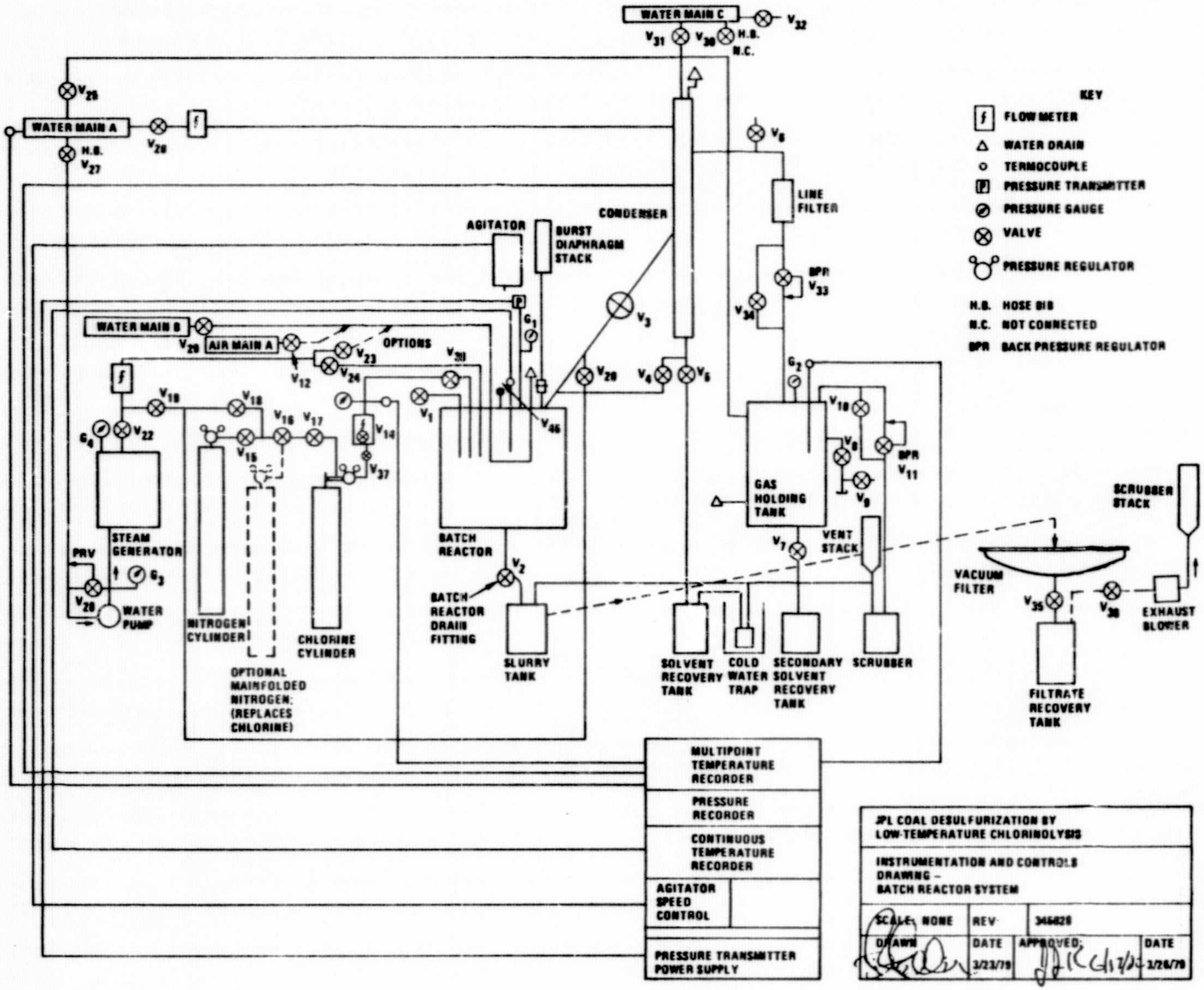


Figure 5. Instrumentation and Controls, Batch Reactor System

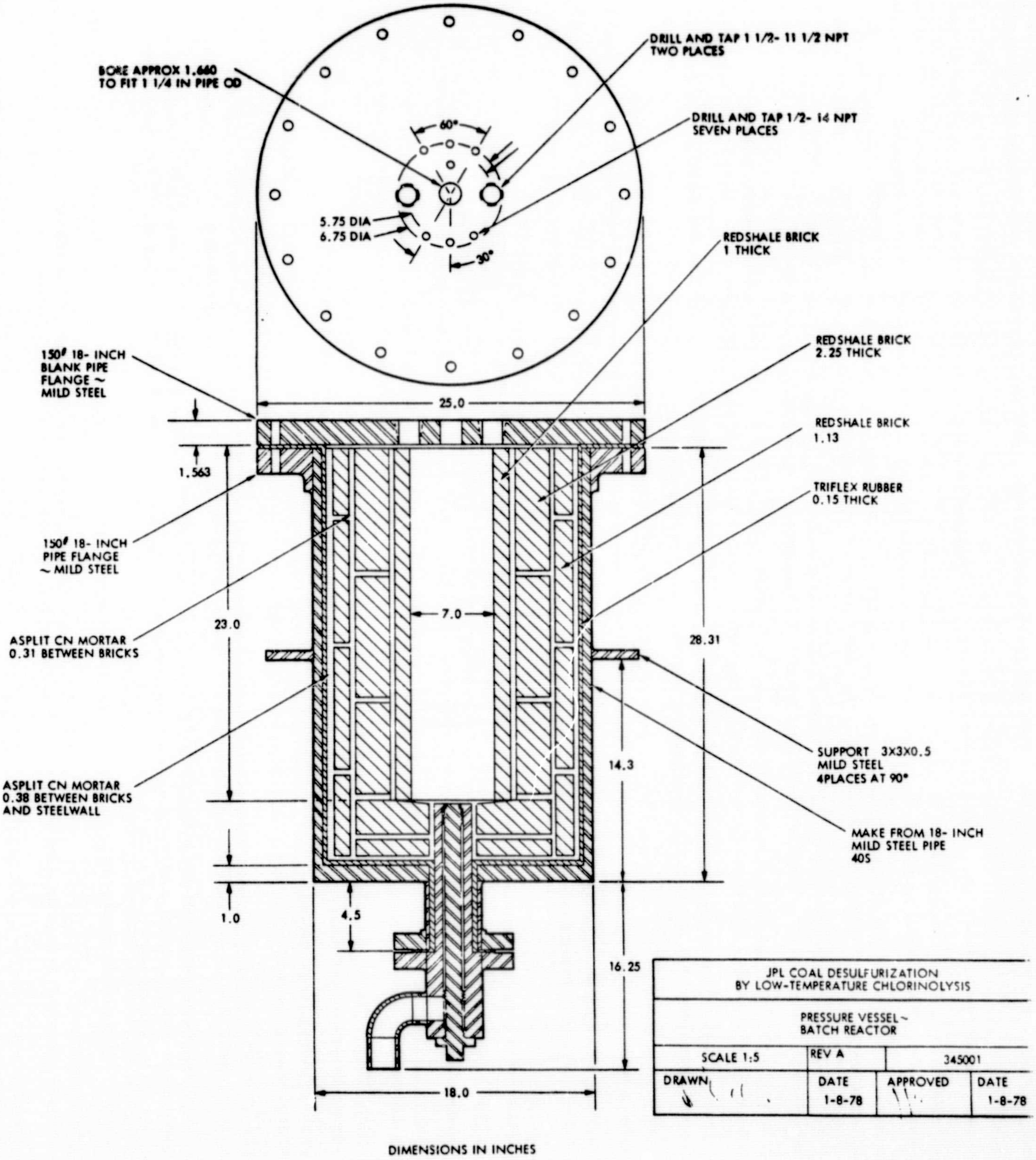
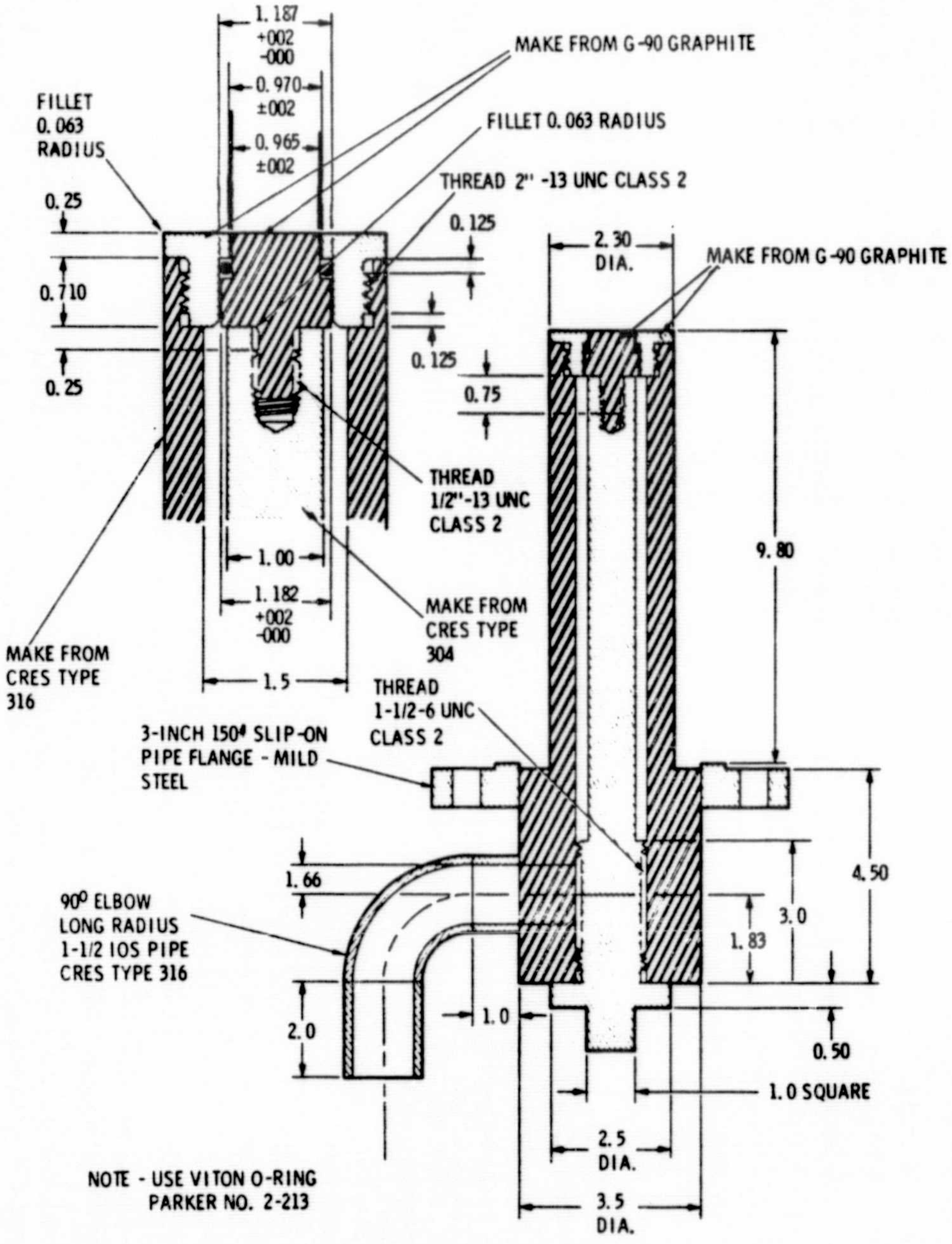


Figure 6. Bench-Scale Batch Reactor



JPL COAL DESULFURIZATION BY LOW TEMPERATURE CHLORINOLYSIS				
DRAIN ASSEMBLY - BATCH REACTOR				
SCALE 1/2	REV. C		345008	
DRAWN	DATE [illegible]	APPROVED		DATE 6/15/80

Figure 7. Drain Assembly - Batch Reactor

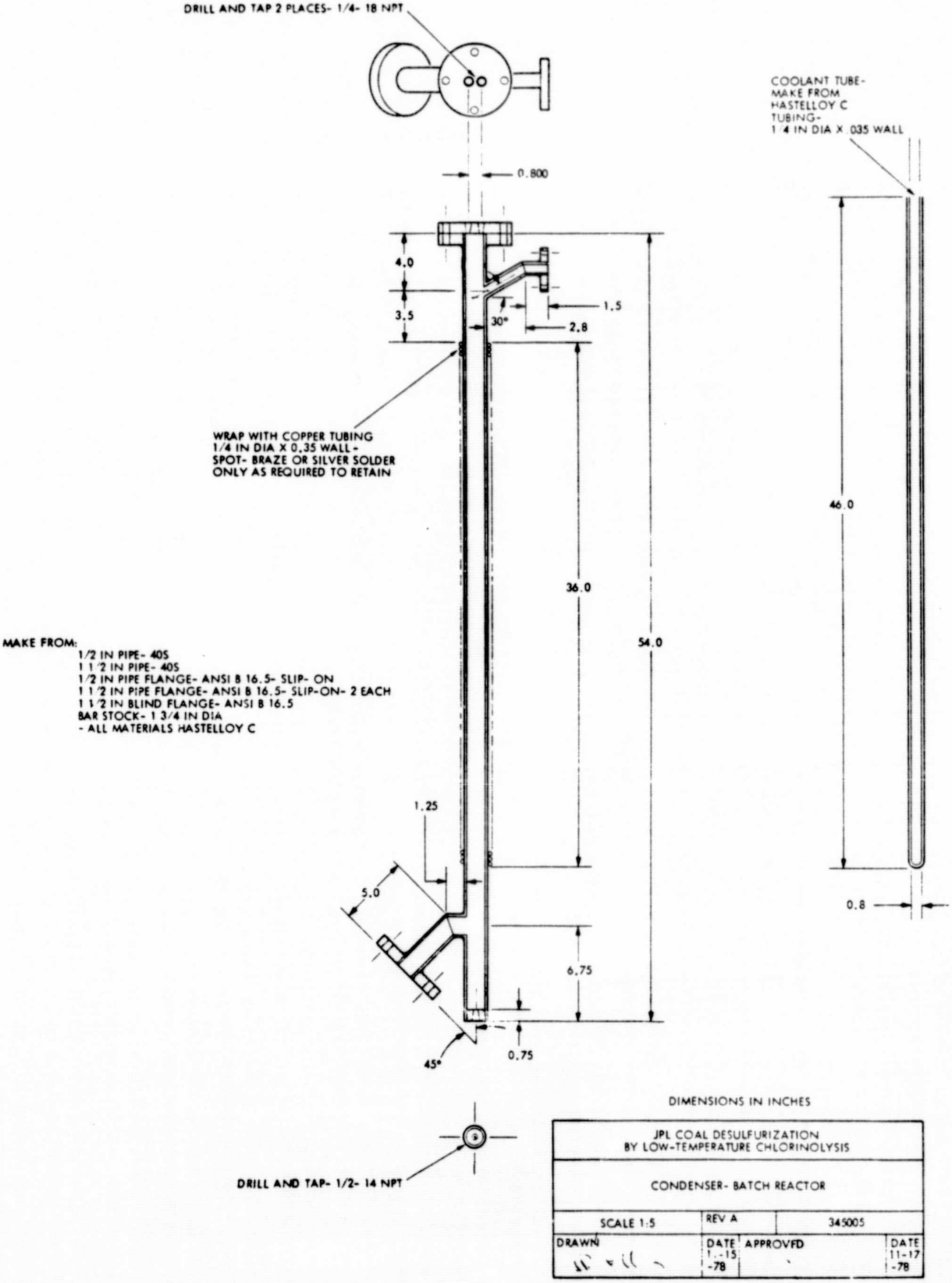


Figure 8. Condenser - Batch Reactor

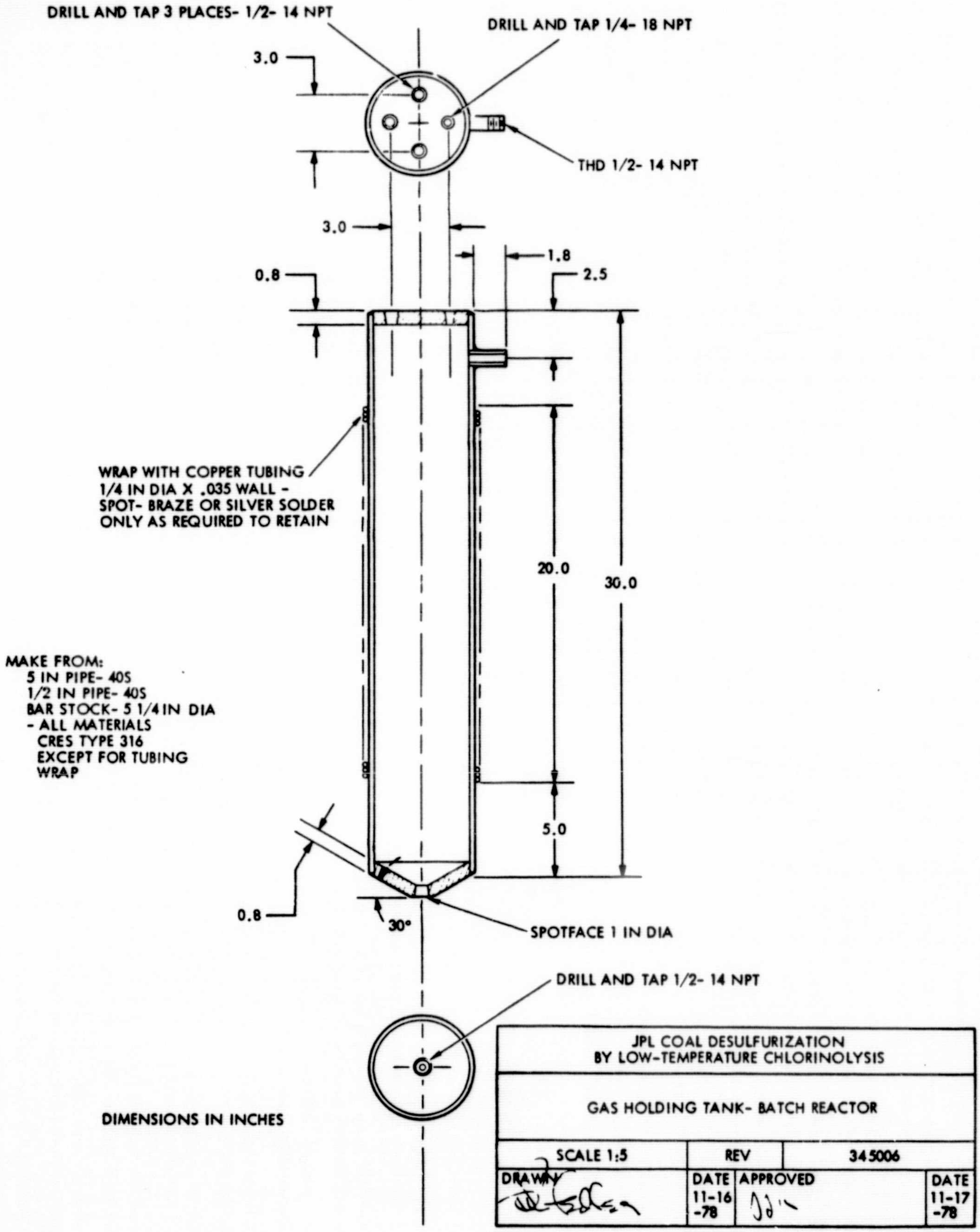


Figure 9. Gas Holding Tank - Batch Reactor

capacity of 20 pounds steam per hour at 100 psig. A Wallace and Tiernan Model 5120 M1 flowmeter monitored steam injection. Gaseous chlorine injection was provided from a standard liquid chlorine storage cylinder equipped with electrical heating and monitored by a Linde Model FM 4311-6 flowmeter with a range of 0.42 to 61.5 SCFH. Chlorine dispersion into the coal slurry was provided by means of a 1/2-inch teflon tubing with 1/32-inch diameter holes. Coal slurry sampling was by means of a 1/2-inch teflon tube located to the side and near the reactor bottom. Pressure was continuously monitored by a Rosemont Model No. 1144G pressure transmitter and Hewlett-Packard No. 7100B pen recorder with a range of 0 to 120 psig. A dial pressure gauge (Series 2554, 3-D Instruments) provides direct readings, 0 to 150 psig with an accuracy of 0.25 %. A Zook carbon rupture disc for rupture pressure of 150 psig ± 5% was obtained from Zook Enterprises. Temperatures were monitored by iron-constantan (Type J) thermocouples with a Leeds and Northrup Speedomax multipoint recorder. Pressure was controlled at 5 to 100 psig ± 10% by a Veriflo 40 series back pressure regulator with 316 stainless steel body and teflon diaphragm, seat, and gasket. A standard nitrogen gas cylinder and regulator was used for a nitrogen purge of the reactor system prior to start-up. A gas holdup tank is located after the reactor pressure control valve. The gas holder construction is of 5-inch, schedule 40, 316 stainless steel pipe with a length of 30-inches for a capacity of 0.34 cubic feet. Maximum operating pressure is 100 psig. A Fisher Type 9811, 316 stainless steel pressure relief valve provides control from 15 to 100 psig. A dial pressure gage provides a direct reading from 0 to 150 psig with ± 0.5 percent accuracy. A needle valve provides bottom tank drainage to a liquid recovery tank.

VACUUM FILTER

The batch vacuum filtration unit, Figure 4, designed to accomodate 2 kilograms of coal was fabricated from a 2:1 elliptical tank head, 18-inch diameter, 12 gauge, 316 stainless steel with a filtration area of 1.8 square feet. A 10 mesh, 304 stainless steel wire screen provides mechanical support to a 325 mesh, polypropylene filtration cloth. An exhaust fan provides vacuum filtration at 20 to 30-inches water column. A manually applied spray water wash was provided. The wash water and filtrate were recovered in a filtrate recovery tank.

DECHLORINATION UNIT

The dechlorination unit, Figure 10, was constructed from a Lindberg Model 58331 tube furnace sized for a 5-inch diameter by 5-foot long tube that could accomodate 2 kilograms of coal. The furnace is designed for operation at 100 to 1100°C with a three zone temperature control for electric power up to 50 amps on 240 VAC, single phase, 50-60 Hz. A 304 stainless steel, 5-inch diameter by 5-foot long, 1/4-inch wall, tube was installed in the furnace and equipped with a variable speed drive for rotation from 1 to 20. Nitrogen at 5 SCFH and 0.5 psig was used to purge HCl to a caustic scrubber. Temperature control is provided within 5°C. A sheafed iron-constantan thermocouple is installed from one end to be in direct contact with the coal bed near the bottom and longitudinal center. Because significant mechanical handling losses of coal were sustained in Phase II testing, a coal containment

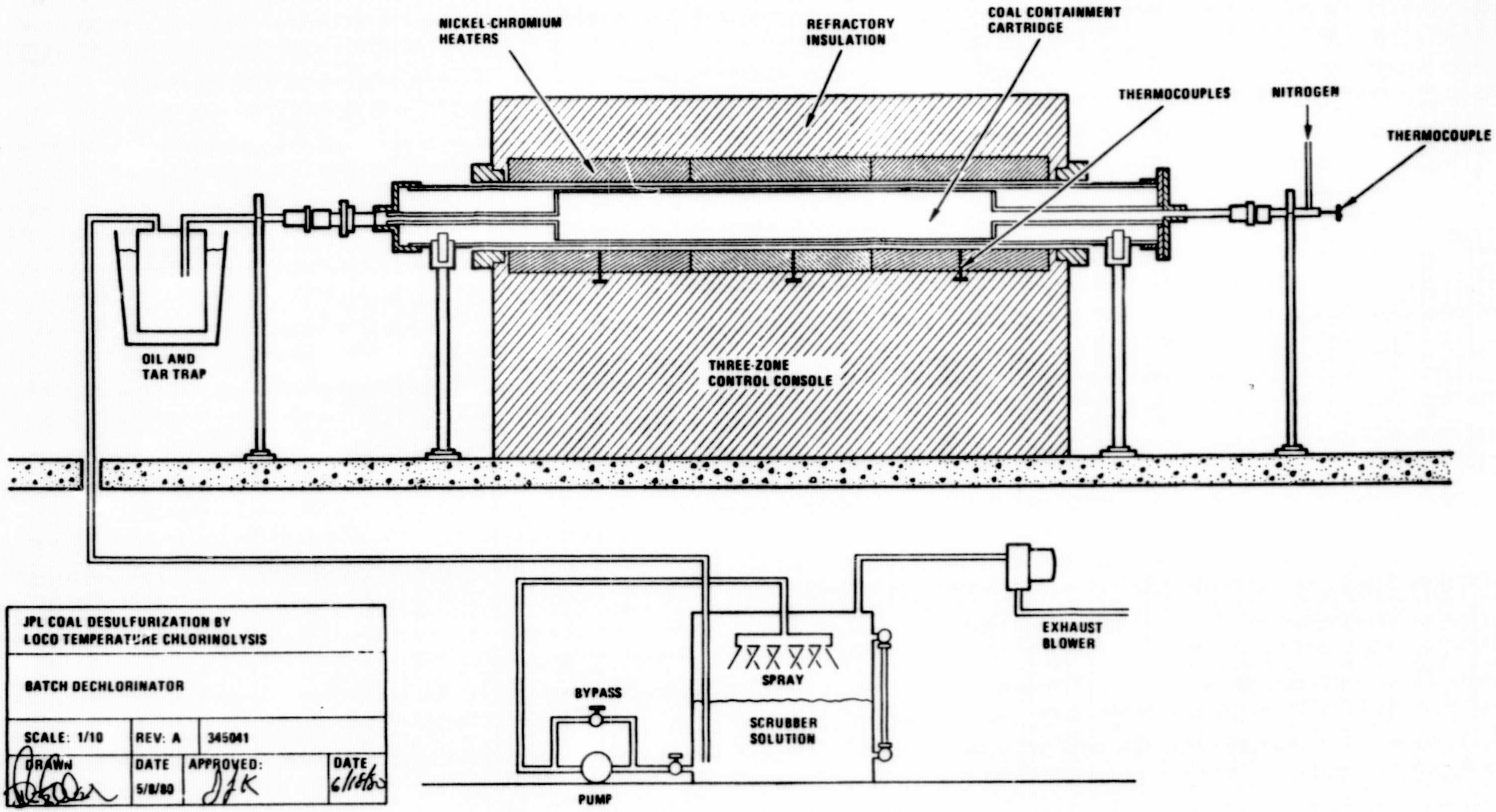


Figure 10. Batch Dechlorinator

cartridge was fabricated that provided for a cartridge insert and withdrawal of the coal. The cartridge is shown in Figure 11. The entire 2 kilograms of dry coal were inserted into the stainless steel cartridge container. Then the cartridge was placed in the preheated dechlorinator furnace unit to dechlorinate the coal. An ice-water trap was installed at the discharge end of the dechlorinator to collect oil and tar from the off gases. Hydrodesulfurization was conducted with the dechlorinator with some minor modifications, Figure 12.

OPERATING PROCEDURE

PRETREATMENT TO CHLORINATION

Chemical coal pretreatment to chlorination experiments (Run Nos. 2 to 4, 17, Table 3) were conducted in the batch reactor with 10% sodium hydroxide solution and 1 methanol-1 carbontetrachloride solution. Two kilograms of coal (100 x 200 mesh, dry weight) with four kilograms of solvent were charged into the reactor. The coal was pretreated in the reactor for one hour at a temperature of 90°C (NaOH solution) and 70°C (methanol and carbon tetrachloride) with agitation at 550 rpm. After pretreatment, the coal slurry was cooled, drained, vacuum filtered, and spray washed to remove pretreatment solution prior to chlorination.

CHLORINATION

The reactor was leak tested under nitrogen pressure, purged with nitrogen and charged with two kilograms (dry weight) of coal (100 x 200, -200, and -325 mesh sizes) and four kilograms of solvent (either methylchloroform or water). In most runs, the reactor off-gas valve to the reflux condenser was open. Injected chlorine was mainly absorbed by the coal slurry but some gaseous chlorine pressure was in the reactor ullage space and condenser. Agitation was set at 550 RPM based on Chemineer design standards. Indirect steam preheated the coal slurry to the desired operating temperature in 20 to 30 minutes. Chlorine flow was then initiated to the reactor (teflon diffuser with 1/32-inch holes) and adjusted to the prescribed flow rate. For operation at elevated pressures, a high initial flow rate of chlorine was set to establish the desired pressure and then reduced to the desired flow rate and/or flow rate compatible with maintaining the pressure level. Cooling water flow was adjusted to control the reactor temperature at prescribed levels. With high chlorine flow rates, exact temperature control was difficult and a substantial temperature rise was obtained above the desired operating point. A graphoil cover was used to protect the cooling coil, thermocouple and agitator shaft. Coal slurry samples were obtained at 15, 30, 45 and in some cases 60 minutes. Samples were approximately 100 grams obtained close to the wall and near the reactor bottom. Stirring was sufficiently intense to ensure a representative coal slurry sample. A detailed operating procedure is included, Appendix C.

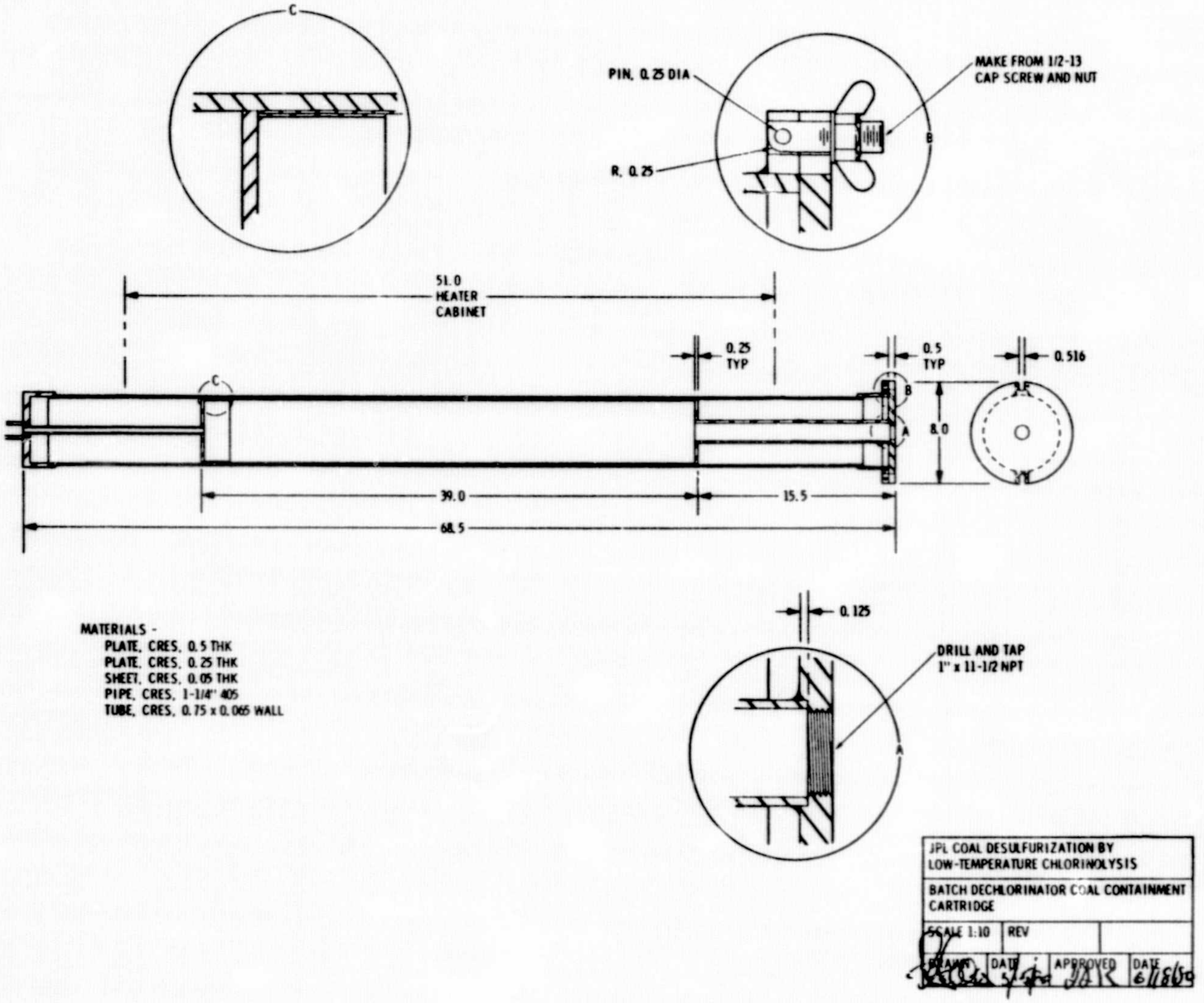


Figure 11. Batch Dechlorinator - Coal Containment Cartridge

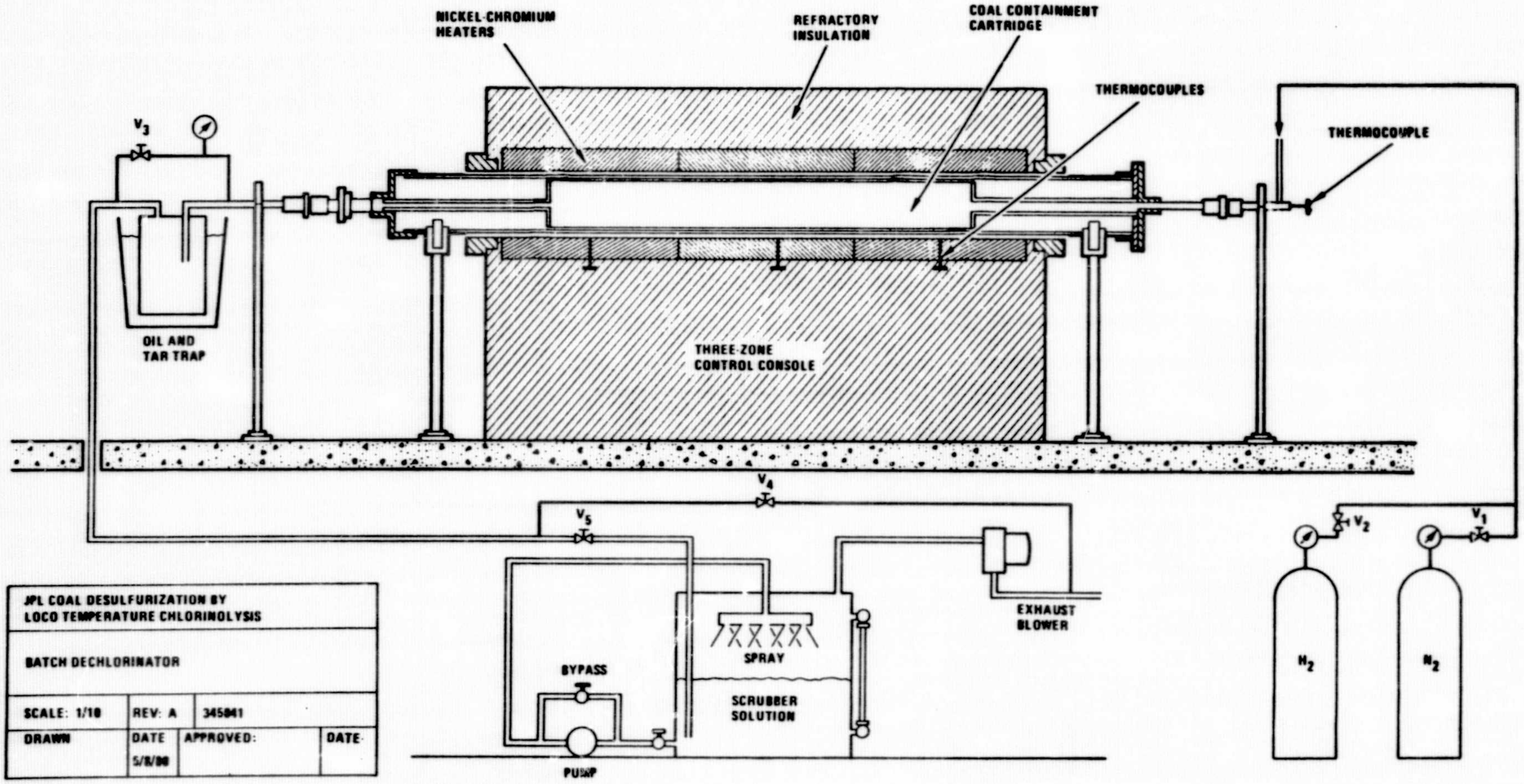


Figure 12. Dechlorinator Modified for Hydrodesulfurization

Table 3. Batch Reactor Experimental Data for Coal Pretreatment/Post-Treatment to Chlorination

Equipment: Batch reactor was used for temp. <100°C - dry weight of coal 2 kg, solvent/coal 2/1, indirect steam heating, 550 RPM; 2 liters autoclave was used for temp. >100°C - dry coal 100g, solvent/coal 7/1, electrical heating, 300 RPM; chlorination conditions: chlorine feed 10 SCFH; dechlorination conditions: nitrogen feed 5 SCFH, 4-5 RPM, temperature 400°C, 60 min.

Run No. and Date	Pretreatment(6)			Pretreated Coal								Chlorination				Chlorinated Coal							
	Conditions			Chlorine	Organic Sulfur		Pyritic Sulfur		Sulfate Sulfur	Total Sulfur		Conditions				Chlorine	Organic Sulfur		Pyritic Sulfur		Sulfate Sulfur	Total Sulfur	
	Solvent	Temp (°C)	Time (min)	(wt.%)	Res(1) (wt.%)	Rem(2) (%)	Res (wt.%)	Rem (%)	Res (wt.%)	Res (wt.%)	Rem. (%)	Solvent	Temp (°C)	Time (min)	Press (psig)	(wt.%)	Res (wt.%)	Rem (%)	Res (wt.%)	Rem (%)	Res (wt.%)	Res (wt.%)	Rem (%)
PSOC-276, HVA, Ohio No. 8, Harrison County, Georgetown No. 24 Mine. -100 to +200 Mesh Sulfur Forms (wt.%): Organic-S 1.17, Pyritic-S 2.63, Sulfate-S 0.06, Total-S 3.87; Chlorine 0.09 (wt.%)																							
26-9/4/80(3)	9% NaOH	230	60	-	1.24	-6.0	0.10	96	0.18	1.52 (1.34)	61 (65)	----	----	----	----	----	----	----	----	----	----	----	----
PSOC-282, HVB, ILL. No. 6, Jefferson County, ILL., Orient No. 6 Mine, Washed, -100 to +200 Mesh Sulfur Forms (wt.%): Organic-S 0.75, Pyritic-S 0.43, Sulfate-S 0.36. Total-S 111.54; Chlorine 0.47 (wt.%)																							
2-6/18/80	10% NaOH	90	60	0.08	0.77	-2.7	0.36	16.3	0.09	1.12 (1.13)	21 (27)	H20	70	45	0.06	11.0	0.62	17.3	0.17	60.5	<0.05	0.79	49
3-6-23/80	10% NaOH	90	60	0.10	0.76	-1.3	0.35	18.6	0.06	1.17 (1.11)	24 (28)	MC(4)	70	45	0-6	6.13	0.75	-	0.34	20.9	<0.05	1.09	29
4-7/7/80	2% NaOH	90	60	0.55	0.78	-4.0	1.16	-170	<0.05	1.94	-26	H_2O	70	45	0-6	7.74	0.99	-32	0.39	9.3	<0.05	1.38	10
13-7/30/80	----	----	----	----	----	----	----	----	----	----	----	H_2O	70	45	0-6	7.33	0.80	-7	0.28	35	<0.05	1.08	30
	----	----	----	----	----	----	----	----	----	----	----	-	-	-	-	-	-	-	-	-	-	-	-
	----	----	----	----	----	----	----	----	----	----	----	-	-	-	-	-	-	-	-	-	-	-	-
	----	----	----	----	----	----	----	----	----	----	----	-	-	-	-	-	-	-	-	-	-	-	-
22-8/25/80(3)	10% NaOH	230	60	0.52	0.64	15	0.14	67	0.10	0.88 (0.78)	43 (49)	----	----	----	----	----	----	----	----	----	----	----	----
16-8/22/80	----	----	----	----	----	----	----	----	----	----	----	10% Na_2CO_3	70	45	0-6	7.80	0.77	-2.7	0.26	40	<0.05	1.03	33
	----	----	----	----	----	----	----	----	----	----	----	-	-	-	-	-	-	-	-	-	-	-	-
	----	----	----	----	----	----	----	----	----	----	----	-	-	-	-	-	-	-	-	-	-	-	-
17-8/11/80	1:1 MeOH :CC14	70	60	1.76	0.76	-1.3	0.42	2	0.21	1.39 (1.18)	10 (23)	H_2O	70	45	0-6	9.61	0.83	-11	0.14	67	<0.05	0.97	37

Run No. and Date	Post-treatment(7)			Post-Treated Coal								Dechlorinated Coal							
	Conditions			Chlorine	Organic Sulfur		Pyritic Sulfur		Sulfate Sulfur	Total Sulfur		Chlorine	Organic Sulfur		Pyritic Sulfur		Sulfate Sulfur	Total Sulfur	
	Solvent	Temp (°C)	Time (min.)	(wt.%)	Res (wt.%)	Rem (%)	Res. (wt.%)	Rem (%)	Res. (wt.%)	Res (wt.%)	Rem (%)	(wt.%)	Res. (wt.%)	Rem (%)	Res (wt.%)	Rem (%)	Res (wt.%)	Res (wt.%)	Rem (%)
PSOC-276, HVA, Ohio No. 8, Harrison County, Georgetown No. 24 Mine. -100 to +200 Mesh Sulfur Forms (wt.%): Organic-S 1.17, Pyritic-S 2.63, Sulfate-S 0.06, Total-S 3.87; Chlorine 0.09 (wt.%)																			
26-9/4/80(3)	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----	----
PSOC-282, HVB, ILL. No. 6, Jefferson County, ILL., Orient No. 6 Mine, Washed, -100 to +200 Mesh Sulfur Forms (wt.%): Organic-S 0.75, Pyritic-S 0.43, Sulfate-S 0.36. Total-S 111.54; Chlorine 0.47 (wt.%)																			
2-6/18/80	10% NaOH	90	120	6.0	0.58	22.7	0.15	65	<0.05	0.73	53	4.92	0.56	25.3	0.13	69.8	<0.05	0.69	55
3-6-23/80	10% NaOH	90	120	1.75	0.71	5.3	0.22	48.8	<0.05	0.93	40	1.54	0.71	5.3	0.27	37.2	<0.05	0.98	36
4-7/7/80	2% NaOH	90	120	8.53	0.84	-12	0.08	81.4	<0.05	0.92	40	1.79	0.61	18.7	0.08	81.4	<0.05	0.69	55
13-7/30/80	----	----	----	----	----	----	----	----	----	----	----	1.02	0.6	20	0.25	42	<0.05	0.85	45
	10% NaOH	230	60	0.58	0.60	20	0.05	88	<0.05	0.65	58	5.46	0.65	13	0.08	81	<0.05	0.73	53
	9% NaOH	260	60	0.30	0.68	9	<0.05	100	<0.05	0.68	56	----	----	----	----	----	<0.05	----	----
	9% NaOH	290	60	0.22	0.68	9	<0.05	100	<0.05	0.68	56	----	----	----	----	----	----	----	----
22-8/25/80(3)	----	----	----	----	----	----	----	----	----	----	----	3.02	0.55	27	0.09	79	0.30	0.94 (0.64)	39 (58)
16-8/22/80	----	----	----	----	----	----	----	----	----	----	----	0.38(L)	-	-	-	-		0.83	46.0
	10% Na_2CO_3	230	60	0.91	0.71	5.3	0.20	53	<0.05	0.91	41	----	----	----	----	----	----	----	----
	10% Na_2CO_3(5)	230	60	0.37	0.71	5.3	0.08	81	<0.05	0.79	49	----	----	----	----	----	----	----	----
17-8/11/80	----	----	----	----	----	----	----	----	----	----	----	1.24	0.62	17.3	0.19	56	<0.05	0.81	47

(1) Residual.
(2) Removal.
(3) Raw coal were subjected to only caustic high temperature pretreatment.
(4) Sulfate sulfur free basis.
(5) Chlorinated/dechlorinated coal was used for this treatment.
(6) Pretreatment to chlorination.
(7) Post-treatment to chlorination.
(L) Leco Analysis.

SOLVENT RECOVERY

After chlorination, reactor pressure was reduced by venting reactor gases through the gas holder and to the caustic scrubber. With methylchloroform in the reactor, four kilograms of water were added and direct steam injection was used to heat the reactor and flash distill the methylchloroform to the condenser and solvent recovery tank. Steam was added until the temperature rose from 65°C to approximately 100°C, indicating that methylchloroform removal was complete. Hydrolysis was considered to be essentially complete during the chlorination reaction because water was present, even with methylchloroform runs. Flash distillation of methylchloroform normally took 45 to 60 minutes. After solvent recovery, the coal-water slurry was cooled, removed through the bottom drain into a holding tank and transferred to the batch vacuum filtration unit. With water as the solvent, the flash distillation step was circumvented. A detailed operating procedure is described in Appendix C.

POST-TREATMENT TO CHLORINATION

Chemical coal post-treatment experiments (Runs 2 to 4) were conducted in the batch reactor with 10% sodium hydroxide solution after coal had been pretreated and chlorinated. Two kilograms (dry basis) of chlorinated coal with four kilograms of 10% sodium hydroxide solution were charged into the reactor. The chlorinated coal was post-treated in the reactor for two hours at a temperature of 90°C with agitation at 550 rpm. The post-treatment experiments at temperatures higher than 100°C and above atmospheric pressure were conducted in a separate 2 liter autoclave. After post-treatment, the coal slurry was cooled, vacuum filtered, spray washed to remove post-treatment solution, and dried prior to dechlorination.

DRYING-DECHLORINATION

Bulk coal samples were removed from the vacuum filter and dried in a vacuum oven overnight at 80°C. Dechlorination of the coal was obtained in a Lindberg furnance equipped with a rotary 5-inch diameter by 5-foot long tube (Figure 10). The furnace and tube were preheated to the operating temperature of 400 to 500°C, flushed with nitrogen and charged with up to 2 kilograms of coal placed in a containment cartridge. Approximately 30 minutes were required to heat the coal charge to 400°C while maintaining a nitrogen purge of 5 SCFH. The coal was then held at 400°C for an additional 60 minutes. Tube rotation was maintained at 4 rpm. After dechlorination, furnace heat was shut down while maintaining the nitrogen purge. After 30 to 60 minutes of cooling, the coal was removed and stored in a closed glass container. The detailed operating procedure is described in Appendix C. The same operating procedure was adopted for hydrodesulfurization experiments except that purge gas was hydrogen instead of nitrogen. The detailed operating procedure for hydrodesulfurization is described in Appendix C.

BATCH REACTOR EXPERIMENTAL DATA

COAL PRETREATMENT/POST-TREATMENT TO CHLORINATION

Coal was pretreated and post-treated relative to the chlorination process in order to enhance coal desulfurization by the chlorinolysis process. Treatment conditions and coal desulfurization results are listed in Table 3. This experimental data obtained on a 2 kilograms of coal scale is complementary to the laboratory scale data (Table 2) obtained on pretreatment and post-treatment of coal relative to the chlorinolysis process.

Coal PSOC 276

Raw coal was treated with 9% NaOH at 230°C for 60 minutes. Pyritic sulfur removal was 96% and total sulfur removal was 61% as a result of the coal pretreatment. The residual sulfate sulfur content after washing was 0.8 wt.%. Total sulfur removal based on complete sulfate removal was 65%.

Coal PSOC 282

Raw Coal was treated with 10% NaOH at 90°C and 230°C for 60 minutes. At 90°C, pyritic sulfur removal was 16-19% and total sulfur removal was 21-24% (27-28% assuming total sulfate removal). At 230°C, the organic sulfur removal was 15%, pyritic sulfur removal was 67 % and total sulfur removal was 43%. Treatment with 2% NaOH at 90°C gave a negative desulfurization, probably due to analytical error from interference by NaOH (NaOH has been noted to provide some analytical problems with sulfur determinations by the Leco acid-base instrument).

Chlorination of the NaOH pretreated coal resulted in a desulfurization of 29-49%. Post-treatment of the chlorinated coal with 10% NaOH at 90°C for 120 minutes increased desulfurization to 40-53%. The dechlorination of the post-treated coal at 400°C showed no significant improvement in desulfurization, i.e., 36-55% desulfurization after dechlorination. Dechlorination of the pretreated coal (10% NaOH at 230°C) at 400°C provided an improved desulfurization to 49%-58% (based on total sulfate sulfur removal).

Chlorination of the coal without pretreatment provided 30% desulfurization and chlorination in the presence of 10% Na_2CO_3 gave 33% desulfurization. Post-treatment of the chlorinated coal (without Na_2CO_3) by 9-10% NaOH at 230, 260 and 290°C for 60 minutes gave 56-58% desulfurization. Dechlorination of the post-treated coal gave 53% desulfurization. The chlorinated coal (with 10% Na_2CO_3) after dechlorination at 400°C achieved 46% desulfurization. Post-treatment with 10% Na_2CO_3 at 230°C, gave a desulfurization of 41-49%.

The conclusion was that the combination of NaOH pretreatments and post-treatments by themselves or in conjunction with chlorination and dechlorination of the treated coal did not provide any substantial increases in coal desulfurization. In fact, 10% NaOH treatment at 230°C, 60 minutes without chlorination achieved close to the maximum desulfurization obtained with chlorination by itself. Other batch reactor runs without pretreatment or post-treatment have achieved up to 60% desulfurization with PSOC 282 coal. Thus, the impact of 10% NaOH in pretreatment or post-treatment is negligible at best.

Pretreatment with a one-to-one mixture of methanol and carbontetrachloride showed a 10% desulfurization (23% assuming zero sulfate sulfur). Chlorination increased desulfurization to 37%. Dechlorination at 400°C increased desulfurization to 47% #. These results with the one-to-one solvent mixture of methanol and carbontetrachloride pretreatment were somewhat better than the laboratory results in which this solvent mixture was used in the chlorination (Table 2). However, no significant advantage in desulfurization was obtained with these solvents over the chlorinolysis process with water.

COAL DESULFURIZATION BY CHLORINOLYSIS

A total of 45 batch runs were conducted with 2 kilograms of coal per batch on 22 bituminous, sub-bituminous and lignite coals, Table 4. The coals were subjected to the chlorinolysis process that included chlorination, filtration-wash and dechlorination.

Chlorinations were carried out with either water or methylchloroform at 2 parts to 1 part of coal, 10 SCFH chlorine feed rate, 0-30 psig, 20-100°C for 30-60 minutes. Coal was 100 x 200, -200 and -325 mesh, as designated. With methylchloroform, the solvent was separated out by distillation after first adding water to the coal slurry. The coal-water slurry was vacuum filtered on a bench-scale unit and manually spray washed. This coal was then dried and dechlorinated. The dechlorination was carried out at 400-500°C for 60 minutes in the bench-scale unit with a nitrogen purge of 5 SCFH at atmospheric pressure and tube rotation at 4 rpm. With PSOC 276 coal, two of the dechlorinations were conducted with hydrogen in place of nitrogen at 600 and 700°C. With the TVA coal, the dechlorination was also with hydrogen at 500°C.

Coal PSOC 276

Four runs were carried out with coal-water chlorinations at 70°C, atmospheric pressure, 60 minutes, with chlorine at 10 SCFH. Run 56 should be disregarded because of the apparent low chlorine input to the coal (1.02 wt.%). The other three runs, after chlorination but before dechlorination indicated a 52-60% desulfurization. Organic sulfur removal was low (0-18%) with pyritic sulfur removal of 78-83%. Dechlorination at 400°C gave 59% desulfurization with 8% organic sulfur removal and 81% pyritic sulfur removal. Subjecting the chlorinated coal to dechlorination at 500°C increased desulfurization to 68% with a 95% pyritic sulfur removal. Treatment of the chlorinated coal with hydrogen at 600°C with batch dechlorination increased desulfurization to 73%. Treatment with hydrogen at 700°C increased desulfurization to 78% with 28% organic sulfur removal and 100% pyritic sulfur removal.

Coal PSOC 282

Staged Chlorination

Runs 5-10 were conducted in sequence on the same batch of coal as indicated (Table 4) with runs 5-6 (stages 1 and 2) with water, runs 7-8 with methylchloroform and runs 9-10 with the processed coal particle size reduced by grinding from 100 x 200 mesh to -325 mesh. Run 9 (stage 5) was with water and run 10 (stage 6) with methylchloroform. Chlorinations were for 30

Table 4. Batch Reactor Experimental Data for Coal Desulfurization by Chlorinolysis(8)

Chlorination Conditions: Dry Weight of Coal 2 kg, for water runs - water/coal 2/1, for methylchloroform runs - methylchloroform/coal 2/1 and water/coal 1/10, chlorine feed 10 SCFH, indirect steam heating, 550 RPM; Distillation (methylchlorform runs only): water/coal 2/1, 65-100°C, indirect steam heating; Filtration-wash: water/coal 2/1, 21°C; Dechlorination: nitrogen (hydrogen) feed 5 SCFH, 4-5 RPM.

RUN NO. AND DATE	RAW COAL						CHLORINATION PROCESS CONDITIONS				CHLORINATED COAL								DECHLORINATION PROCESS CONDITIONS		DECHLORINATED COAL							
	Coal Mesh Size	Chlorine	Organic S	Pyritic S	Sulfate S	Total S	Solvent	Temp.	Time	Press.	Chlorine	Organic-S		Pyritic-S		Sulfate -S	Total-S		Temp.	Time	Chlorine	Organic-S		Pyritic-S		Sulfate-S	Total-S	
												Res.(1)	Rem.(2)	Res.	Rem.	Res.	Res.	Rem.				Res.	Rem.	Res.	Rem.	Res.	Res.	Rem.
		(wt.%)	(wt.%)	(wt.%)	(wt.%)	(wt.%)		(°C)	(min)	(psig)	(wt.%)	(wt.%)	(%)	(wt.%)	(%)	(wt.%)	(wt.%)	(%)	(°C)	(Min.)	(wt.%)	(wt.%)	(%)	(wt.%)	(%)	(wt.%)	(wt.%)	(%)
PSOC-276, HVA, Ohio No. 8, Harrison County, Ohio (Georgetown No. 24 Mine)																												
38-10/29/80	-200	0.09	1.17	2.63	0.06	3.87	H_2O	70	60	0-6	7.08	0.96	18	0.58	78	0.19	1.73	55 (3)	400	60	1.17	1.08	8	0.50	81	<0.05	1.58	59
																	(1.54)	(60)										
48-01/06/81	-325	0.09	1.17	2.63	0.06	3.87	H_2O	70	60	0-6	9.36	1.15	1.7	0.45	83	0.11	1.72	56	500	60	0.37	1.11	5.0	0.13	95	<0.05	1.25	68
																	(1.61)	(58)	600	60in H_2	0.09	1.06	9.4	<0.05	100	<0.05	1.06	73
48-01/08/81	-325	0.09	1.17	2.63	0.06	3.87	H_2O	70	60	0-6	8.45	1.23	-5.1	0.54	79.5	0.10	1.87	52	500	60	-	-	-	-	-	-	-	-
																	(1.77)	(54)	700	60in H_2	<0.05	0.84	28.2	<0.05	100	0.19	1.03	73
																											(0.84)	(78)
57-01/16/81	-325	0.09	1.17	2.63	0.06	3.87	H_2O	70	60	0-6	1.02	1.18	-0.8	1.66	37	0.13	2.97	23	500	60	0.18	1.50	-28.2	0.69	73.8	<0.05	2.20	43
																	(2.84)	(27)										
PSOC-282, HVB, Illinois No. 6, Jefferson County, Illinois (Orient No. 6 Mine, Washed)																												
(5) 5-07/10/80	100-200	0.47	0.75	0.43	0.36	1.54	H_2O	(6) RT	30	0-6	4.58	0.63	16	0.37	14	0.15	1.15	25	-	-	-	-	-	-	-	-	-	-
																	(1.00)	(35)										
6-07/10/80	100-200	-	-	-	-	-	H_2O	RT	30	0-6	8.76	0.66	12	0.19	56	0.17	1.02	34	-	-	-	-	-	-	-	-	-	-
																	(0.85)	(45)	-	-	-	-	-					
7-07/11/80	100-200	-	-	-	-	-	(4) MC	70	30	0-6	9.88	0.67	11	0.2	53	<0.05	0.87	44	-	-	-	-	-	-	-	-	-	
8-07/15/80	100-200	-	-	-	-	-	MC	70	30	0-6	11.1	0.67	11	0.16	63	<0.05	0.83	46	-	-	-	-	-	-	-	-	-	
9-07/17/80	-325	-	-	-	-	-	H_2O	RT	30	0-6	20.8	0.69	8	<0.05	100	<0.05	0.69	55	-	-	-	-	-	-	-	-	-	-
10-07/18/80	-325	-	-	-	-	-	MC	70	30	0-6	23.7	0.62	17	<0.05	100	<0.05	0.62	60	400	60	2.2	0.54	28	0.05	88	<0.05	0.59	62
(7) 14-08/06/80	-325	0.47	0.75	0.43	0.36	1.54	H_2O	RT	45	0-6	-	-	-	-	-	-	-	-	400	60	2.11	0.62	17	0.08	81	<0.05	0.70	55
15-08/07/80	-325	-	-	-	-	-	MC	70	45	0.6	18.2	0.65	13	<0.05	100	<0.05	0.65	58	400	60	3.10	0.54	28	0.07	84	<0.05	0.61	60
18-08/14/80	100-200	0.47	0.75	0.43	0.36	1.54	H_2O	RT	45	0-6	24.4	0.78	-4	<0.05	100	<0.05	0.78	49	400	60	3.22	0.64	15	<0.05	100	<0.05	0.64	58
23-08/20/80	100-200	0.47	0.75	0.43	0.36	1.54	H_2O	RT	45	30	23.3	0.74	1	<0.05	100	<0.05	0.74	52	400	60	3.79	0.61	19	<0.05	100	<0.05	0.61	60
19-08/18/80	100-200	0.47	0.75	0.43	0.36	1.54	H_2O	70	45	30	21.0	0.81	8	<0.05	100	<0.05	0.81	47	400	60	2.69	0.68	9	<0.05	100	<0.05	0.68	56
24-08/28/80	100-200	0.47	0.75	0.43	0.36	1.54	H_2O	70	45	30	14.6	0.73	3	0.10	77	<0.05	0.83	46	400	60	2.0	0.78	-4	<0.05	100	<0.05	0.78	49
20-08/26/80	100-200	0.47	0.75	0.43	0.36	1.54	H_2O	100	45	30	13.6	0.82	9	0.06	86	<0.05	0.88	43	400	60	2.19	0.84	-12	<0.05	100	<0.05	0.84	45
39-11/18/80	-325	0.47	0.75	0.43	0.36	1.54	H_2O	70	60	0-6	10.2	0.59	21	0.16	63	0.2	0.95	38	500	60	0.47	0.71	5.3	<0.05	100	<0.05	0.71	54
																	(0.75)	(51)										
43-12/04/80	-325	0.47	0.75	0.43	0.36	1.54	H_2O	70	60	0-6	8.99	0.81	-8	0.16	63	<0.05	0.97	37	500	60	0.44	0.68	9	<0.05	100	<0.05	0.68	56
44-12/09/80	-325	0.47	0.75	0.43	0.36	1.54	H_2O	70	60	0-6	10.1	0.93	-24	<0.05	100	<0.05	0.93	40	500	60	0.45	0.68	9	<0.05	100	<0.05	0.68	56
PSOC-219, HVB, Kentucky No. 4, Hopkins County, Kentucky																												
32-09/10/80	-200	0.07	0.81	0.73	0.60	2.15	H_2O	70	45	0-6	6.25	0.83	-2.5	0.37	49	0.1	1.3	40	400	60	0.97	0.71	12	0.31	57	<0.05	1.02	53
																	(1.20)	(44)	450	60	0.51	0.77	5	0.25	66	<0.05	1.02	53
																			500	60	0.33	0.75	7	0.19	74	<0.05	0.94	56
PSOC-230, Rosebud Colstrip Field, Rosebud County, Montana																												
11-07/23/80	100-200	<0.05	0.52	0.35	<0.05	0.87	H_2O	70	45	0-6	7.6	0.47	10	<0.05	100	<0.05	0.52	40	400	60	1.24	0.46	11.5	<0.05	100	<0.05	0.46	47
																			400	120	0.60	0.33	36	0.13	63	<0.05	0.46	47
12-07/25/80	100-200	<0.05	0.52	0.35	<0.05	0.87	MC	70	45	0-6	6.96	0.48	8	<0.05	100	<0.05	0.48	45	400	60	0.64	0.37	29	0.09	74	<0.05	0.46	47
PSOC-090, Gust, Richland County, Montana (Savage Mine)																												
27-09/02/80	100-200	0.05	0.47	<0.05	<0.05	0.47	H_2O	70	45	0-6	5.51	0.43	9	<0.05	-	<0.05	0.43	9	400	60	0.62	0.37	21	<0.05	-	<0.05	0.37	21
37-10/22/80	100-200	0.05	0.47	<0.05	<0.05	0.47	MC	70	45	0-6	10.5	0.38	19	<0.05	-	<0.05	0.38	19	400	60	1.97	0.37	21	<0.05	-	<0.05	0.37	21
PSOC,126 (Washed), HVA, Lower Kittanning, Cambria County, Pennsylvania (Cambria Slope No. 33)																												
28-09/03/80	100-200	0.1	0.61	0.07	<0.05	0.68	H_2O	70	45	0-6	7.27	0.58	5	<0.05	100	<0.05	0.58	15	400	60	1.53	0.57	6.5	<0.05	100	<0.05	0.57	16
33-09/15/80	100-200	0.1	0.61	0.07	<0.05	0.68	MC	70	45	0-6	7.27	0.54	11	<0.05	100	<0.05	0.54	21	400	60	1.56	0.52	15	<0.05	100	<0.05	0.52	24
34-09/17/80	100-200	0.1	0.61	0.07	<0.05	0.68	MC	70	45	0-6	16.1	0.50	18	<0.50	100	<0.50	0.50	26	400	60	3.07	0.50	18	<0.05	100	<0.05	0.50	26
PSOC-126, HVA, Lower Kittanning, Cambria County, Pennsylvania (Cambria Slope No. 33)																												
29-09/04/80	100-200	0.06	0.52	0.51	<0.05	1.03	H_2O	70	45	0-6	6.95	0.50	4	0.11	78	<0.50	0.61	41	400	60	1.40	0.50	4	0.09	82	<0.05	0.59	43
36-10/21/80	100-200	0.06	0.52	0.51	<0.05	1.03	MC	70	45	0-6	-	-	-	-	-	-	-	-	400	60	2.67	0.41	21	<0.05	100	<0.05	0.41	60
PSOC-074, Beulah-Zap, Mercer County, North Dakota (Beulah Mine)																												
30-09/09/80	100-200	<0.05	0.58	0.29	<0.05	0.87	H_2O	70	45	0-6	4.20	0.55	5.2	0.25	14	<0.05	0.80	8	400	60	0.65	0.45	22.4	0.26	10	<0.05	0.71	18
[illegible]-09/19/80	100-200	<0.05	0.58	0.29	<0.05	0.87	MC	70	45	0-6	9.16	0.48	17.2	0.18	38	<0.05	0.66	24	400	60	0.86	0.54	7	0.10	65.5	<0.05	0.64	26

Table 4. (cont'd)

Chlorination Conditions: Dry Weight of Coal 2 kg, for water runs - water/coal 2/1, for methylchloroform runs - methylchloroform/coal 2/1 and water/coal 1/10, chlorine feed 10 SCFH, indirect steam heating, 550 RPM; Distillation (methylchlorform runs only): water/coal 2/1, 65-100°C, indirect steam heating; Filtration-wash: water/coal 2/1, 21°C; Dechlorination: nitrogen (hydrogen) feed 5 SCFH, 4-5 RPM.

RUN NO. AND DATE	RAW COAL						CHLORINATION PROCESS CONDITIONS				CHLORINATED COAL								DECHLORINATION PROCESS CONDITIONS		DECHLORINATED COAL							
	Coal Mesh Size	Chlorine (wt.%)	Organic S (wt.%)	Pyritic S (wt.%)	Sulfate S (wt.%)	Total S (wt.%)	Solvent	Temp. (°C)	Time (min)	Press. (psig)	Chlorine (wt.%)	Organic-S		Pyritic-S		Sulfate -S	Total-S		Temp. (°C)	Time (Min.)	Chlorine (wt.%)	Organic-S		Pyritic-S		Sulfate-S	Total-S	
												Res.(1) (wt.%)	Rem.(2) (%)	Res. (wt.%)	Rem. (%)	Res. (wt.%)	Res. (wt.%)	Rem. (%)				Res. (wt.%)	Rem. (%)	Res. (wt.%)	Rem. (%)	Res. (wt.%)	Res. (wt.%)	Rem. (%)
											HVA, Mary Lee, Jefferson County, Alabama (Chetopa Mine)																	
40-11/19/80	-325	<0.05	0.33	0.41	<0.05	0.74	H_2O	70	60	0-6	9.84	0.44	-33	<0.05	100	<0.05	0.44	41	500	60	0.45	0.41	-24	<0.05	100	<0.05	0.41	45
											PSOC-274A, HVA, Sewell, Nicholas County, West Virginia (Quinwood No. 7)																	
41-11/25/80	-325	0.10	0.58	<0.05	<0.05	0.58	H_2O	70	60	0-6	11.6	0.45	22	<0.05	-	<0.05	0.45	22	500	60	0.50	0.43	26	<0.05	-	<0.05	0.43	26
											PSOC-371, HVA, Imboden, Letcher County, Kentucky (Scotia Mine)																	
42-12/01/80	-325	<0.05	0.60	0.36	<0.05	0.96	H_2O	70	60	0-6	9.46	0.62	-3	<0.05	100	<0.05	0.62	35	500	60	0.35	0.51	15	<0.05	100	<0.05	0.51	47
											PSOC-241, SB-B, Monarch & Dietz No. 3, Sheridan County, Wyoming (Big Horn)																	
45-12/11/80	-325	<0.05	0.55	0.19	0.11	0.85	H_2O	70	60	0-6	7.71	0.72	-31	<0.05	100	<0.05	0.72	15	500	60	0.26	0.55	0	<0.05	100	<0.05	0.55	35
											Rosebud-McKay & Robinson, Big Horn County, Montana (Absaloka Mine)																	
46-12/16/80	-325	<0.05	0.57	0.17	<0.05	0.75	H_2O	70	60	0-6	8.62	0.59	-4	<0.05	100	<0.50	0.59	21	500	60	0.31	0.50	12	<0.05	100	<0.05	0.50	33
											No. 2 Lehigh Bed, Stark County, North Dakota																	
47-12/31/80	-325	<0.05	0.72	1.48	0.20	2.39	H_2O	70	60	0-6	7.34	1.09	-51	0.58	61	<0.05	1.68	30	500	60	0.29	1.18	-64	0.30	80	<0.05	1.48	38
											West Kentucky #11 (Washed), obtained from TVA																	
50-01/09/81	-325	<0.05	1.99	1.34	<0.05	3.32	H_2O	70	60	0-6	5.95	1.89	5.0	0.7	47.8	<0.05	2.60	22	400 500	60 60 in H_2	- 0.23	- 1.78	- 10.6	- <0.05	- 100	- <0.05	- 1.78	- 46
											Western Kentucky No. 9 Bed, Union County, Kentucky (Hamilton Mine NO. 1)																	
51-01/12/81	-200	0.29	1.25	2.22	0.22	3.69	H_2O	70	60	0-6	4.56	1.36	-9	1.41	35.6	0.07	2.85 (2.78)	23 (25)	500	60	0.34	1.58	-26	0.51	77	<0.05	2.10	43
											Lower Kittanning Bed, Armstrong County, Pennsylvania (C. H. Snyder Mine)																	
52-01/12/81	-200	0.27	0.98	4.04	0.1	5.12	H_2O	70	60	0-6	5.96	1.35	-38	1.07	73.5	<0.05	2.41	53	500	60	0.51	1.64	-67	0.57	86	<0.05	2.22	57
											Pittsburgh Bed, Harrison County, Ohio (Franklin Mine)																	
53-01/13/81	-200	0.2	0.9	1.31	<0.05	2.21	H_2O	70	60	0-6	7.74	0.92	-2	0.45	65.6	<0.05	1.38	38	500	60	0.34	0.88	2	0.18	86	<0.05	1.06	52
											Illinois No. 6 Bed, St. Clair County, Illinois (River King Mine, Washed)																	
55-01/15/81	-200	0.12	1.86	1.49	0.14	3.49	H_2O	70	60	0-6	4.65	2.09	-12.4	0.99	33.6	<0.05	3.07	12	500	60	0.27	1.94	-4	0.24	84	<0.05	2.18	38
											Lucas Co. No. 5 Bed, Monroe County, Iowa (Lovilia No. 4 Mine)																	
56-01/15/81	-200	0.09	0.7	1.31	0.12	2.13	H_2O	70	60	0-6	1.37	0.85	-23	1.35	-3	<0.05	2.19	-2.8	500	60	0.32	1.07	-53	0.71	46	<0.05	1.79	16
											Texas Lignite (Dow Chemical)																	
54-01/14/81	30-100	0.07	0.82	0.27	0.14	1.23	H_2O	70	60	0-6	-	-	-	-	-	-	-	-	400	60	1.1	0.59	28	0.14	48	<0.05	0.73	41

(1) Residual
(2) Removal
(3) Sulfate sulfur free basis
(4) Mechylchloroform
(5) Six consecutive step process where same coal was treated under six different process conditions
(6) Room temperature, 21°C
(7) Two consecutive step process
(8) Sulfur forms are dry and chlorine free basis, alternate method.

minutes with Cl_2 at 10 SCFH. Total sulfur reduction was 25-35% (stage 1), 34-45% (stage 2), 44% (stage 3), 46% (Stage 4), 55% (stage 5) and 60% (stage 6). The extent of desulfurization appeared to be the same with water and methylchloform. The desulfurization reached a maximum value with stage 2 with 100 x 200 mesh coal. The added stages of chlorination (stages 3-4) had no apparent effect on desulfurization until the coal was reground to -325 mesh (stage 5). Regrinding the coal from 100 x 200 mesh to -325 mesh had a substantial effect of increasing the desulfurization from 45 to 55-60% (stages 5,6).

A subsequent 2 stage chlorination (runs 14, 15) at 45 minutes for each stage with -325 mesh coal provided comparable (55-60%) desulfurization to that achieved in the 6 stage treatment. The desulfurization of the first stage with the water (after dechlorination) was 55% and after the second stage with methylchloroform was 60%. The combination of these runs indicates the importance of reduced coal particle size in achieving maximum desulfurization with PSOC 282 coal. Solvent differences between water and methylchloroform showed no substantial influence.

Chlorinolysis Process Parameters

A series of eight runs were conducted with water at temperatures from 20°C to 100°C, 45-60 minutes, 0-30 psig, 100 x 200 mesh and -325 mesh coal and Cl_2 at 10 SCFH (Table 4). The chlorinated coal before dechlorination showed 28-52% desulfurization with 0-21% organic sulfur removal and 63-100% pyritic sulfur removal. Dechlorination at 400-500°C increased desulfurization to 45-60% with organic sulfur removal of 0-19% and pyritic sulfur removal of 100%. Variations in temperature, pressure, mesh size and retention time over the range indicated showed no correlation with desulfurization. Some analytical bias in organic sulfur and pyritic sulfur determinations is indicated by the occurrence of some negative values of organic sulfur removal in both the chlorinated and dechlorinated samples.

Coal PSOC 219

Chlorinolysis of PSOC 219 coal (run 32) showed 40-44% desulfurization after chlorination and 53-56% desulfurization after dechlorination at 400-500°C (Table 4). Organic sulfur removal was 5-12% and pyritic sulfur removal 57-74%.

Low Sulfur Coals

PSOC 230 Coal with 0.87% wt.% sulfur gave 40% desulfurization in water and 45% desulfurization in methylchloroform at 70°C and 45 minutes (Table 4). After dechlorination at 400°C, desulfurization is 47% with organic sulfur removal at 11-36% and pyritic sulfur removal at 63-100%.

PSOC 090 coal with 0.47 wt.% sulfur (<0.05 wt.% pyritic sulfur) showed 9% desulfurization with water and 19% desulfurization with methylchloroform (Table 4). After dechlorination at 400°C, desulfurization was 21% in both runs.

PSOC 126 washed coal with 0.68 wt.% sulfur (0.07 wt.% pyritic sulfur) gave 15% desulfurization with water and 21-26% desulfurization with methylchloroform (Table 4). Dechlorination at 400°C increased desulfurization slightly to 16-26%.

PSOC 126 unwashed coal with 1.03 wt.% sulfur gave 43% desulfurization with water and 60% desulfurization with methylchloroform after dechlorination at 400°C (Table 4).

PSOC 074 coal with 0.87 wt.% sulfur showed only 8% desulfurization with water and 24% desulfurization with methylchloroform (Table 4). Dechlorination at 400°C increased the desulfurization to 18-26%.

The above five low sulfur coals were generally characterized by low levels of desulfurization with methylchloroform providing significantly more desulfurization than water. Dechlorination at 400°C provided significant improvements in desulfurization for some of the coals.

Chetopa Mine - Mary Lee, Jefferson County, Ala. coal with 0.74 wt.% total sulfur gave 41% desulfurization with the chlorinated coal and 45% desulfurization with the dechlorinated coal. Pyritic sulfur removal was complete.

PSOC 274A with 0.58 wt.% sulfur which is totally organic sulfur showed 22% desulfurization after chlorination and 26% after dechlorination at 500°C (Table 4).

PSOC 371 with 0.96 wt.% sulfur showed 35% desulfurization after chlorination and 47% after dechlorination at 500°C (Table 4).

PSOC 241 with 0.85 wt.% sulfur showed 15% desulfurization after chlorination and 35% after dechlorination at 500°C (Table 4).

Rosebud-McKay and Robinson (Absaloke Mine), Montana coal with 0.75 wt.% sulfur showed 21% desulfurization after chlorination and 33% after dechlorination at 500°C (Table 4).

No. 2 Lehigh Bed, North Dakota with 2.39 wt.% sulfur gave 30% desulfurization after chlorination and 38% after dechlorination (Table 4).

TVA Test Coal

West Kentucky No. 11 (washed) coal with 3.32 wt.% sulfur showed 22% desulfurization after chlorination and 46% after dechlorination at 500°C (Table 4).

DOE Test Coals

West Kentucky No. 9 coal with 3.69 wt.% sulfur gave 23% desulfurization after chlorination and 43% after dechlorination at 500°C (Table 4).

Lower Kittaning Bed, PA., coal with 5.12% sulfur gave 53% desulfurization after chlorination and 57% after dechlorination at 500°C (Table 4).

Pittsburgh Bed, Ohio coal with 2.21 wt.% sulfur gave 38% desulfurization after chlorination and 52% after dechlorination (Table 4).

Illinois No. 6 Bed (River King Mine, washed) coal with 3.49 wt.% sulfur gave 12% desulfurization after chlorination and 38% after dechlorination (Table 4).

Lovilia No. 4 Mine, Iowa with 2.13 wt.% sulfur showed no desulfurization after chlorination and 16% after dechlorination (Table 4). It is suggested that the chlorine feed rate was erroneously very low (sticking flowmeter).

Dow Chemical/Texas Lignite

Texas Lignite (Dow Chemical) with 1.23 wt.% total sulfur showed 41% desulfurization after dechlorination (Table 4). No sample was analyzed after chlorination. Later laboratory test with hydrodesulfurization at 700°C indicates a 80% sulfur reduction (Table 4).

ADVANCED DECHLORINATION/DESULFURIZATION OF RAW/CHLORINOLYSIS PROCESSED COAL

Eight bituminous, sub-bituminous and lignite coals with a total sulfur content of 0.47 wt.% to 3.87 wt.% were first treated by the chlorinolysis process in the bench-scale, batch reactor (2 kg coal) that included chlorination and dechlorination (Table 4). The bench scale dechlorination condition was normally at 400°C, 60 minutes, with 5 SCFH of nitrogen purge, atmospheric pressure, and tube rotation at 4 rpm. The laboratory scale processing was done on a 2 to 4 grams sample in a one-inch diameter quartz tube, rotating at 2 rpm, held in a muffle furnace with provisions for metering a variety of purge gas streams through the rotating coal bed. Hydrodesulfurization (H_2 treatment) was conducted with H_2 replacing N_2 at the designated conditions and atmospheric pressure.

Coal PSOC 282

A total of 28 laboratory scale tests runs, Table 5, were conducted on PSOC 282 coal (1.54 wt.% total sulfur). Initial laboratory scale tests were conducted with nitrogen at temperatures of 400 to 700°C, 45-60 minutes, with a nitrogen purge of 90 std. cm^3/min. over a 2 to 4 gram sample. The tests with nitrogen at 400°C were in essence a repetition of the earlier dechlorination conditions to which the chlorinated batch coal was subjected. Typical results were a further decrease in coal chlorine content from 2 wt.% to less than 1 wt.% or a proportionate reduction if the starting chlorine content in the processed coal was lower. Some slight increase in desulfurization also occured in some instances at 400°C. However, increasing the temperature to 500°C with nitrogen did in some instances increase the level of desulfurization by 5 to 10%, up to a maximum desulfurization of 60%. Increasing the temperature from 500°C to 600 and 700°C with nitrogen did not increase the level of desulfurization. Product coal recovery ranged from 72 to 94%, with oil and tar recovery accounting for another 0 to 9% of the coal. Some spillage and also volatiles as low molecular weight gases accounted for the loss.

A raw coal sample (PSOC 282) subjected to 400°C, for 60 minutes in nitrogen showed a 12% desulfurization, an 88% coal product recovery with 6% of the coal as oil and tar for a coal accounting of 94%.

The chlorinolysis-processed coal that was treated came from several different bench-scale batch runs (as indicated in Table 5). The desulfurization levels were from 43 to 62%. Elevated temperature treatment up to 700°C with nitrogen was able to increase desulfurization levels up to 60%, as a maximum. As indicated, this level of desulfurization could be achieved in the chlorinolysis process without requiring treatment with nitrogen above 400°C. At temperatures above 400°C, chlorine levels were reduced to 0.1-0.2 wt.%.

Table 5. Laboratory Scale Runs of Batch Coals for Advanced Dechlorination and Desulfurization

Note: a-dry basis, b-moisture, chlorine free basis; c-cold trap replaced scrubber; d-one-inch diam. quartz tube, 2 RPM. e-pyritic sulfur determination by direct sulfur analysis (barium ppt.) not Fe determination except PSOC 276, 219 raw coals are ASTM analyses.

Lab Run/ Date	Chlorinolysis Processed Coal Product for Advanced Dechlorination/Desulfurization							Advanced Dechlorination/Desulfurization[d]													
								Conditions				Product Coal					Coal Accounting				
	Coal Batch Run	Sulfur[a,e]					Chlorine[a]	Temp	Time	Gas Flow		Sulfur[e]				Chlorine[a]	Coal Feed[a]	Coal Recov.		Oil/Tar Recov.	Total Acct.
		Org. (wt.%)	Pyr. (wt.%)	Sulf. (wt.%)	Total (wt.%)	Rem. (%)	(wt.%)	(°C)	(min)	Type	(Scm^3/min)	Org. (wt.%)	Pyritic (wt.%)	Total[b] (wt.%)	Rem. (%)	(wt.%)	(g)	(g)[a]	(%)[b]	(g)	(%)
PSOC 282, HVB, Ill. No. 6 Jefferson County, Ill. Orient Mine, Total Sulfur 1.54 Wt.% (Runs 1-25, 100 x 200 mesh, Runs 25-53, -325 mesh)																					
14-9/15/80	Raw	0.70	0.50	0.34	1.54	-	0.47	420	60	N_2	20	-	-	1.40	12	0.10	3.08	2.71	88	0.19	94
15-9/16/80	24	0.73	0.10	<0.05	0.83	46	14.6	400	45	N_2	900[c]	-	-	0.62	60	0.42	4.17	2.57	72	0	72
13-9/16/80	"	0.78	<0.05	<0.05	0.78	49	2.00	450	60	N_2	20	-	-	0.74	52	0.55	4.11	3.81	94	0.09	96
	13 Prod.	-	-	-	0.74	52	0.55	500	60	N_2	20	-	-	0.67	57	0.21	1.89	1.75	93	0.02	94
11-9/10/80	24	0.78	<0.05	<0.05	0.78	49	2.00	500	60	N_2	20	-	-	0.62	60	0.24	4.03	3.47	88	0.12	91
16-9/29/80	"	"	"	"	"	"	"	550	60	N_2	20	-	-	0.67	57	0.27	4.40	3.67	85	0.13	88
19-10/6/80	"	"	"	"	"	"	"	600	60	N_2	85	-	-	0.72	53	0.10	4.51	3.66	83	0.41	92
25-10/22/80	"	"	"	"	"	"	"	700	60	N_2	90	-	-	0.64	58	0.45	1.93	1.47	77	0.19	83
22-10/15/80	"	0.73	0.10	<0.05	0.83	46	14.6	400	45	1% Cl_2/N_2	90	-	-	0.77	50	8.00	1.92	2.19	123	0.18	134
18-10/2/80	"	0.78	<0.05	<0.05	0.78	49	2.00	400	60	1% NO_2/N_2	46	-	-	0.78	49	0.82	3.99	3.69	93	0.20	99
20-10/6/80	"	"	"	"	"	"	"	490	60	1% SO_2/N_2	84	-	-	0.75	51	0.14	3.04	2.61	88	0.14	93
28-10/31/80	10	0.54	<0.05	<0.05	0.59	62	2.20	500	60	N_2	90	-	-	0.59	62	0.79	1.95	1.49	78	0.19	85
12a-9/12/80	20	0.82	0.06	<0.05	0.88	43	13.6	400	66	N_2	20	-	-	0.84	45	-	-	-	-	-	-
12b-9/12/80	"	"	"	"	"	"	"	"	"	NH_3	55	-	-	0.71	54	0.57	-	-	-	-	-
12c-9/12/80	"	"	"	"	"	"	"	"	"	"	"	-	-	0.69	55	0.58	-	-	-	-	-
27-10/31/80	15	0.54	0.07	<0.05	0.61	60	3.10	500	60	N_2	90	-	-	0.66	57	0.55	1.96	1.45	76	0.03	76
23-10/16/80	"	"	"	"	"	"	"	400	45	0.5% O_2/N_2	90	-	-	0.63	59	0.98	2.90	2.51	88	0.24	94
26-10/28/80	"	"	"	"	"	"	"	400	45	5% O_2/N_2	90	-	-	0.63	59	3.56	1.95	1.51	77	0.12	81
30-11/7/80	"	"	"	"	"	"	"	400	45	21% O_2/N_2	90	-	-	0.61	60	2.14	1.98	1.41	72	0.19	80
24-10/17/80	"	"	"	"	"	"	"	390	60	0.91% H_2/N_2	90	-	-	0.61	60	2.20	1.95	1.68	87	0.09	90
33-11/12/80	"	"	"	"	"	"	"	400	60	H_2	90	-	-	0.58	62	1.70	1.99	1.81	92	0.20	101

Table 5. (cont'd)

Lab Run/ Date	Chlorinolysis Processed Coal Product for Advanced Dechlorination/Desulfurization							Advanced Dechlorination/Desulfurization[d]													
								Conditions				Product Coal					Coal Accounting				
	Coal Batch Run	Sulfur[a,e]					Chlorine[a] (wt.%)	Temp (°C)	Time (min)	Gas Flow		Sulfur[e]				Chlorine[a] (wt.%)	Coal Feed[a] (g)	Coal Recov.		Oil/Tar Recov. (g)	Total Acct. (%)
		Org. (wt.%)	Pyr. (wt.%)	Sulf. (wt.%)	Total (wt.%)	Rem. (%)				Type	(Scm^3/min)	Org. (wt.%)	Pyritic (wt.%)	Total[b] (wt.%)	Rem. (%)			(g)[a]	(%)[b]		
38-12/8/80	"	"	"	"	"	"	"	700	60	H_2	90	-	<0.05	0.29	81	0.00	1.98	1.36	71	0.17	78
41-12/11/80	"	"	"	"	"	"	"	700	60	H_2	90	-	<0.05	0.32	79	0.04	1.98	1.44	75	0.05	76
50/12/29/80	"	"		"	"	"	"	700	60	H_2	90		<0.05	0.26	83	0.00	4.39 4.10	3.36 3.68	79 93	- 0.46	- 102
53-1/13/81	"	"	"	"	"	"	"	700	60	H_2	90	-	<0.05	0.40	74	<0.05	5.9	4.2	73	-	-
42-12/12/80	Raw	0.70	0.50	0.34	1.54	-	0.47	700	60	H_2	90	-	<0.05	0.57	63	0.00	1.98	1.24	63	0.39	80
51-1/13/81	"	"	"	"	"	"	"	700 "	60 "	H_2	90		<0.05 "	0.87 "	44 "	0.00 "	4.88 5.85	3.20 3.70	66 64	- -	- -
PSOC 276, HVA, Ohio No. 8, Harrison County, OH, Georgetown No. 24 Mine, Total Sulfur 3.87 Wt.% (-200 mesh)																					
46-12/18-80	Raw	1.17	2.63	0.06	3.87	-	0.16	700	30	H_2	90	-	<0.05	2.43	37	0.05	1.98	1.58	80	-	-
52-1/7/80	Raw	"	"	"	"	-	"	700 "	60 "	H_2 "	90 "	-	<0.05 "	2.45 "	37 "	0.05 "	6.54 5.76	3.83 4.7	58 82	-	-
44-12/17/80	38	1.08	0.50	<0.05	1.58	60	1.17	510	30	H_2	90	-	<0.05	1.22	68	0.04	1.97	1.62	83	-	-
45-12/17/80	"	"	"	"	"	"	"	610	30	H_2	90	-	<0.05	1.21	69	0.03	1.97	1.40	72	-	-
43-12/17/80	"	"	"	"	"	"	"	700	30	H_2	90	-	<0.05	0.81	79	0.01	1.98	1.11	57	-	-
47-12/23/80	"	"	"	"	"	"	"	700	15	H_2	90	-	<0.05	0.99	74	0.01	1.99	-	-	-	-
48-12/23/80	"	"	"	"	"	"	"	700	60	H_2	90	-	<0.05	0.55	86	0.01	1.98	1.57	79	-	-
49-12/29/80	"	"	"	"	"	"	"	700 "	60 "	H_2 "	90 "	-	<0.05 "	0.78 "	80 "	0.27 "	4.31 4.0	- -	- -	- -	- -
PSOC 219, HVB, KY No. 4, Hopkins County, KY, Total Sulfur 2.15 Wt.% (-200 mesh)																					
54-1/14/81	Raw	0.82	0.73	0.60	2.15	-	0.07	700	60	H_2	90	-	<0.05	1.71	20	-	4.45	2.97	67	-	-
55-1/14/81	32	0.71	0.31	<0.05	1.02	53	0.97	700	60	H_2	90	-	<0.05	0.48	78	-	4.93	3.05	62	-	-
PSOC 230, Rosebud Colstrip Field, Rosebud County, MT, Total Sulfur 0.87 wt.% (100-200 mesh)																					
56-1/14/81	Raw	0.36	0.51	<0.05	0.87	-	0.05	700	60	H_2	90	-	<0.05	0.22	75	-	5.97	4.77	80	-	-
57-1/15/81	11	0.46	<0.05	<0.05	0.46	47	1.24	700	60	H_2	90	-	<0.05	0.18	79	-	4.39	3.40	78	-	-
PSOC 090 Gust, Richland County, MT., Savage Mine, Total Sulfur 0.47 wt.% (100-200 mesh)																					
58-1/15/81	Raw	0.47	<0.05	<0.05	0.47	-	0.05	700	60	H_2	90	-	<0.05	0.44	6	-	3.93	2.41	61	-	-
59-1/15/81	27	0.37	<0.05	<0.05	0.37	21	0.62	700	60	H_2	90	-	<0.05	0.17	64		4.49	3.21	71	-	-
PSOC 126, HVA, Lower Kittanning, Cambria County, PA., Cambria Slope No. 33, Total Sulfur 1.03 wt.% (100-200 mesh)																					
60-1/16/81	Raw	0.52	0.51	<0.05	1.03	-	0.06	700	60	H_2	90	-	<0.05	0.66	36	-	4.49	3.79	84	-	-
61-1/16/81	29	0.50	0.09	<0.05	0.59	43	1.40	700	60	H_2	90	-	<0.05	0.24	77	-	4.56	3.94	88	-	-
PSOC 074, Beulah-Zap, Mercer County, N.D., Beulah Mine, Total Sulfur 0.87 wt.% (100-200 mesh)																					
62-1/16/81	Raw	0.51	0.36	<0.05	0.87	-	<0.05	700	60	H_2	90	-	<0.05	0.88	0	-	3.55	2.11	59	-	-
63-1/16/81	30	0.45	0.26	<0.05	0.71	18	0.65	700	60	H_2	90	-	<0.05	0.42	52	-	4.59	3.10	68	-	-
TEXAS LIGNITE (DOW CHEMICAL), Total Sulfur 1.23 wt.% (30-100 mesh)																					
64-1/19/81	Raw	0.82	0.27	0.14	1.23	-	0.07	700	60	H_2	90	-	<0.05	1.09	11	-	4.52	2.76	61	-	-
65-1/19/81	54	0.59	0.14	<0.05	0.73	41	1.10	700	60	H_2	90	-	<0.05	0.24	80	-	4.52	3.31	73	-	-

With PSOC 282 coal, the introduction of 1% Cl_2, 1% NO_2, 1% SO_2, 0.5% O_2, 5% O_2, 21% O_2 and 0.91% H_2 in nitrogen were tried at 400°C (Table 5) without showing any added desulfurization although added dechlorination was achieved. Ammonia gas in lieu of nitrogen at 400°C showed an improved desulfurization from 43 - 55% with a previously undechlorinated coal sample. However, a similar improvement in desulfurization from 46 - 60%, occured with nitrogen at 400°C on a previously undechlorinated sample.

Treatment of the chlorinolysis processed samples with H_2 at temperatures of 400 to 700°C for 60 minutes indicated a significant increase in desulfurization from 60 to 72% at 600°C. A significant increase in dechlorination from 3.1 wt.% to 0.17 wt.% chlorine was observed with H_2 at 500°C (Table 5). By increasing the temperature to 700°C, the level of desulfurization was increased from 60% to 74-83%. The accompanying chlorine levels were reduced to less than 0.01 wt.%. A level of 80% desulfurization with 0.3 wt.% residual sulfur exceeds EPA sulfur emission requirements for New Source Performance Standards (NSPS).

Raw PSOC 282 coal was treated with hydrogen at 700°C for 60 minutes. The level of desulfurization without any prior processing was 44-63% but with a low 63-66% coal product recovery. Oil and tar recovery increased the coal accounting to 80%.

Coal PSOC 276

A total of eight test runs were made with raw and chlorinolysis-processed coal with H_2 at 510 to 700°C for 15-60 minutes (Table 5). The chlorinolysis-processed coal before treatment was at a 60% desulfurization level (reduced from 3.87 wt.% sulfur to 1.58 wt.% sulfur).

The raw coal showed a 37% desulfurization after treatment with H_2 at 700°C for 60 minutes with a 58-82% coal product recovery.

PSOC 276 chlorinolysis-processed coal showed a significant increase in desulfurization from 60% to 68% with H_2 at 510°C, 30 minutes with 83% coal recovery. Hydrogen treatment at a temperature of 700°C gave 74% desulfurization in 15 minutes, 79% in 30 minutes and 80-86% in 60 minutes. Coal recoveries were from 57 to 83%.

Coal PSOC 219

At 700°C with H_2 for 60 minutes, raw PSOC 219 had 20% desulfurization and 67% coal recovery (Table 5). Chlorinolysis-processed coal (53% desulfurization) after H_2 treatment at 700°C had 78% desulfurization and 62% recovery.

Coal PSOC 230

At 700°C, with H_2 for 60 minutes, raw PSOC 230 coal is 75% desulfurized with 80% recovery (Table 5). Chlorinolysis-processed coal (47% desulfurized) after H_2 treatment at 700°C had 79% desulfurization with 78% recovery.

Coal PSOC 090

At 700°C, with H_2 for 60 minutes the raw coal had 6% desulfurization, 61% recovery (Table 5). Chlorinolysis-processed coal (21% desulfurization) after H_2 treatment at 700°C had 64% desulfurization and 71% recovery.

Coal PSOC 126

At 700°C, with H_2 for 60 minutes, the raw coal was 36% desulfurized with 84% recovery (Table 5). Chlorinolysis-processed coal (43% desulfurization) after H_2 treatment at 700°C was 77% desulfurized with 88% recovery.

PSOC 074

At 700°C with H_2 for 60 minutes, raw coal had 0% desulfurization with 59% recovery (Table 5). Chlorinolysis processed coal (18% desulfurized) after H_2 treatment at 700°C had 52% desulfurization and 68% recovery.

Texas Lignite (Dow Chemical)

At 700°C, with H_2 for 60 minutes, raw coal had 11% desulfurization with 61% recovery. Chlorinolysis-processed coal (41% desulfurized) after H_2 treatment at 700°C had 80% desulfurization with 73% recovery (Table 5).

Test Summary for Eight Coals

For all eight test coals, the hydrogen treatment in the range of 500 to 700°C and times of 15-60 minutes increased the level of desulfurization substantially for the chlorinolysis-processed coal. Coal recoveries were in the range of 57 to 88%. In some cases, the hydrogen treatment of raw coal at 700°C for 60 minutes showed substantial desulfurization (75%) but in the majority of cases, the level of desulfurization of the raw coal was low, 0 to 37%, with coal recoveries of 59-85%.

COAL PROXIMATE-ULTIMATE ANALYSES- BATCH REACTOR AND LABORATORY SCALE TESTS

Coal PSOC 282

Proximate and ultimate analyses of raw and chlorinolysis-processed PSOC 282 coal are included in Table 6. Dechlorination was carried out at 500°C with nitrogen. Two additional runs are included, one run with raw coal treated with hydrogen at 700°C for 60 minutes and one run with chlorinolysis-processed coal treated with hydrogen at 700°C for 60 minutes.

The chlorinoysis-processed coal dechlorinated at 500°C shows a 56% decrease in volatiles, a 32% increase in fixed carbon, no change in ash content, a 2.6% increase in heating value as a result of a pronounced decrease in oxygen (10 vs. 5.53 wt.%). Carbon content is increased by 9.4%, hydrogen decreased by 16.2%, nitrogen increased by 14.2%, sulfur decreased by 56%, chlorine unchanged at 0.47 wt.%.

Treatment of the raw PSOC 282 coal in the laboratory dechlorinator with hydrogen at 700°C provided a 44% sulfur decrease. However, the loss of volatiles was very substantial (81%), fixed carbon increased from 59.5 to 83.8 wt.%, ash increased by 47% and heating value increased by 1.2% despite the hydrogen reduction and ash increase because of the large reduction in oxygen content from 10.0 to 1.59 wt.%. Ultimate analyses indicated an increase in carbon from 74.8 to 84.8 wt.% and a 69% decrease in hydrogen, 21% decrease in nitrogen.

Table 6. Proximate and Ultimate Analyses [a,b] of Raw and Chlorinolysis Coal
(Batch Reactor and Laboratory Glassware System)

Coal[e] Source	Run No. and Treatment	Temp (°C)	Volatiles (wt.%)	Fixed Carbon (wt.%)	Ash (wt.%)	Moisture (wt.%)	HHV (Btu/lb.)	Carbon (wt.%)	Hydrogen (wt.%)	Nitrogen (wt.%)	Sulfur (wt.%)	Chlorine (wt.%)	Oxygen[d] (wt.%)
PSOC-276, HVA OHIO, NO. 8, HARRISON COUNTY, OHIO (GEORGETOWN NO. 24 Mine)													
Raw	-	-	37.2	51.3	11.5	1.89	12,755	71.6	5.67	1.28	3.91	0.16	5.87
Chlorinolysis Processed[c] Batch Run 48-1/6/81	Batch Run 48-1/6/81 Dechlorinated	500	15.1	73.9	11.0	0.17	12,703	77.8	3.57	1.55	1.24	0.37	4.54
"	Batch Run 48-1/16/81 Hydrodesulfurized	600	12.8	75.1	12.1	<0.1	13,069	80.5	2.46	1.62	1.06	0.09	2.17
Chlorinolysis Processed Batch Run 49-1/8/81	Batch Run 49-1/8/81 Hydrodesulfurized	700	3.88	83.1	13.0	1.08	12,843	82.7	1.49	1.34	1.03	<0.05	0.44
Raw	Lab. Run 52-12/29/80 Hydrodesulfurized	700	5.14	76.4	18.5	0.43	12,113	76	1.37	1.11	2.45	-	0.57
Chlorinolysis Processed Batch Run 38-10/29/80	Lab. Run 49-1/7/81 Hydrodesulfurized	700	5.71	80.2	14.1	0.62	12,632	82	2.21	1.21	0.78	-	0
PSOC 282, HVB, ILL. No. 6, JEFFERSON COUNTY, ILL. (ORIENT NO. 6 MINE, WASHED)													
Raw	-	-	33.8	59.5	6.7	3.1	13,092	74.8	4.82	1.69	1.54	0.47	10.0
Chlorinolysis Processed Batch Run 39-11/18/80	Batch Run 39 11/18/80 Dechlorinated	500	15.0	78.4	6.56	0.52	13,436	81.8	3.04	1.93	0.67	0.47	5.53
Raw	Lab. Run 51-1/13/81 Hydrodesulfurized	700	6.36	83.8	9.88	0.38	13,252	84.8	1.52	1.34	0.87	-	1.59
Chlorinolysis Processed Batch Run 15-8/7/80	Lab. Run 50-12/29/80 Hydrodesulfurized	700	5.12	87.1	7.72	0.53	13,600	87.1	1.69	1.41	0.26	-	1.82

[a] Reference Tables 4 and 5.

[b] Dry basis.

[c] Coal has been chlorinated, filtration-wash, and dechlorinated under nitrogen.

[d] By difference

[e] Feed coal.

Treatment of the chlorinolysis processed coal with hydrogen at 700°C for 60 minutes showed similar trends in coal properties. However, desulfurization was much greater at 83%. Volatiles were reduced to 5.12 wt.%, fixed carbon increased to 87.1 wt.% and ash was increased by 15%, and heating value increased by 3.9%. Ultimate analyses indicated a 16.4% increase in carbon, 65% decrease in hydrogen, 17% decrease in nitrogen and a 82% decrease in oxygen.

Coal PSOC 276

Raw and chlorinolysis-processed PSOC 276 coal were subjected to hydrogen treatment at 700°C for 60 minutes. In addition, chlorinolysis-processed coal was subjected to dechlorination at 500°C with nitrogen and also subjected to hydrogen treatment at 600°C (Table 5). Proximate and ultimate analyses of raw and chlorinolysis processed coal are included in Table 6.

Volatiles were reduced from 37.2 wt.% in the raw coal to decreasing levels with increasing treatment temperatures. Volatiles were reduced to 15.1 wt.% at 500°C (N_2) and to 12.8 wt.% at 600°C (H_2) and to 3.88-5.71 wt.% at 700°C (H_2).

Fixed carbon levels were increased with increasing temperature from 51.3 wt.% in raw coal to 73.9 wt.% at 500°C (H_2), 75.1 wt.% at 600°C (H_2) and 76.4-83.1 wt.% at 700°C (H_2).

Ash levels also changed for chlorinolysis-processed coal with increasing temperature from 11.5 wt.% in raw coal to 11.0 wt.% at 500°C (H_2), 12.1 wt.% at 600°C (H_2), and 12.1-14.1 wt.% at 700°C (H_2). For the raw coal sample treated with H_2 at 700°C, ash increased to 18.5 wt.% indicating a much larger loss of hydrocarbons than the chlorinolysis-processed coal.

Heating value changed from 12,755 Btu/lb from the raw coal to 12,703 Btu/lb at 500°C (N_2), to 13,069 Btu/lb at 600°C (H_2) and 12,632 - 12,843 Btu/lb at at 700°C (H_2). Raw coal processed with H_2 at 700°C has a reduced heating value of 12,113 Btu/lb, probably as a result of the high ash buildup.

Carbon content increases with treatment temperature from 71.6 wt.% for raw coal to 77.8 wt.% at 500°C (N_2), 80.5 wt.% at 600°C (H_2) and 82-82.7 wt.% at 700°C (H_2). Raw treated coal with H_2 at 700°C has a lower carbon increase to 76 wt.% primarily as a result of the increased ash content.

Hydrogen is decreased with increasing temperatures from 5.67 wt.% in the raw coal to 3.57 wt.% at 500°C (N_2), 2.46 wt.% at 600°C (H_2) and 1.49 - 2.21 wt.% at 700°C. H_2 in the raw coal with hydrogen treatment at 700°C is reduced to 1.37 wt.%.

Nitrogen is changed from 1.28 wt.% in the raw coal to 1.55 wt.% at 500°C (N_2), 1.62 wt.% at 600°C (H_2), 1.21-1.34 wt.% at 700°C (H_2). Raw coal treated with H_2 at 700°C is reduced to 1.11 wt.%.

Sulfur values are reduced from 3.91 wt.% in the raw coal to 1.24 wt.% (500°C, N_2) to 1.06 wt.% (600°C, H_2) to 0.78-1.03 wt.% (700°C, H_2). Raw treated coal at 700°C with H_2 has sulfur reduced to 2.45 wt.%. Sulfur removal appears to be more effectively removed in PSOC 276 coal with prior chlorination of the coal.

Chlorine levels are changed from 0.16 wt.% in raw coal to 0.37 wt.% after treatment at 500°C with N_2 and to 0.09 wt.% at 600°C (H_2) and to 0.00-0.05 wt.% at 700°C (H_2).

Oxygen is decreased from 5.87 wt.% in raw coal to 4.54 wt.% at 500°C (N_2), to 2.17 wt.% at 600°C (H_2), to 0-0.44 wt.% at 700°C (H_2). Raw coal treated at 700°C with H_2 has oxygen reduced to 0.57 wt.%.

COAL MATERIAL BALANCE - LABORATORY SCALE TESTS

Dechlorination/Hydrodesulfurization

Coal samples charged to the laboratory scale dechlorinator were in the range of 1.9 to 5.9 grams. Chlorinolysis processed coal samples obtained from the batch reactor runs included a prior dechlorination at 400°C. Coal product recoveries in the dechlorination/hydrodesulfurization ranged from 59 to 123% (Table 5). The poor accounting in some instances is attributed to the small coal sample size with even small handling losses being magnified to indicate poor coal recovery. A more detailed discussion of the coal mass balances for the laboratory-scale tests is included in the "Advanced Dechlorination/Desulfurization" section discussing the experimental data.

COAL MATERIAL BALANCE - BATCH REACTOR TESTS

Coal material balances (Table 7) were conducted on 35 batch reactor chlorinations with filtration-washes for 20 bituminous, sub-bituminous and lignite coals. A separate coal material balance was made across the dechlorination stage, Table 7.

Chlorination/Filtration-Wash

Coal feed to the chlorinator was 2000 grams in all cases. A net weight of coal was obtained after correction for moisture, chlorine and sulfur content. Coal slurry samples were normally obtained from the reactor at 15, 30 and 45 minutes of the run time. These coal slurry samples were weighed and corrected for chlorine and sulfur content. Chlorine content was based on the chlorine feed rate over the reaction time period. The processed coal from the filtration-wash stage was weighed and corrected for moisture, chlorine and sulfur content. The moisture was obtained by an "Ohaus" balance. The chlorine and sulfur were obtained by CSMRI analyses.

Three of the coal material balances (Table 7) were poor, i.e., accounting of 79-88%. Four runs were 91-93% coal accounting. The remaining 28 runs gave 95-106% coal accounting with the majority in the range of 97-101% coal accounting. The indication is that there is relatively little coal loss in the chlorination and filtration/wash stages of the chlorinolysis process.

Dechlorination/Hydrodesulfurization

The majority of dechlorinations were at 400°C and 500°C with a nitrogen purge gas of 5 SCFH for 60 minutes at temperature with a tube rotation of 4

Table 7. Coal Mass Balance - Batch Reactor System(3)

Run #	Raw Coal Feed(1)				Samples Removed(2)				Chlorinated, Filtered, Washed and Dried Coal				Coal Accounting		Dechlorinated Product Coal									
	Coal (g)	Chlorine (g)	Sulfur (g)	Coal-Cl_2-S (g)	Coal (g)	Chlorine (g)	Sulfur (g)	Coal-Cl_2-S (g)	Coal (g)	Chlorine (g)	Sulfur (g)	Coal-Cl_2-S (g)	Coal (g)	Recov. (%)	Temp (°C)	Input Coal (g)	Coal (g)	Chlorine (g)	Sulfur (g)	Coal-Cl_2-S (g)	Recov. (%)	Oil & Tar Mass (g)	Oil & Tar Recov. (%)	Total Recov. (%)
PSOC 276, HVA, Ohio NO. 8, Harrison County, Ohio (Georgetown, No. 24 Mine)																								
38	2000	1.8	77.4	1921	422.5	23.6	7.3	391	1586	112.3	27.4	1446	1837	96	400	1446	1349	15.8	21.3	1312	91	27	1.8	93
48	2000	1.8	77.4	1921	67.0	6.3	1.1	60	2048	191.7	35.2	1821	1881	98	500	1821	1503	5.6	18.8	1479	81	73	4.0	85
															600	984	904	0.8	9.6	894	91	24	2.4	93
49	2000	1.8	77.4	1921	83.0	7.0	1.6	74	1802	152.2	33.7	1616	1690	88	700	1616	941	0.0	9.7	931	58	56	3.5	62
57	2000	1.8	77.4	1921	72.0	0.7	2.1	69	1865	19.0	55.4	1791	1860	97	500	1791	1438	2.6	31.6	1403	78	82	4.6	83
PSOC 282, HVB, ILL. NO. 6, Jefferson County, ILL. (Orient No. 6 Mine, Washed)																								
18	2000	9.4	30.8	1960	664.5	115.1	5.2	544	1869	456	15	1398	1942	99	400	1398	1277	41.0	8.0	1228	88	15	1.1	89
23	2000	9.4	30.8	1960	630.6	137.0	4.7	489	1984	456	15	1513	2002	102	400	1513	1395	52.9	8.5	1334	88	14	0.9	89
19	2000	9.4	30.8	1960	657.4	127.0	5.3	525	1812	380.5	14.5	1417	1942	99	400	1417	1247	33.5	8.5	1205	85	89	6.3	91
24	2000	9.4	30.8	1960	475.3	57.0	4.0	414	1828	267	15	1546	1960	100	400	1546	1445	31.0	12.0	1402	91	11	0.7	92
20	2000	9.4	30.8	1960	692.8	78.4	6.1	608	1724	234	15	1475	2083	106	400	1475	1270	27.8	10.7	1231	83	6	0.4	83
39	2000	9.4	30.8	1960	322.6	23.0	3.1	297	1869	191	18.0	1660	1957	100	500	1660	1298	6.1	9.2	1283	77	107	6.5	84
43	2000	9.4	30.8	1960	106	9.5	1.0	95	2207	198.4	21.4	1987	2082	106	500	1987	1568	6.9	10.7	1550	78	53	2.7	81
44	2000	9.4	30.8	1960	97.8	9.9	0.9	87	2167	218.9	20.1	1928	2015	103	500	1928	1606	7.2	10.9	1588	82	43	2.2	84
PSOC 219, HVB, KY, No. 4, Hopkins County, KY.																								
32	2000	1.4	43	1957	240.8	13.5	3.1	22.4	1442	90	19	1333	1557	80	500	1333	1069	3.5	10	1055	79	53	4.0	83
PSOC 230, Rosebud Colstrip Field, Rosebud County, Montana																								
11	2000	0.0	17.4	1983	608.0	39.7	2.8	566	1536.5	116.8	8.0	1412	1978	100	400	1412	1081	6.5	5.0	1069	76	9	0.6	77
12	2000	0.0	17.4	1983	219.3	15.2	1.0	203	1775.0	123.5	8.5	1643	1846	93	400	1643	1458	9.3	6.7	1452	88	11	0.8	89
PSOC 090 Gust, Richland County, Montana (Savage Mine)																								
27	2000	1.0	9.4	1990	308.8	15.1	1.3	292	1613	88.9	7.0	1517	1809	91	400	1517	1279	7.9	4.7	1267	84	15	0.1	84
37	2000	1.0	9.7	1989	289.9	23.7	1.1	265	1725	181.0	7.0	1537	1802	91	400	1537	1345	26.5	5.0	1314	85	27.3	1.8	87

Table 7. (cont'd)

Run #	Raw Coal Feed$^{(1)}$				Samples Removed$^{(2)}$				Chlorinated, Filtered Washed and Dried Coal				Coal Accounting		Dechlorinated Product Coal									
	Coal (g)	Chlorine (g)	Sulfur (g)	Coal-Cl_2-S (g)	Coal (g)	Chlorine (g)	Sulfur (g)	Coal-Cl_2-S (g)	Coal (g)	Chlorine (g)	Sulfur (g)	Coal-Cl_2-S (g)	Coal (g)	Recov. (%)	Temp (°C)	Input Coal (g)	Coal (g)	Chlorine (g)	Sulfur (g)	Coal-Cl_2-S (g)	Recov. (%)	Oil & Tar Mass (g)	Oil & Tar Recov. (%)	Total Recov. (%)
PSOC 126, HVA, Lower Kittanning, Cambria County, Pennsylvania (Cambria Slope No.33)																								
28	2000	2.0	13.6	1984	442.6	28.7	2.6	411	1696	123.3	9.8	1563	1974	100	400	1563	1575	24.1	9.0	1542	99	5.9	0.4	99
33	2000	2.0	13.6	1984	305.1	16.7	1.6	287	1811	131.6	9.8	1670	1957	99	400	1670	1660	25.9	8.6	1625	97	23	1.4	98
34	2000	2.0	13.6	1984	360.6	44.0	1.8	315	1977	318.0	10.0	1649	1964	99	400	1649	1569	48.2	7.8	1513	92	112	6.8	99
PSOC 126 (Washed), HVA, Lower Kittanning, Cambria County, Pennsylvania (Cambria Slope No. 33)																								
29	2000	1.0	21.0	1978	361.5	22.2	2.2	337	1760	122	10.7	1627	1964	99	400	1627	1636	23.0	10.0	1603	98	5.2	0.3	98
PSOC 074, Beulah-Zap, Mercer County, North Dakota (Beulah Mine)																								
30	2000	0.0	17.0	1983	362.3	13.2	2.9	346	1620	68.0	13.0	1539	1885	95	400	1539	1316	8.6	9.3	1298	84	5.1	0.3	84
35	2000	0.0	17.4	1983	366.3	25.0	2.4	339	1626	149.0	11.0	1466	1805	91	400	1466	1180	10.0	8.0	1162	79	43	3.0	82
HVA, Mary Lee, Jefferson County, Alabama (Chetopa Mine)																								
40	2000	0.0	14.8	1985	331.9	24.4	0.7	307	1401	137.8	6.2	1257	1564	79	500	1257	1174	5.3	4.8	1164	93	13.5	1.1	94
PSOC 274A, HVA, Sewell, Nicholas County, West Virginia (Quinwood No. 7)																								
41	2000	2.0	11.6	1986	347.0	29.3	1.6	316	1896	219.9	8.5	1668	1984	100	500	1668	1541	7.7	6.6	1527	92	19	1.1	93
PSOC 371, HVA, IMBODEN, LETCHER COUNTY, KENTUCKY (SCOTIA MINE)																								
42	2000	0.0	19.2	1981	398.9	27.3	2.5	369	1742	164.8	10.8	1566	1935	98	500	1566	1438	5.0	7.3	1426	91	30	1.9	94
PSOC 241, SB-B, Monarch & Dietz No. 3, Sheridan County, Wyoming (Big Horn)																								
45	2000	0.0	17.0	1983	361.3	20	2.6	339	1713	132.1	12.3	1569	1908	96	500	1569	1138	2.9	6.3	1129	72	40	2.5	75
Rosebud-McKay & Robinson, Big Horn County, Montana (Absaloka)																								
46	2000	0.0	15.0	1985	341.2	21.7	2.0	318	1815	156.5	10.7	1648	1966	99	500	1648	1222	3.8	6.1	1212	74	45	2.7	77
No. 2, Lehigh Bed, Stark County, North Dakota																								
47	2000	0.0	47.8	1952	274.8	14.4	4.6	256	1713	125.7	28.8	1559	1815	93	500	1559	1103	3.2	16.3	1084	70	27	1.7	72
West Kentucky No. 11 (Washed), Obtained from TVA																								
50	2000	0.0	16.4	1934	394.5	17.4	10.3	367	1741	103.6	45.3	1592	1959	101	500	1592	1261	2.9	22.4	1236	78	78	4.9	84
Western Kentucky No. 9, Bed, Union County, Kentucky (Hamilton Mine No. 1)																								
51	2000	5.8	73.8	1920	67	3.1	1.9	62	1952	89	55.6	1807	1869	97	500	1807	1485	5.0	31.2	1449	80	60	3.3	83
Lower Kittanning Bed, Armstrong County, Pennsylvania (C.H. Snyder Mine)																								
52	2000	5.4	102.4	1892	60	3.6	1.4	55	1973	117.6	47.5	1808	1863	98	500	1808	1527	7.8	33.9	1485	82	62	3.4	85
Pittsburgh Bed, Harrison County, Ohio (Franklin Mine)																								
53	2000	4.0	44.2	1952	71	5.5	0.98	65	2108	163.1	29.1	1916	1981	101	500	1916	1590	5.4	16.9	1568	82	55	2.9	85
Illinois No. 6 Bed, St. Clair County, Illinois (River King Mine, Washed)																								
55	2000	2.4	69.8	1928	57	2.7	1.7	53	2018	93.8	62	1862	1915	99	500	1862	1430	3.9	31.2	1395	75	93	5.0	80
Lucas Co. No. 5 Bed, Monroe County, Iowa (Lovilia No. 4 Mine)																								
56	2000	1.8	42.6	1956	58	0.8	1.3	56	1907	26.1	41.8	1839	1897	97	500	1839	1285	4.1	23.0	1258	68	231	12.6	81

(1) Dry weight

(2) Includes dry weight of all samples collected during an experimental run.

(3) Reference Table 4.

rpm (Table 7). Three runs were with a hydrogen gas at temperatures of 500, 600 and 700°C in the bench-scale batch dechlorinator. (A large number of runs were made in the laboratory with hydrogen treatment at temperatures up to 700°C with accompanying material balances that are listed separately in Table 5 and are included with the laboratory scale advanced dechlorination/desulfurization discusssion of experimental data).

The tabulated dechlorination data include the dechlorination temperature as well as the coal feed to the dechlorinator, and weight of dechlorinated coal. Corrections are made for chlorine and sulfur on both the input and output coals from the dechlorinator. Oil and tar values collected in the trap for the off-gases is indicated.

Coal PSOC 276

Five dechlorinations were made. Three dechlorinations with nitrogen showed 91% coal product recovery at 400°C and 78-81% at 500°C. Oil and tar amounted to 1.8-4.6% of the coal which increased coal accounting to 93% at 400°C and 83-85% at 500°C.

Two runs with hydrogen in place of nitrogen, one at 600°C and one at 700°C showed a 91% coal product at 600°C and only 58% at 700°C. Oil and tar accounted for an additional 2.4-3.5% of the coal providing a total accounting of 93% at 600°C and 62% at 700°C. An apparent explanation is that the 600°C treatment with hydrogen was subsequent to a dechlorination at 500°C, thus minimizing the loss of volatiles. The 62% recovery is low relative to laboratory results at 700°C with hydrogen treatment.

Coal PSOC 282

A total of eight dechlorinations were carried out with five at 400°C and three at 500°C. Coal product recovery at 400°C was 83-91% with an additional 0.4 to 6.3% as oil and tar for an accounting of 83-92%. Coal product recovery at 500°C was 77-82% with an additional oil and tar recovery of 2.2-6.5% for an overall coal accounting of 81-84%.

Coals PSOC 230, 090, 074, 126 (washed and unwashed)

All five coals were dechlorinated at 400°C for 60 minutes after chlorination. Coal product recoveries were 76-99% with oil and tar recovery representing an additional 0.1-6.8%.

Twelve Additional Coals

Twelve other bituminous, sub-bituminous and lignite coals are listed, (Table 7) that were dechlorinated at 500°C. Coal product recoveries were:

Coals	% Product	% Oil and Tar	% Accounting
3	91-93	1.1-1.9	93-94
3	80-82	2.9-3.4	83-85
4	72-78	2.5-5.0	75-84
2	68-70	1.7-12.6	72-81

ANALYSES OF TVA TEST COAL

Analyses of the raw and chlorinolysis processed TVA coal were made by both TVA and the CSMRI, Table 8. The analyses included sulfur forms, proximate, ultimate, ash elemental and ash fusion temperatures - reducing and oxidizing. Some small differences are noted between the TVA and CSMRI analyses.

Chlorinolysis process conditions for the TVA coal (Kentucky No. 11) are included in Table 4. Total sulfur was reduced by 45-46% with organic sulfur reduction of 11-15% and pyritic sulfur reduction of 96-100%.

Heating value was increased from 12,945 Btu/lb to 13,364 Btu/lb, primarily as a result of the reduced oxygen content from 8.8 to 4.9 wt.%. Ash values remained unchanged at 8.3-8.4 wt.%. Volatile matter was decreased from 39 to 14.7 wt.%. Chlorine in the processed coal was zero (Table 8).

Ash fusion temperatures in both the reducing and oxidizing mode were noted to increase in all cases (Table 8).

Table 8. Analyses of TVA Test Coal[c]

TYPES OF ANALYSES[e]	RAW COAL TVA[b] ANALYSES	FEED COAL (WASHED)		PROCESSED COAL[d]	
		CSMRI[a] ANALYSES	TVA ANALYSES	CSMRI ANALYSES	TVA ANALYSES
SULFUR FORMS (WT.%)					
Total	3.82	3.32	3.53	1.78(46)[f]	1.96(45)[f](49)[g]
Organic	1.21	1.98	2.25	1.78(11)[f]	1.91(15)[f]
Pyritic	2.56	1.34	1.09	<0.05(100)[f]	0.04(96)[f]
Sulfate	0.04	<0.05	0.19	<0.05(100)[f]	0.01(95)[f]
PROXIMATE ANALYSIS (WT.%)					
Moisture	-	4.95	5.6	-	0.2
Volatile Matter	25.2	38.5	39.2	-	14.7
Ash	48.8	8.5	8.4	-	8.3
Fixed Carbon	26.0	53.0	52.4	-	77.0
HEATING VALUE, BTU/LB					
Dry	6,769	12,957	12,945	-	13,364
Ash & Moisture Free	-	-	14,635	-	14,576
ULTIMATE ANALYSIS (WT.%)					
Carbon	-	72.8	72.9	-	79.6
Hydrogen	-	5.2	4.9	-	3.5
Nitrogen	-	1.4	1.5	-	1.7
Total Sulfur	3.8	3.3	3.5	1.78	2.0
Chlorine	-	<0.05	-	-	-
Oxygen (by difference	-	8.7	8.8	-	4.9
Ash	-	8.5	8.4	-	8.3
ASH ELEMENTAL ANALYSIS (WT.% OF ASH)					
SiO_2	-	-	49.5	-	57.3
$Al2O_3$	-	-	20.7	-	23.1
$Fe2O_3$	-	-	21.8	-	13.8
CaO	-	-	2.0	-	0.7
MgO	-	-	1.0	-	1.0
SO_3	-	-	1.1	-	0.4
Na_2O	-	-	0.7	-	0.4
K_2O	-	-	2.4	-	2.5
TiO_2	-	-	0.3	-	0.3
ASH FUSION TEMP (°F)					
Reducing					
Initial deformation	-	-	1,940	-	2,130
Softening	-	-	2,050	-	2,410
Fluid	-	-	2,260	-	2,560
Oxidizing					
Initial deformation	-	-	2,320	-	2,440
Softening	-	-	2,470	-	2,640
Fluid	-	-	2,530	-	2,680

. Colorado School of Mines Research Institute
. Tennessee Valley Authority
. West Kentucky No. 11, Washed
. Coal has been chlorinated, dechlorinated, and then hydrodesulfurized at 500°C
. Dry basis
. % sulfur removal
. % sulfur removal is based on 3.8 wt.% sulfur in unwashed coal.

PART III - CONTINUOUS FLOW MINI-PILOT PLANT

EQUIPMENT

The mini-pilot plant for coal desulfurization by low temperature chlorination is designed to feed pulverized coal (14-300 mesh) at a nominal rate of 2 kg/hr. Nominal solvent flow rates are 4 kg per hour. With methylchloroform there is an attendant water flow rate of 1.4 kg per hour. The plant is designed to operate at a pressure and temperature ranging from 0 to 100 psig and 50 to 150°C. The equipment flow schematic and layout for the mini-pilot plant are shown in Figures 13, 14. Nominal design variations in flow rates with corresponding changes of retention time are in the range of -50 to +100% variation. Special provisions for increased coal and solvent feed rates allowed up to a 450% increase in feed rate with a proportionate reduction in retention time. Stainless steel surfaces in the chlorinator are protected by Teflon coating to overcome corrosion problems.

The coal desulfurization mini-pilot plant is comprised of nine major units and several auxiliary systems to support them (Table 9, Figures 15-23). The instrumentation for the mini-pilot plant is included, Table 10. The nine remaining major units, listed consecutively from start to completion of the desulfurizing process, are as follows:

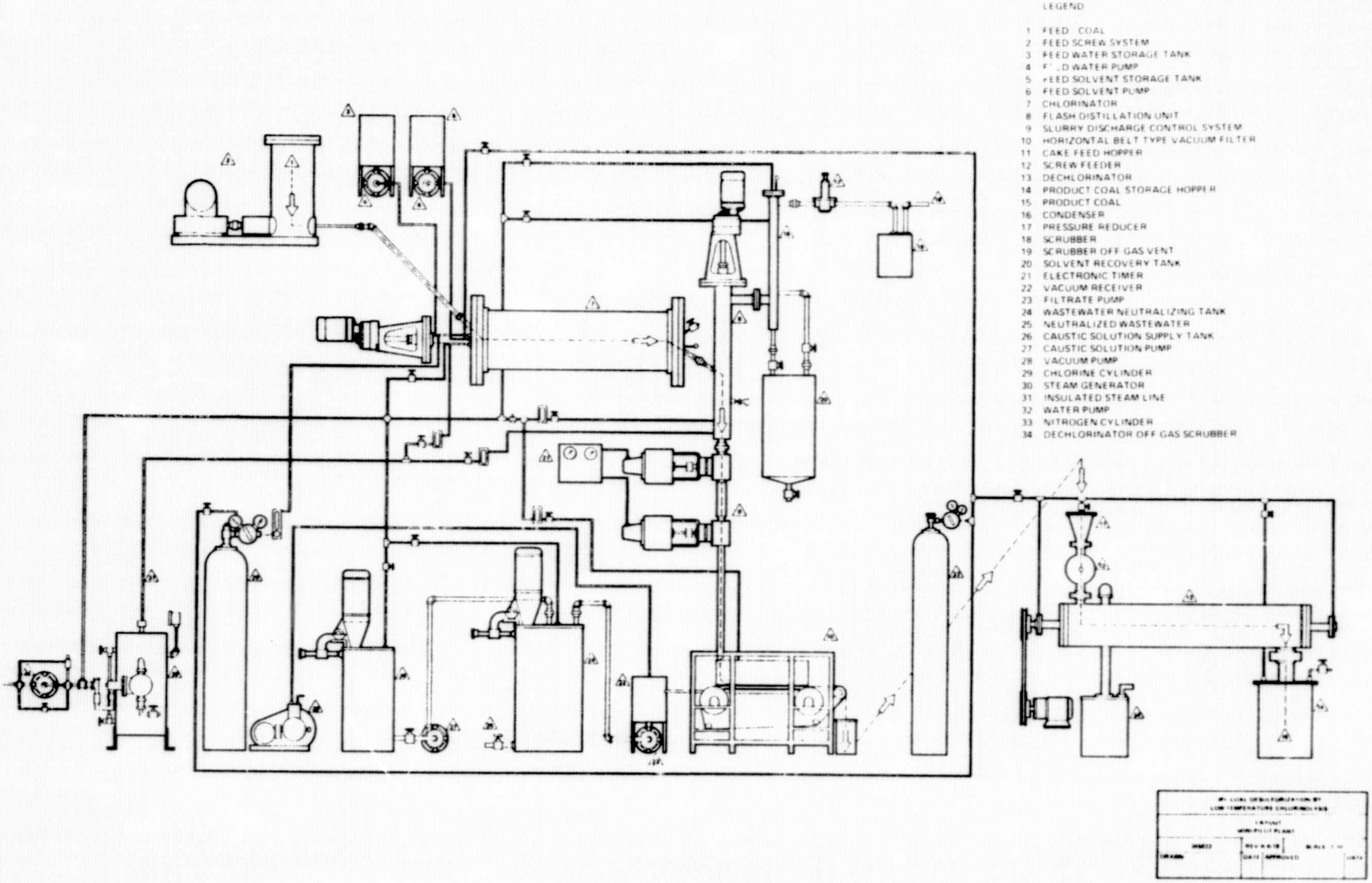
1. Dry coal pressure screw feeder.
2. Solvent and water metering pumps.
3. Chlorinator, Figures 15, 16.
4. Flash distillation unit, Figure 17.
5. Condenser, Figure 18.
6. Solvent recovery tank, Figure 19.
7. Horizontal belt vacuum filter and spray wash, Figure 20.
8. Dechlorinator, Figures 21, 22.
9. Product coal storage hopper, Figure 23.

DRY COAL PRESSURE SCREW FEEDER

This unit is designed to feed dry pulverized coal to the chlorinator at pressures up to 100 psig. It consists of a pressure vessel coated with 35 mils teflon, an agitator to break bridging of coal particles, and a 1/2 hp motor to drive the coal feed screw. The pressure vessel has the capacity to hold 23 kg of coal for 10 hours of operation at a nominal design flow rate of 2 kg/hr of coal. The coal is fed to the chlorinator via a 3/4-inch OD square wire type feed screw or a 13/16-inch OD wood screw installed at a feed angle of 45° with respect to the horizontal plane. Coal feed rate can be varied from 1 to 10 kg/hr.

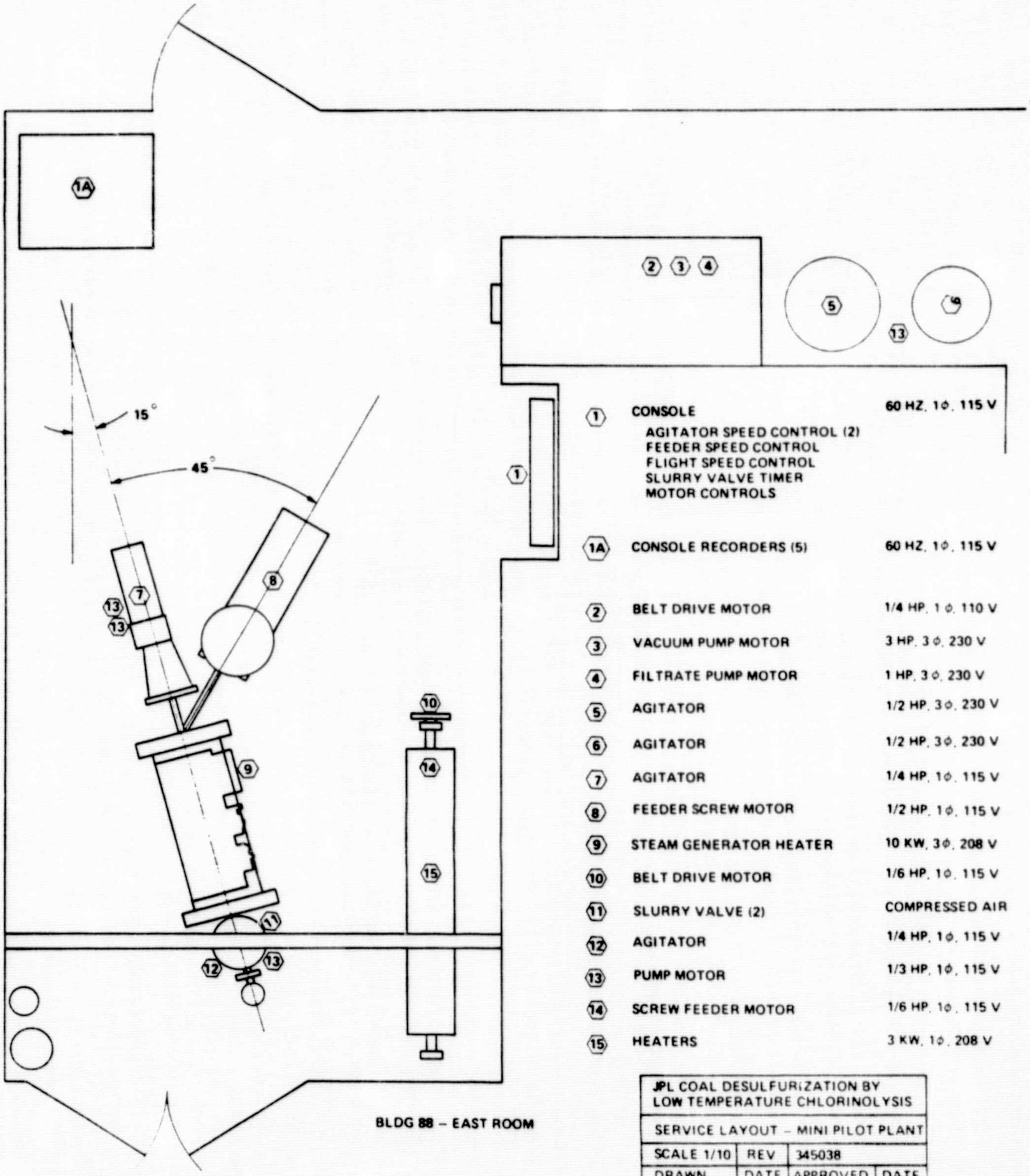
SOLVENT AND WATER METERING PUMPS

Neptune chemical metering pumps are used to feed solvent and water to the chlorinator. Minimum pumping capacities are 1 gph for water and 2.3 gph for solvent at discharge pressures up to 100 psig.



	LEGEND
1	FEED COAL
2	FEED SCREW SYSTEM
3	FEED WATER STORAGE TANK
4	FEED WATER PUMP
5	FEED SOLVENT STORAGE TANK
6	FEED SOLVENT PUMP
7	CHLORINATOR
8	FLASH DISTILLATION UNIT
9	SLURRY DISCHARGE CONTROL SYSTEM
10	HORIZONTAL BELT TYPE VACUUM FILTER
11	CAKE FEED HOPPER
12	SCREW FEEDER
13	DECHLORINATOR
14	PRODUCT COAL STORAGE HOPPER
15	PRODUCT COAL
16	CONDENSER
17	PRESSURE REDUCER
18	SCRUBBER
19	SCRUBBER OFF GAS VENT
20	SOLVENT RECOVERY TANK
21	ELECTRONIC TIMER
22	VACUUM RECEIVER
23	FILTRATE PUMP
24	WASTEWATER NEUTRALIZING TANK
25	NEUTRALIZED WASTEWATER
26	CAUSTIC SOLUTION SUPPLY TANK
27	CAUSTIC SOLUTION PUMP
28	VACUUM PUMP
29	CHLORINE CYLINDER
30	STEAM GENERATOR
31	INSULATED STEAM LINE
32	WATER PUMP
33	NITROGEN CYLINDER
34	DECHLORINATOR OFF GAS SCRUBBER

Figure 13. Equipment Flow Schematic - Mini-Pilot Plant



①	**CONSOLE** AGITATOR SPEED CONTROL (2) FEEDER SPEED CONTROL FLIGHT SPEED CONTROL SLURRY VALVE TIMER MOTOR CONTROLS	60 HZ, 1ϕ, 115 V
1A	CONSOLE RECORDERS (5)	60 HZ, 1ϕ, 115 V
②	BELT DRIVE MOTOR	1/4 HP, 1 ϕ, 110 V
③	VACUUM PUMP MOTOR	3 HP, 3 ϕ, 230 V
④	FILTRATE PUMP MOTOR	1 HP, 3 ϕ, 230 V
⑤	AGITATOR	1/2 HP, 3 ϕ, 230 V
⑥	AGITATOR	1/2 HP, 3 ϕ, 230 V
⑦	AGITATOR	1/4 HP, 1ϕ, 115 V
⑧	FEEDER SCREW MOTOR	1/2 HP, 1ϕ, 115 V
⑨	STEAM GENERATOR HEATER	10 KW, 3ϕ, 208 V
⑩	BELT DRIVE MOTOR	1/6 HP, 1ϕ, 115 V
⑪	SLURRY VALVE (2)	COMPRESSED AIR
⑫	AGITATOR	1/4 HP, 1ϕ, 115 V
⑬	PUMP MOTOR	1/3 HP, 1ϕ, 115 V
⑭	SCREW FEEDER MOTOR	1/6 HP, 1ϕ, 115 V
⑮	HEATERS	3 KW, 1ϕ, 208 V

JPL COAL DESULFURIZATION BY LOW TEMPERATURE CHLORINOLYSIS			
SERVICE LAYOUT – MINI PILOT PLANT			
SCALE 1/10	REV	345038	
DRAWN	DATE 5/16/79	APPROVED	DATE 5/16/79

Figure 14. Equipment Layout - Mini-Pilot Plant

Table 9. Major Units - Coal Desulfurization by Low Temperature Chlorinolysis Mini-Pilot Plant
Nominal Design Basis: 2 kg/hr of coal, 1.0 kg/hr of Water, and 4 kg/hr of Solvent in Continuous Feed.

System/Treatment	Manufacturer/ Fabricator	Specifications
Pressure Screw Feeder for Chlorinator	Priority Systems, Inc. Covina, California	1/2 HP motor to feed 2 kg/hr of dry coal against 100 psig pressure. Feed rate adjustable from 1 to 10 kg/hr. Coal particle size 40 to 300 mesh.
Metering Pumps for Solvent and Water Feed	Vossler & Co. N. Hollywood, CA	1/3 HP motor, minimun capacity 1 GPH for water and 2.3 GPH for solvent, discharge pressure 100 psig.
Chlorinator-Provide chlorination of agitated ground coal solvent slurry. Figure Nos. 15, 16	Stebbins Engineering and Manufacturing Co., Watertown, N.Y.	Carbon steel pipeline reactor lined with fiberglass membrane, and one layer of semacid brick laid with Stebbins' AR-20-C carbon filled furan mortar and another layer of visil brick laid with Pennwalt K-14 Silicate mortar. Cavity dimensions are: 3-1/4-inch ID by 48-inch long. Separable reactor head ported for raw and chlorinated coal slurry, agitator shaft, teflon bushing, steam, chlorine, thermocouple, pressure transmitter, pressure gauge, pressure relief, rupture disc, and cooling water. Maximum operating pressure: 100 psig.
Agitator for Chlorinator	Chemineer Agitator Dayton, Ohio	Chemineer Model No. VLA-2. 1/4 HP at 565 rpm maximum, SCR variable speed, 1 inch shaft diameter, 60 inches long supported at far end by teflon bushing, nine 2 in. x 3/8 in. radial impellers, 6 ring teflor stuffing box, 6 inch 150 pound ASA flange, all parts in contact with the slurry are Hastelooy C-276

Table 9. (Cont'd)

System/Treatment	Manufacturer/ Fabricator	Specifications
Flash Distillation Figure No. 17	JPL, Pasadena,	Stainless steel 316 vessel equipped with Chemineer agitator model No. VLA-2, volume liquid space 0.096 ft^3, gas space: 0.056 ft^3, maximum operating pressure, 100 psig. Maximum operating temperature, 100°C.
Agitator for Flash Distillation Unit	Chemineer Agitator, Dayton, Ohio	Chemineer Model No. VLA-2. Top entering agitator, 1/4 HP at 565 rpm maximum, SCR variable speed drive, 3/4 inch shaft diameter, 35 inches long, 2 inch propeller, 6 ring teflon stuffing box, 6 inch 150 pound ASA flange, all parts in contact with the slurry are Hastelloy C-276.
Slurry Valve	CS Company Torrance, CA	Air operated Red Slurry Valve. They completely open and close by the action of air on an acid resistant rubber sleeve (Nordel rubber) installed within a valve housing. Valve size: 1" ID, 7-1/4" length, 5-1/4" width.
Condenser-Condense and recover solvent. Figure No. 18	JPL, Pasadena, California	Stainless steel 316 condenser cooling surface area: 0.59 ft^2. Maximum operating pressure: 100 psig.
Solvent Recovery Tank. Figure No. 19	JPL, Pasadena, California.	Stainless steel 316 pressure vessel. Capacity 1.8 cubic ft.
Vacuum Filter	Straight Line Filters, Inc. Wilmington, Delaware	Top feed horizontal belt vacuum filter. DC variable speed belt drive, 0.08 to 0.008 feet per minute. Filtration area 0.5 ft^2. Equipped to provide spray water wash of cake.

Table 9. (Cont'd)

System/Treatment	Manufacturer/ Fabricator	Specifications
Dechlorinator Remove chlorine form coal. Figure Nos. 21, 22	JPL Pasadena, California	Cylindrical reactor, 5 in. schedule 80 pipe, length 38 in. Equipped with rotary flights, 1-5 rpm. Externally heated with 3 heaters 1 KW each. Operating temperature, 700-900°F. Cylinder material, stainless steel 316. Feed rate, 2 kg/hr dry coal.
Product Coal Storage Hopper Figure No. 23	JPL Pasadena, California	1.26 ft^3 (50 kg) cylindrical hopper equipped with nitrogen purge.
Volumetric Twin Screw Feeder for Dechlorinator	Priority Systems, Inc.	1/6 HP motor to provide coal feed rate from 1 to 10 kg/hr.
Agitator for Caustic Tank and Wastewater Neutralizing Tank	Chemineer Agitator, Dayton, Ohio	Chemineer Model No. PD-2. Top entering portable clamp type agitator, 1/2 HP at 430 rpm maximum, SCR variable speed drive, 3/4 inch shaft diameter, three blades axial propeller, shaft and impeller are 316 stainless steel.
Steam Generator	Steam Sales & Service Co., Long Beach, California	Steam flow rate, 20 lbs/hr, at 100 psig. Automatic feed, pressure range 0 to 100 psig.

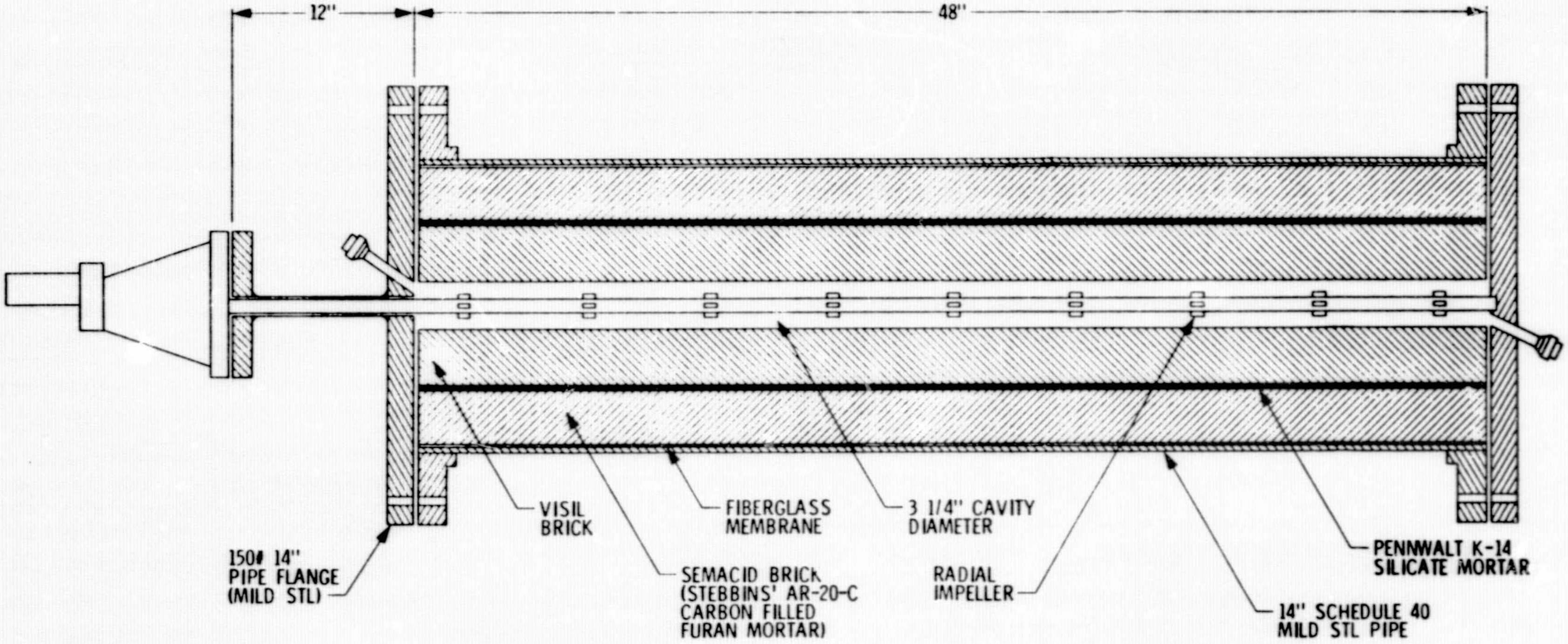


Figure 15. Chlorinator - Mini-Pilot Plant

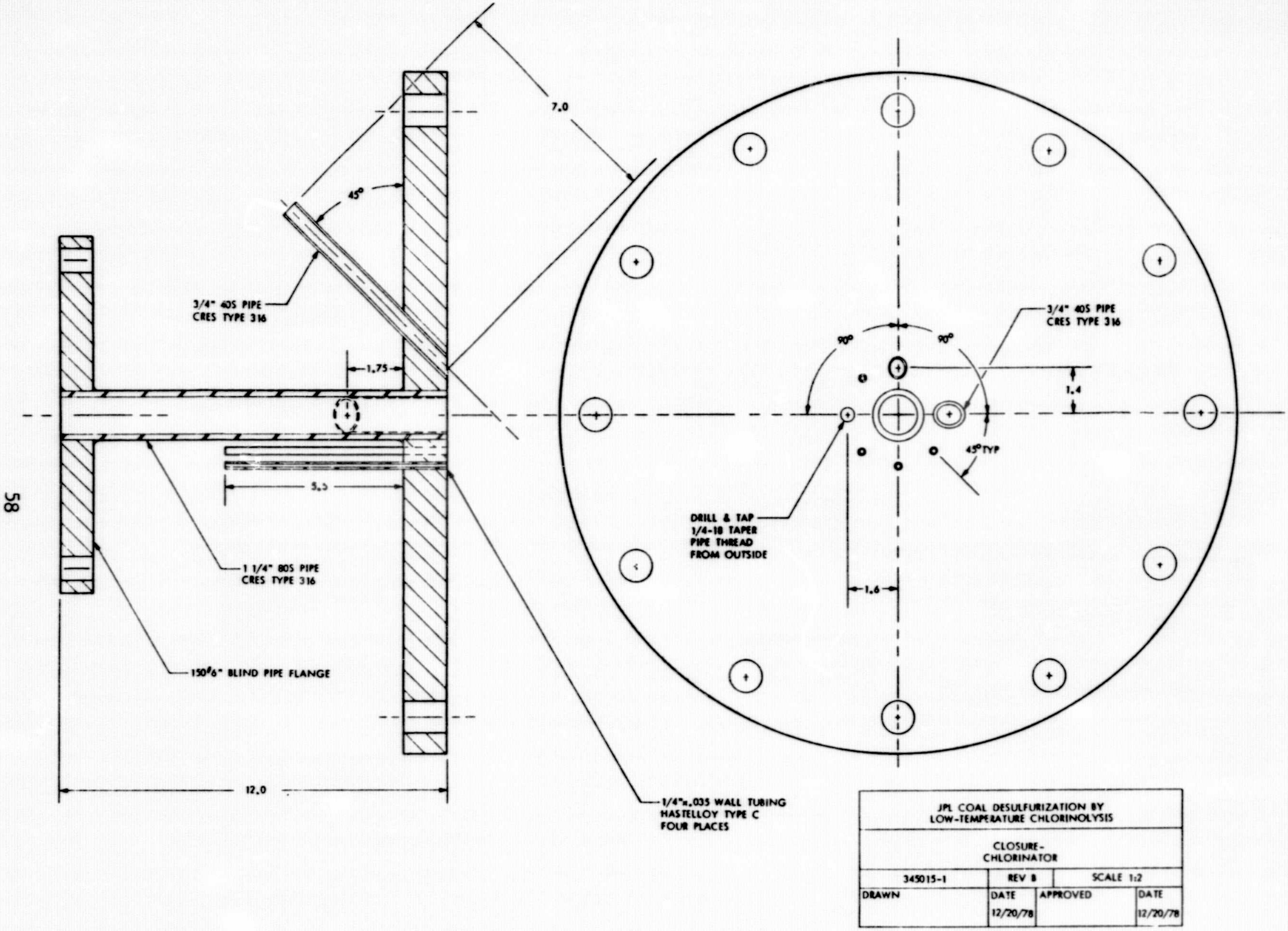


Figure 16. Closure-Chlorinator - Mini-Pilot Plant

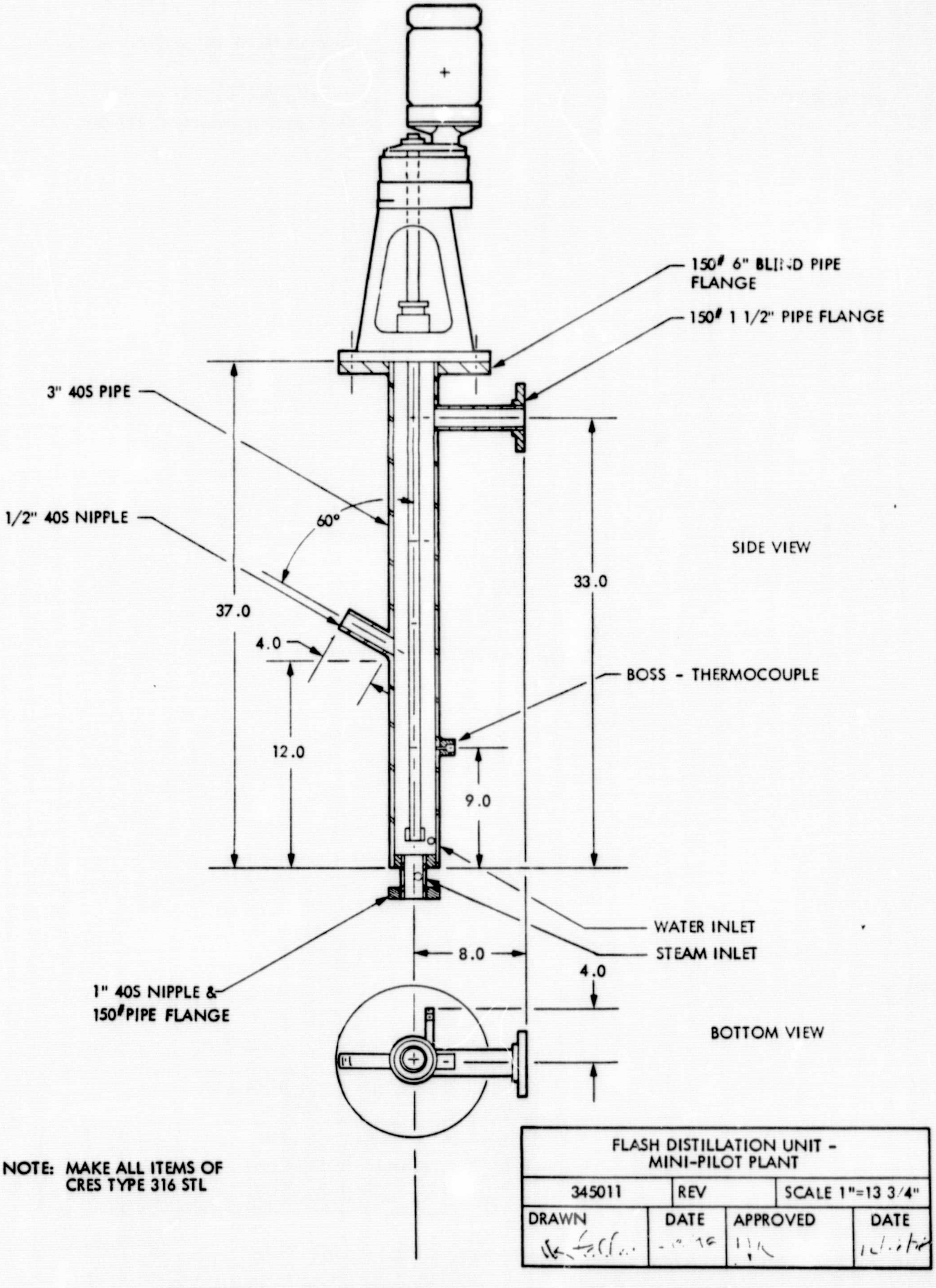


Figure 17. Flash Distillation Unit - Mini-Pilot Plant

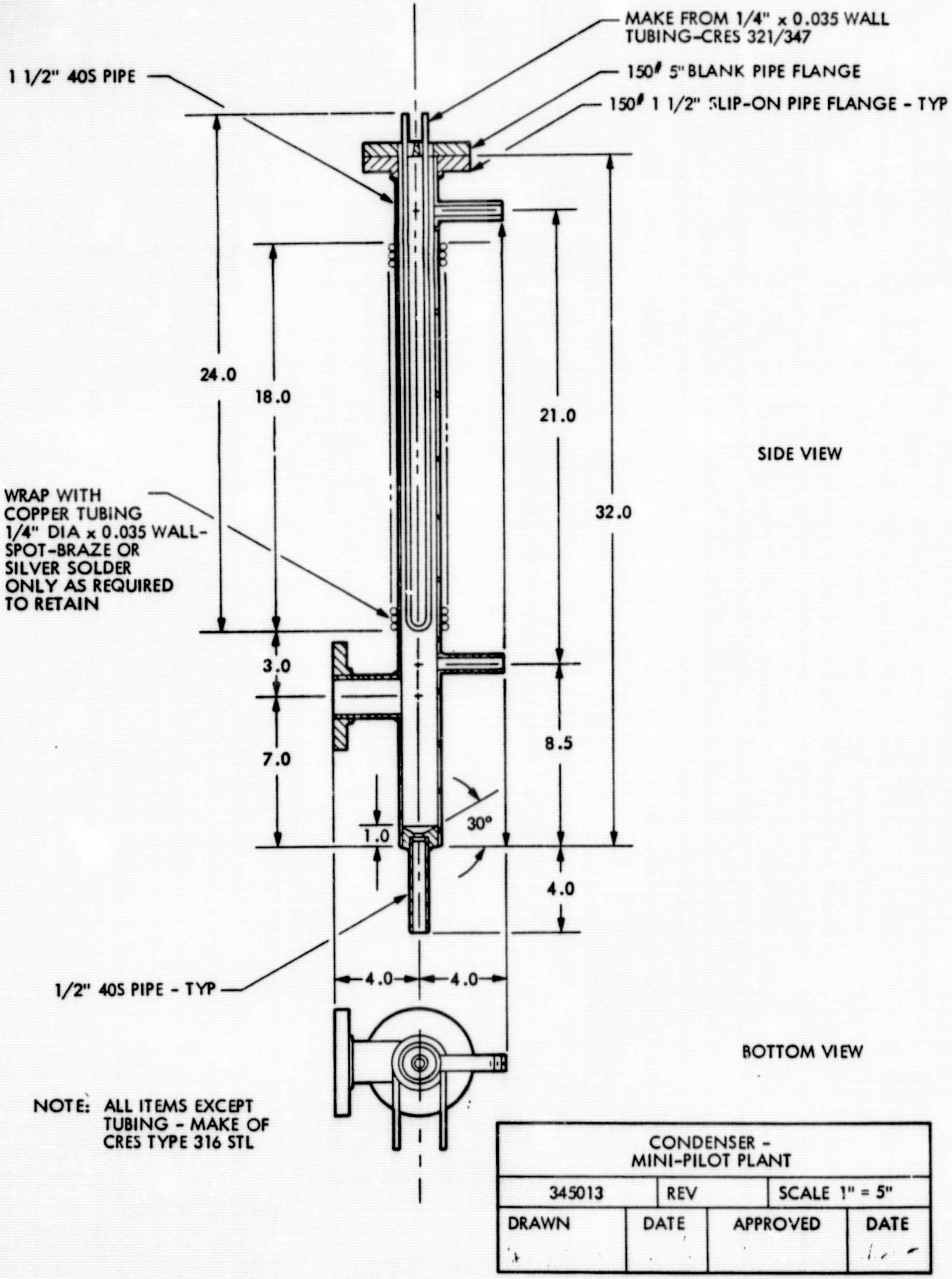
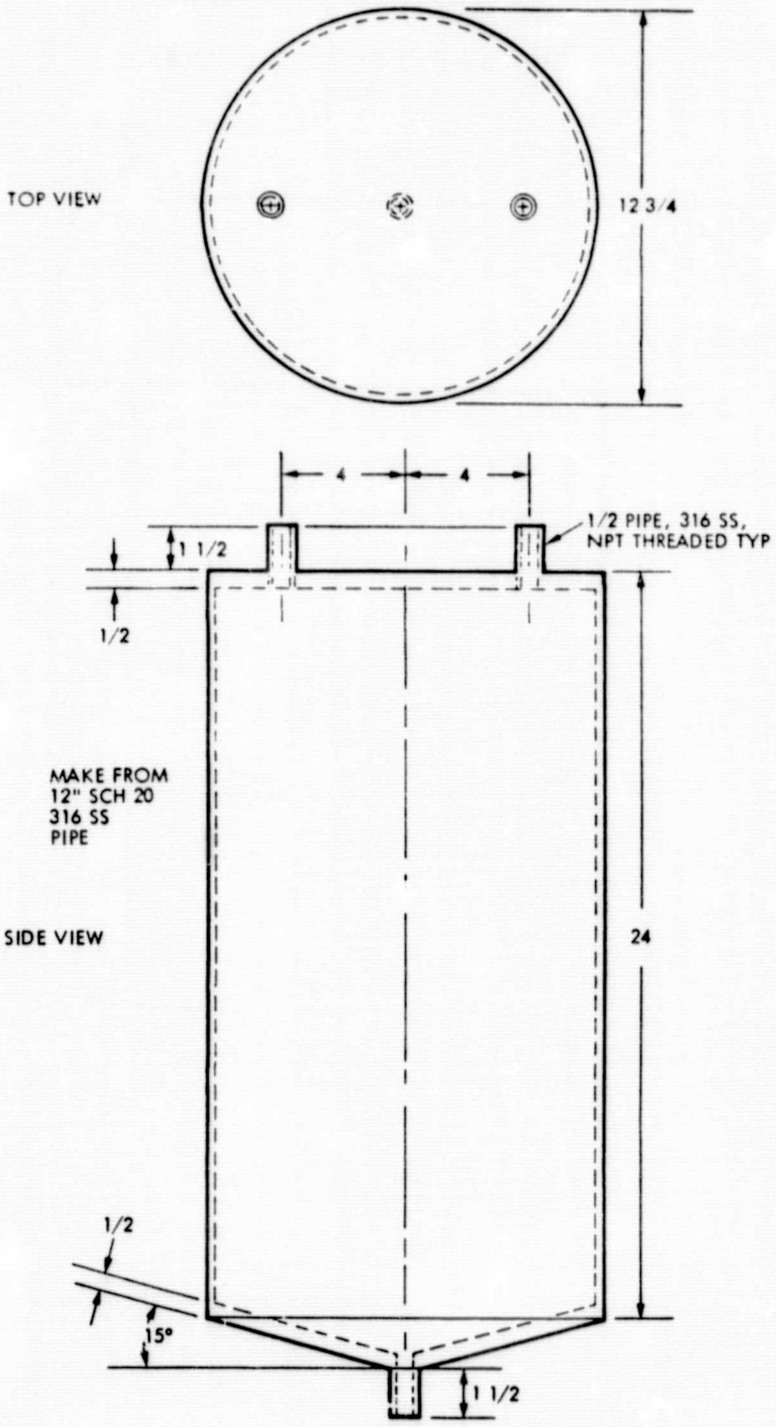


Figure 18. Condenser - Mini-Pilot Plant



NOTE: WELDED CONSTRUCTION

DIMENSIONS IN INCHES

SOLVENT RECOVERY TANK- MINI-PILOT PLANT			
345020	REV	SCALE: 1:4	
DRAWN	DATE 12/21/78	APPROVED	DATE 12/27/78

Figure 19. Solvent Recovery Tank - Mini-Pilot Plant

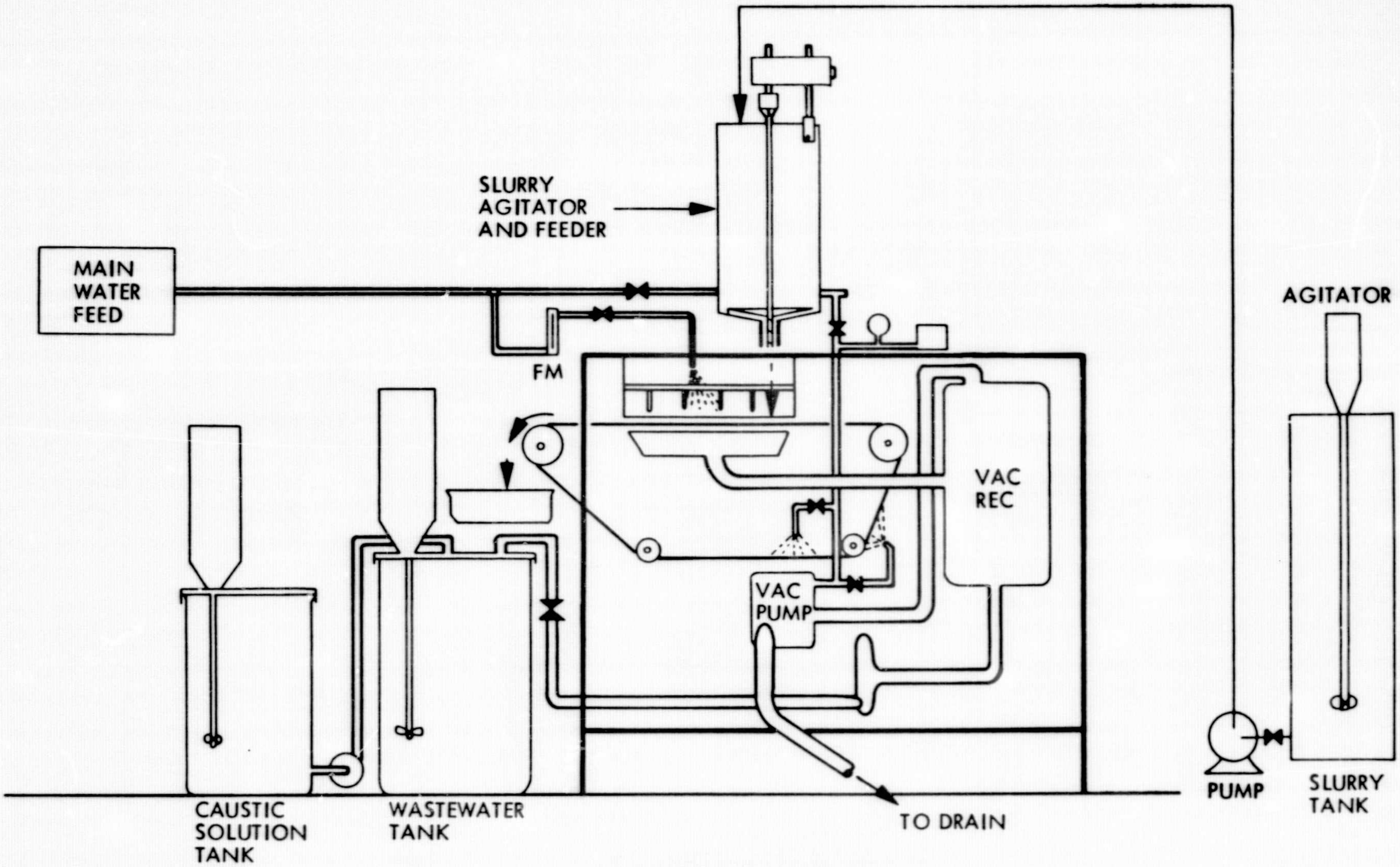
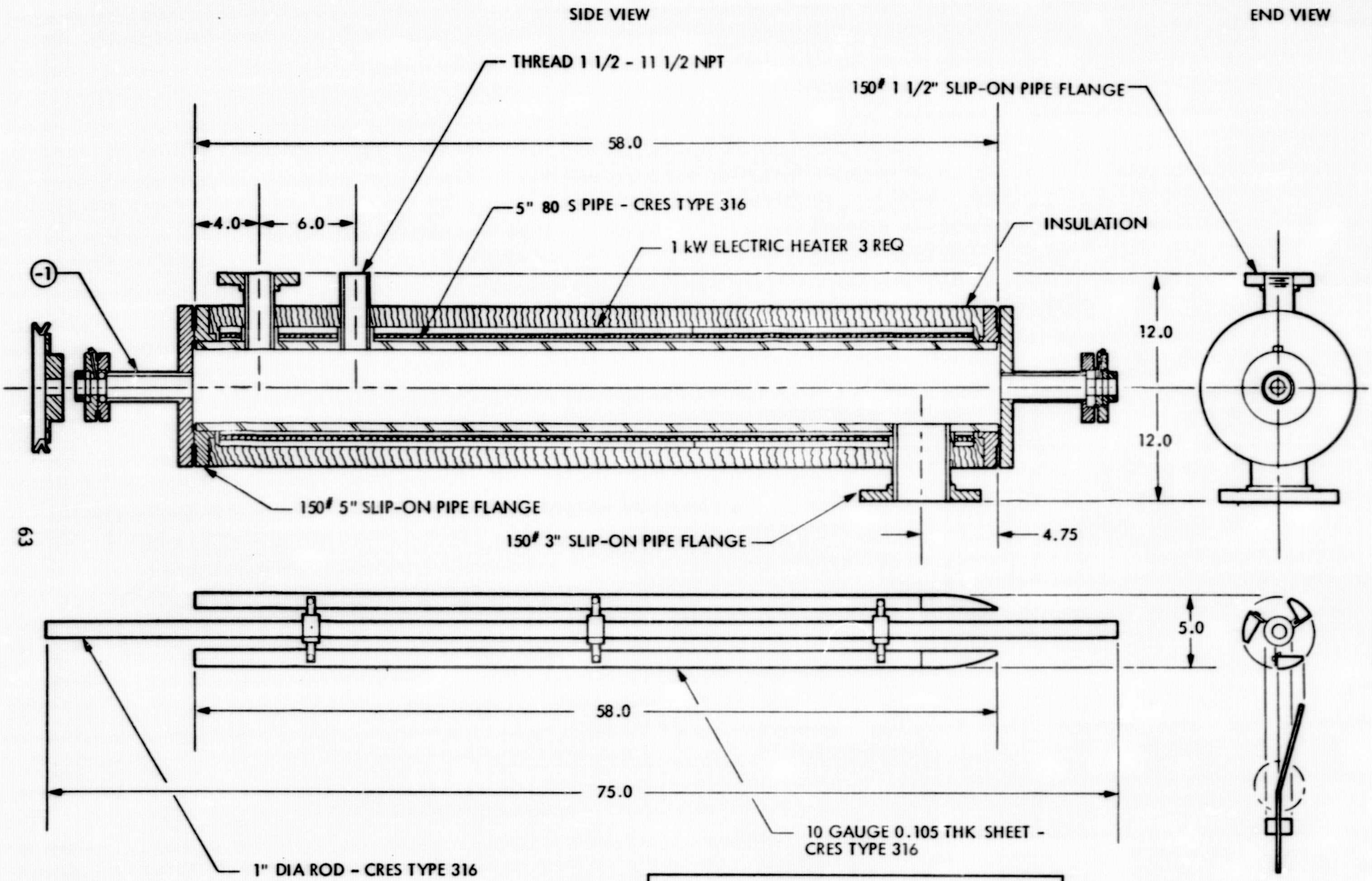


Figure 20. Horizontal Belt Vacuum Filter and Spray Wash - Mini-Pilot **Plant**



DECHLORINATOR - MINI-PILOT PLANT			
345010	REV	SCALE 1" =3 29/32"	
DRAWN	DATE	APPROVED	DATE
[illegible]	[illegible]	[illegible]	[illegible]

Figure 21. Dechlorinator - Mini-Pilot Plant

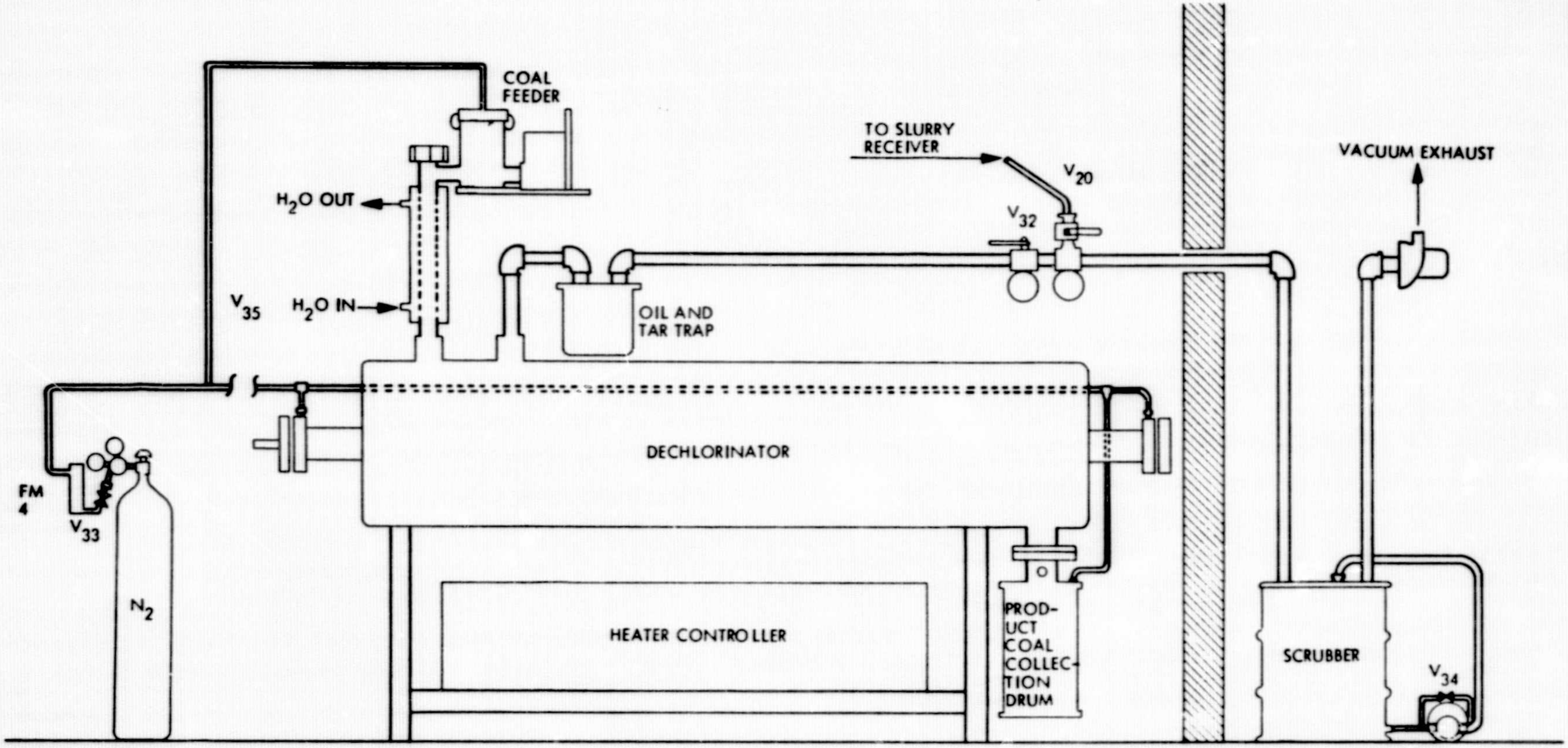
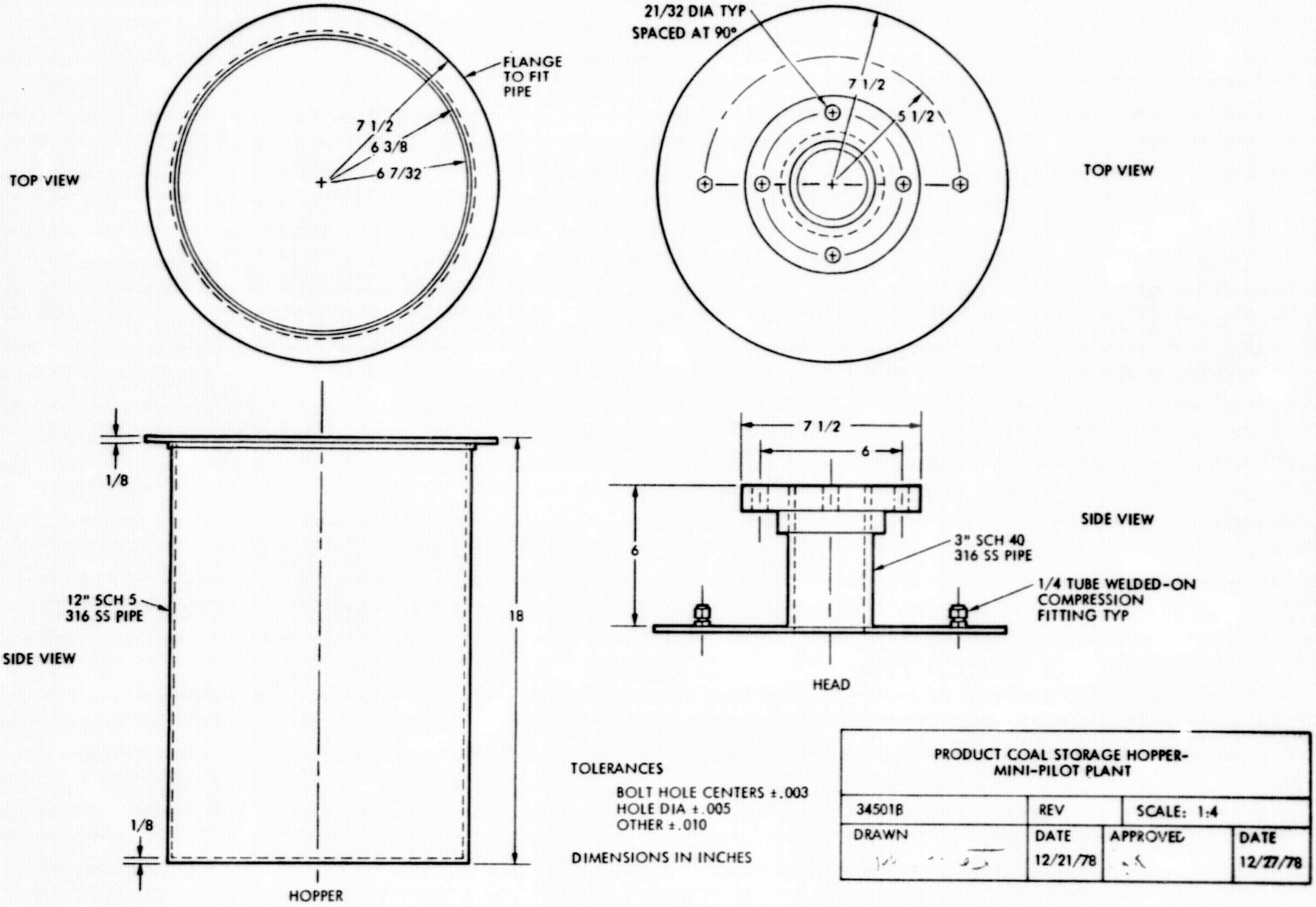


Figure 22. Dechlorinator Equipment System - Mini-Pilot Plant



TOLERANCES

BOLT HOLE CENTERS ±.003
HOLE DIA ±.005
OTHER ±.010

DIMENSIONS IN INCHES

PRODUCT COAL STORAGE HOPPER- MINI-PILOT PLANT			
34501B	REV	SCALE: 1:4	
DRAWN	DATE 12/21/78	APPROVED	DATE 12/27/78

Figure 23. Product Coal Storage Hopper - Mini-Pilot Plant

Table 10. Instrumentation - Mini-Pilot Plant

System	Manufacturer/ Supplier	Specifications
Chlorinator		
Pressure Transmitter	Rosemont, Inc. Chatsworth, CA	Model No. 1144G, range 0 to 120 psig. The output is 4 to 20 milliamperes and will be recorded on a pen recorder. The pressure transmitter is excited by a 24 volt power supply. The process flange and diaphragm of the pressure transmitter are made of Hastelloy C-276.
Pressure Gauge	3-D Instruments Huntington Beach, CA	Series 2554. A dial pressure gauge with ± 0.25% accuracy. The gauge has a range of 0 to 150 psig, and is protected from the corrosive environment by 316 stainless steel isolator with Teflon diaphram.
Rupture Disc	Vossler & Co. Hollywood, CA	1-inch Zook carbon rupture disc for rupture pressure of 150 psig ±5%.
Thermocouple	California Alloy Co. El Monte, CA	Temperatures are monitored by means of iron-constant (Type J) thermocouples calibrated from 0 to 1200°F.
Chlorine Flowmeter Controller	Union Carbide Corp. Long Beach, CA	Lindberg Model FM4311-6. The chlorine flowmeter has a special calibration for gaseous chlorine under standard conditions. The calibrated range is from 0.2 to 29 standard liters per minute as Cl.
	Tylan Torrance, CA	Tylan Mass Flow Controller Model No. FC-261, calibrated range is from 0.2 to 10 standard liters per minute as Cl.
Steam Flowmeter	Decker Industrial Supply Co. Beverly Hills, CA	Wallace and Tiernan Model 5120 M1. Calibrated from 0 to 20 lb/hr., at 100 psig.
Flash Distillation Unit		
Thermocouple	California Alloy Co. El Monte, CA	Temperature are monitored by means of iron-constant (Type J) thermocouples calibrated from 0 to 1200°F.

Table 10. (Cont'd)

System	Manufacturer/ Supplier	Specifications
Flash Distillation Unit (Cont'd)		
Steam Flowmeter	Decker Industrial Supply Co. Beverly Hills, CA	Wallace and Tiernan Model 5120 M1. Calibrated from 0 to 120 lbs/hr, at 100 psig.
Level Sensor and Automatic Time	JPL, Pasadena California	Two carbon electrode to control minimum and maximum slurry level in the distillation unit.
Condenser		
Thermocouple	California Alloy Co. El Monte, CA	Temperatures are monitored by means of iron-constant (Type J) thermocouples calibrated from 0 to 1200°F.
Back Pressure Regulator	Fluid-Tech Sales Garden Grove, CA	Veriflow 40 series regulator to control pressure from 5 to 100 psig ±10%.
Dechlorinator		
Thermocouple	California Alloy Co. El Monte, CA	Temperatures are monitored by means of iron-constant (Type J) thermocouples calibrated from 0 to 1200°F.
Temperature Controller	Scientific Products Irvine, CA	Lindberg Model No. 5831, three zone, operating voltage 240, current rating 20 amps.

CHLORINATOR

The mini-pilot plant chlorinator is shown in Figure 15. The reactor was made from 14-inch, schedule 40, mild steel pipe lined with fiberglass membrane and two layers of different types of acid proof bricks. The first outside layer (close to inside surface of pipe) is semacid brick laid with 1/8-inch joints using Stebbins' AR-20-C carbon filled furan mortar. The second inside layer (exposed to corrosive environment) is Visil brick laid with 1/8-inch joints using Pennwalt K-14 silicate mortar. The bricks and mortars were selected on the basis of recommendations made by the Stebbins Engineering and Manufacturing Company. The reactor cavity dimensions are 3-1/4" I.D. by 48-inches long. The reactor is provided with two removable 150 pound, 14-inch blank pipe flanges for the feed and discharge ends of the reactor. The reactor head at the feed end is drilled to accomodate a centrally mounted agigator unit and port openings for instrumentation and process lines. The agitator is a Chemineer Model No. VLA-2 with a six rings teflon stuffing box, 1/4 hp electric motor drive controlled by a SCR variable drive unit for shaft speeds of 40 to 565 rpm. The agitator shaft is of Hastelloy C-276 construction, 1-inch diameter by 60-inch long and supported at the discharge end flange by a teflon bushing. It has nine 2-inch by 3/8-inch radial impellers to keep coal in suspension. An outer cover of graphoil tape was provided to protect both agitator shaft and impellers from the corrosive environment. The dry coal was fed to the reactor by a precalibrated pressure screw feeder. Water and solvent were fed to the reactor by precalibrated neptune chemical metering pumps. Gaseous chlorine injection was provided from a standard liquid chlorine storage cylinder equipped with a 150 watt electrical heater and monitored by a Tylan mass flow controller Model No. FC-261 with a range of 0.42 to 21 SCFH and a Linde Model FM 4311-6 flowmeter with a range of 0.42 to 61.5 SCFH. Chlorine dispersion into the coal slurry was provided by means of a 1/2-inch teflon tubing with 1/32-inch diameter holes. Temperature control of the reactor is provided by a cooling water coil and indirect steam heating (through cooling coil). The cooling water coil consists of a straight 1/4-inch 316 stainless steel tubing with one turn on a 3-inch diameter circle. An outer cover of graphoil tape was provided to protect the cooling coil tubing from the highly corrosive environment. Steam injection was provided for the reactor by a Steam Sales and Service Company steam generator, capacity of 20 pound steam per hour at 100 psig. A Wallace and Tiernan Model 5120 M1 flowmeter monitored steam injection. Pressure was continuously monitored by a Rosemont Inc. Model No. 1144G pressure transmitter and Leeds and Northrup Speedomax Mark III miniature two pen recorder. A dial pressure gauge (Series 2554, 3-D Instruments) provided direct reading, 0-150 psig with an accuracy of 0.25 percent. Temperatures were monitored by a iron-constantan (type J) thermocouple with a Leeds and Northrup Speedomax Multipoint Recorder Model No. 251. A Zook carbon rupture disc for rupture pressure of 150 psig ± 5% was installed and obtained from Zook Enterprises. Pressure was controlled at 5 to 100 psig ± 10% by a Veriflo 40 series back pressure regulator with 316 stainless steel body and teflon diaphram, seat, and gasket. The reactor head at the discharge end is drilled to provide a 1/2-inch vent line to release excess chlorine gas and 1/2-inch line to discharge coal slurry into the flash distillation unit. Coal slurry samples were collected by means of a 1/2-inch, graphoil tape covered 316 stainless steel tubing located at the longitudinal center of the reactor.

FLASH DISTILLATION UNIT

This unit, Figure 17, is a 316 stainless steel cylinder vessel, 3-inch ID by 37-inch long, with the inside surface covered with 35 mils of teflon. The unit is equipped with a side port feed, coal slurry discharge line at the bottom and a Chemineer agitator model No. VLA-2 for stirring the coal slurry to prevent settling of coal and solvent. The slurry is heated to 100°C with live steam to flash distill solvent from the coal-water slurry. Provisions are made for water addition if needed. The vessel has ports for installation of a thermocouple and two carbon electrodes to control with a timer minimum and maximum slurry levels in the distillation unit. Two Red Slurry Valves equipped with automatic timers are installed in series at the bottom of the flash distillation unit to provide controlled discharge of the coal slurry. For operation involving only water, the flash distillation unit is disconnected from the system and coal slurry is directly discharged to the Red Slurry Valves.

CONDENSER

This unit, Figure 18, is a 316 stainless steel vessel, 1-1/2-inch ID by 32-inch long, with a copper cooling coil wrapped around it. The solvent vapors are condensed in this unit and collected in a solvent recovery tank for reuse. For experiments involving only water, the condenser was also disconnected from the system.

SOLVENT RECOVERY TANK

This unit, Figure 19, is a 316 stainless steel pressure vessel designed to collect solvent from the condenser. This unit was also disconnected from the system during the water solvent runs.

HORIZONTAL BELT VACUUM FILTER AND SPRAY WASH

The coal slurry from the flash distillation unit is discharged into a coal slurry receiver and manually transported to the vacuum filter (Figure 20). The filter consists of a horizontal belt covered with polypropylene filter cloth. The center of the belt is under vacuum, which draws the coal slurry filtrate through the porous filter cloth as the belt moves. The filtration unit is equipped to provide a spray or weir overflow displacement wash. The vacuum dried coal filter cake is disengaged from the belt by a mother knife as the belt turns under across a pulley and falls into a receiver. The coal is manually transported to the dechlorinator feed hopper.

DECHLORINATOR

The dechlorinator, Figures 21 and 22, consists of a stationary cylinder fabricated from 316 stainless steel 5-inch schedule 80 pipe. Heating is accomplished by three electric heaters (1 kW each) wrapped around the dechlorinator cylinder. Two additional heaters (400 watts each) were installed to compensate for excessive heat loss near the discharge end of the dechlorinator. The rotary flights inside the dechlorinator cylinder provide continuous mixing as well as a forward feed of coal particles. Dry coal is fed into the dechlorinator by a twin screw feeder. At the discharge end of the dechlorinator, product coal drops into a storage hopper. Operating temperatures up to 500°C are possible. Maximum operating pressure is 4-inches water column.

PRODUCT COAL STORAGE HOPPER

This is a closed bin, Figure 23, provided with a nitrogen purge to prevent oxidation of the coal heated in the dechlorinator.

WASTEWATER AND CAUSTIC SOLUTION TANKS

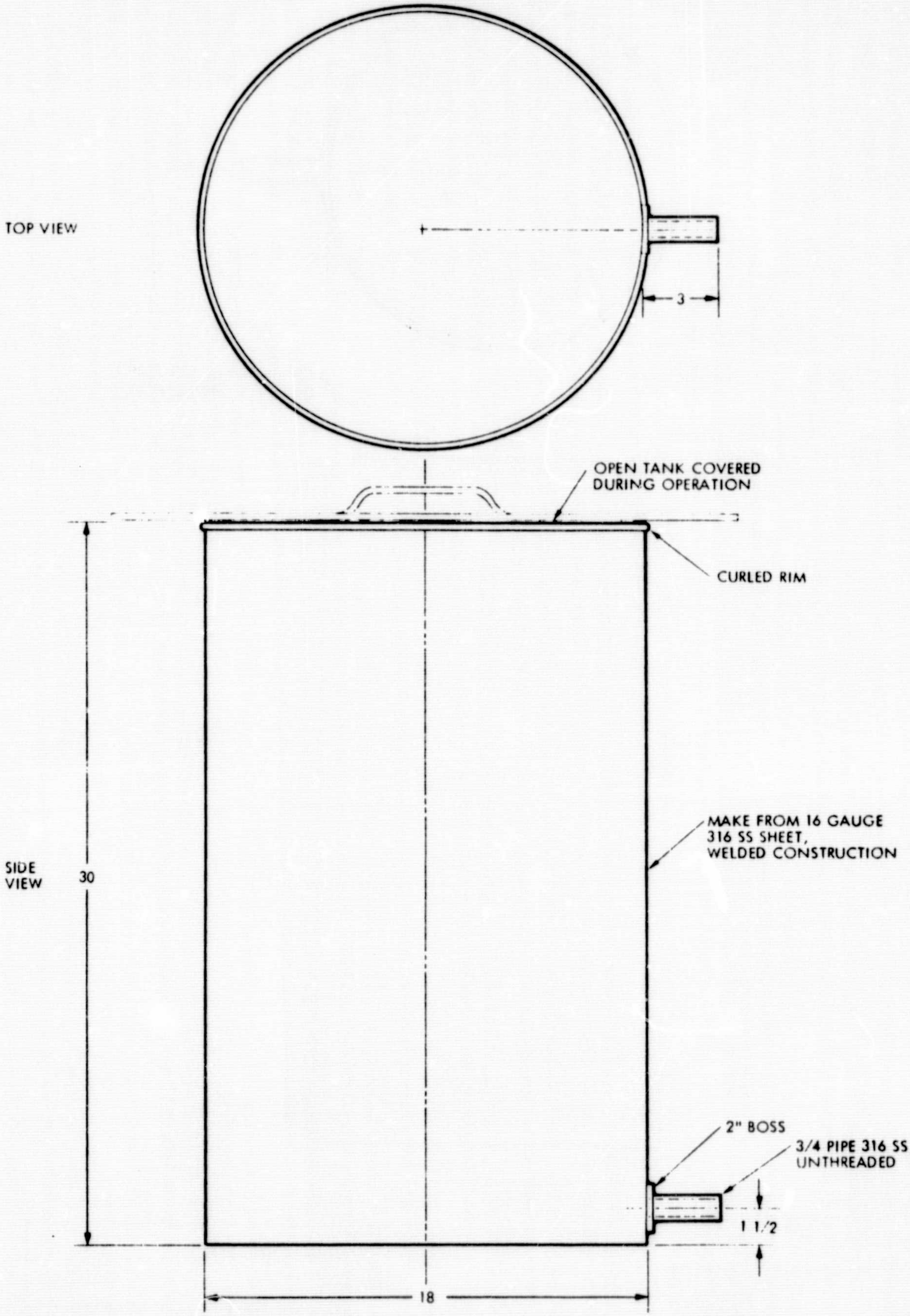
Wastewater and caustic solution tanks are included, Figures 24 and 25.

OPERATING PROCEDURE

Start-up of the mini-pilot plant requires bringing the equipment to operating temperature and introducing flow through the chlorinator and into the flash distillation unit to establish steady-state operating conditions. Phasing of feed material may be required to avoid problems of caking, etc. Schematic diagrams for the chlorinator with methylchloroform and water are shown in Figures 26 and 27, respectively. Mechanical operation of the equipment is described as follows:

The reactor, pressure screw feeder, distillation unit, and condenser were first leak tested under nitrogen pressure. The start-up procedure involves filling of the chlorinator with fresh water and then the dry pulverized coal (-200 mesh) is fed to the chlorinator via a pressure screw feeder designed to operate at 100 psig back-pressure. Water and solvent are transported from holding tanks to the chlorinator via metering pumps at a prescribed flow rate and pressures up to 100 psig. The coal slurry is continuously agitated in the chlorinator with a variable speed Chemineer agitator equipped with nine radial impellers to provide coal suspension and plug flow. Chlorine flow was then initiated to the reactor (teflon diffuser with 1/32-inch holes) and adjusted to the prescribed flowrate. The chlorinated coal slurry samples were taken from the middle and discharge end of the reactor after steady-state was reached. The time required to reach steady-state was defined as the residence time plus 30 minutes. The residence time in the chlorinator is governed by the coal and solvent flow rates and volume of the chlorinator. In the chlorinator, the sulfur contained in the coal is oxidized by gaseous chlorine to water-soluble sulfate compounds. Operating temperatures are in the range of 50 to 150°C. The chlorination reaction is exothermic and requires a cooling coil to maintain temperature control.

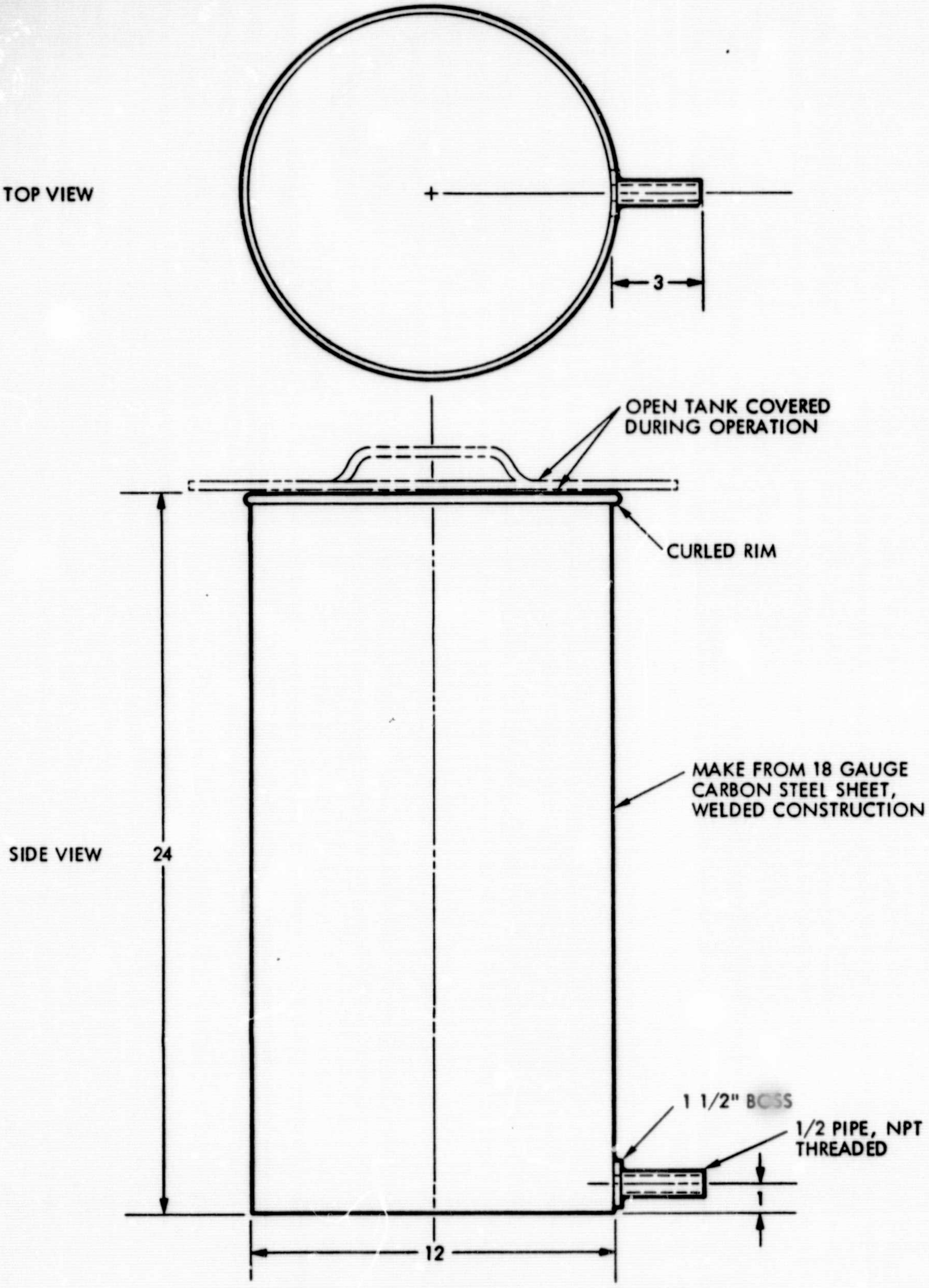
The chlorinated coal slurry with methylchloroform solvent discharges to the flash distillation unit where live steam injection is used to flash the organic solvent to a condenser and collection in a solvent recovery tank. Any HCl off-gas from the condenser is neutralized in a 5 gallon caustic solution scrubber. When only water was used as a solvent, the flash distillation unit, condenser, and solvent recovery tank were disconnected from the system (Figure 27). The coal slurry from the chlorinator was directly discharged through to the Red Slurry Valves. The rate of chlorinated slurry discharge from the chlorinator to the slurry receiving tank is determined by the frequency of the opening and closing of Red Slurry



DIMENSIONS IN INCHES

345021	REV	SCALE: 1:4	
DRAWN	DATE 12-20-78	APPROVED	DATE 12-27-78

Figure 24. Wastewater Neutralizing Tank - Mini-Pilot Plant



DIMENSIONS IN INCHES

CAUSTIC SOLUTION SUPPLY TANK- MINI-PILOT PLANT			
345017	REV		SCALE: 1:4
DRAWN	DATE 12-21-78	APPROVED	DATE 12-27-78

Figure 25. Caustic Solution Supply Tank - Mini-Pilot Plant

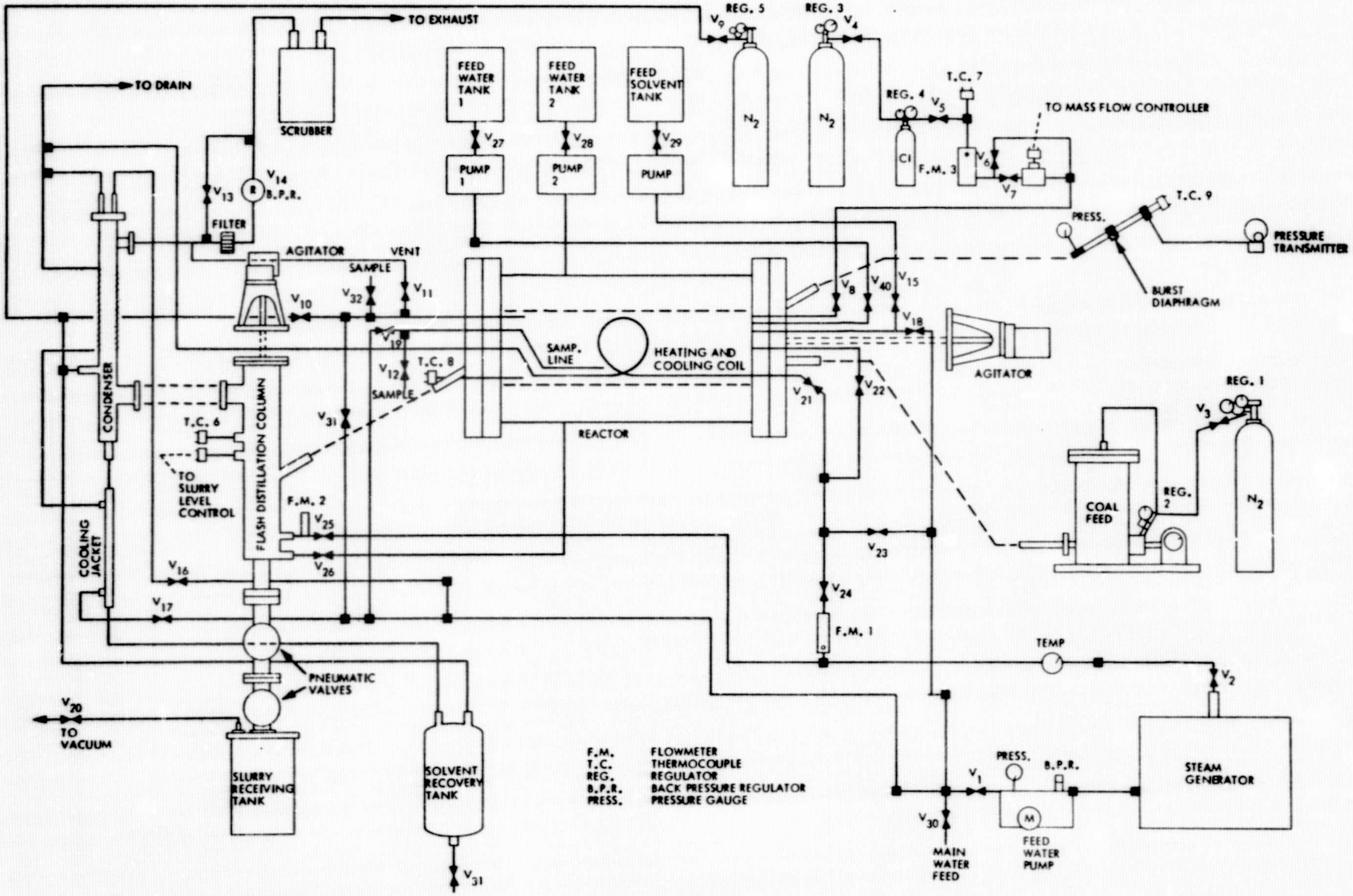


Figure 26. Chlorinator for Continuous Flow Mini-Pilot Plant (Methylchloroform System)

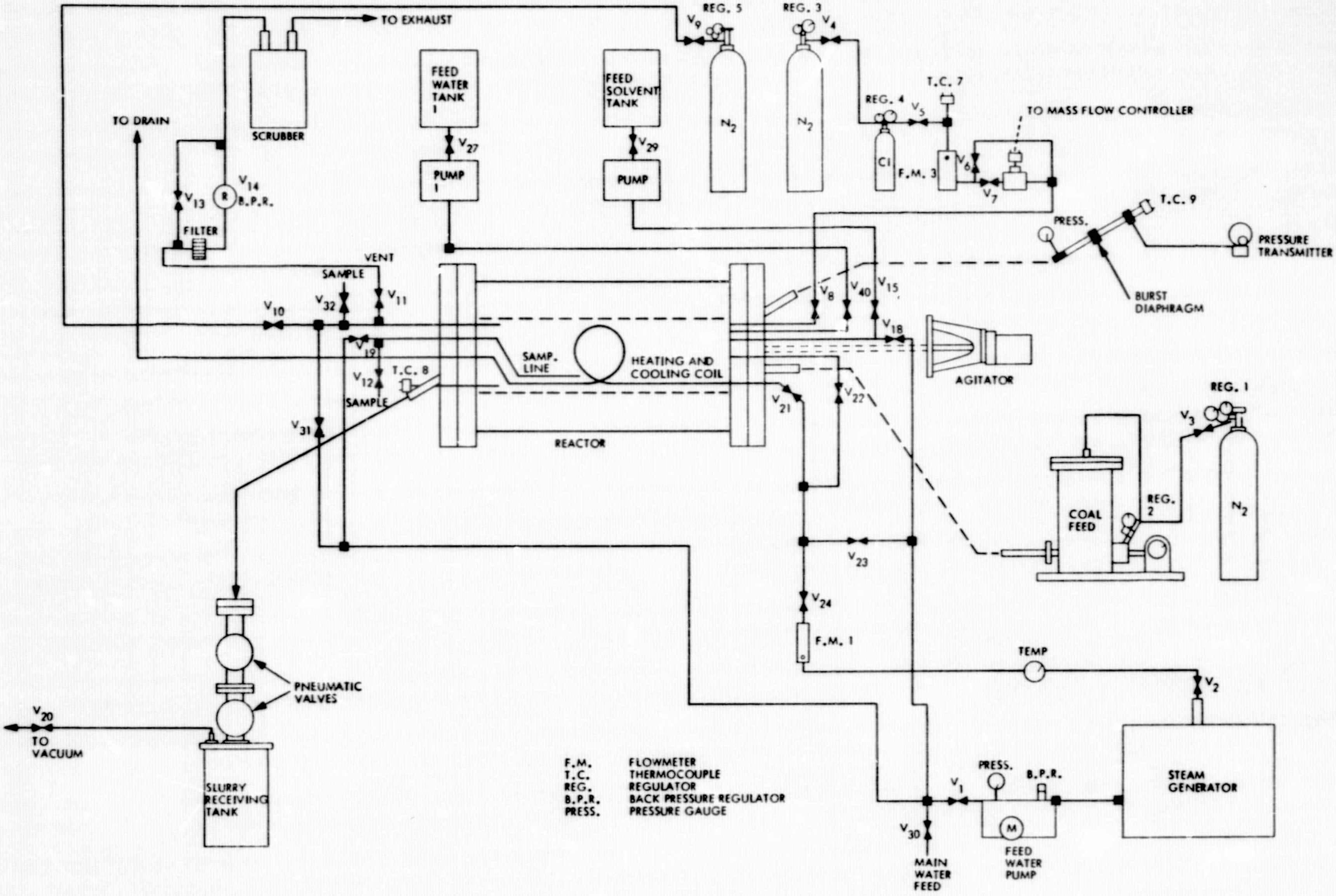


Figure 27. Chlorinator for Continuous Flow Mini-Pilot Plant (Water System)

Valves which is controlled by the carbon electrode level sensor and/or automatic timer. The chlorinated coal slurry is collected in a holding tank for periodic transfer to the slurry feed tank of the horizontal belt vacuum filter. As the filter belt moves, the coal forms a thin, damp cake on the belt. The cake is flushed with fresh water to displace sulfate-containing wash water from the coal. The coal filter cake is vacuum-dried as the belt moves forward. The filter cake is removed by a mother knife into a cake hopper as the belt turns over a pulley wheel. The coal is dried overnight in an 80°C oven and then transported to the dechlorinator coal feed hopper. The acid filtrate solution from the vacuum filter is neutralized with caustic soda before being discharged from the process. The detailed operating procedure for the mini-pilot plant chlorinator is described, Appendix D.

The chlorinated coal is fed by a twin-screw feeder into the dechlorinator where it is dechlorinated at a temperature of 400°C. The dechlorinator is electrically heated to provide the required temperature. Retention time of coal in the rotary kiln is governed by the angle of inclination and rotational speed of flights. Off-gases consist primarily of traces of steam, oil and tar, HCl, and nitrogen purge gas. Oil and tar are collected in an ice water trap. A caustic scrubber collects the HCl in the off gas. In a commercial unit, the HCl will be recovered for recycling to a Kel-chlor plant. The detailed operating procedure of the mini-pilot plant dechlorinator is described in Appendix D.

Coal from the dechlorinator is discharged into a product coal hopper contained under a nitrogen blanket. Quantities are small enough so that the hot coal will be cooled by natural convection of air to the coal hopper walls.

MINI-PILOT PLANT EXPERIMENTAL DATA

Operating data and coal desulfurization results are indicated in Table 11 for the mini-pilot plant. The mini-pilot plant is designed to operate as continuous flow units, the three major stages of chlorination, horizontal belt vacuum filtration-spray wash and dechlorination. A total of one run was conducted with PSOC 282 coal and six runs with PSOC 276 coal with one of the runs aborted.

CHLORINATION

CHLORINATION operating conditions were at atmospheric pressure, 70°C (except for run 7-1/12/8 at 21-60°C), residence times of 20-120 minutes with coal feed rates of 1.5-8.8 kg/hour and solvent/coal at 2/1, with chlorine feed near stoichiometric for the coal sulfur removal, i.e., 3-31.4 SCFH. Water was used in all but one run in which methylchloroform was used. Steady state in the chlorinator was assumed to be achieved after having coal slurry and chlorine feed for a time equal to the residence time plus 30 minutes. Monitoring of the coal slurry concentration at the discharge established that the coal concentration was steady at 33 wt.% after a time elapse of 30 minutes plus the residence time for the slurry. After steady state was established, a series of five coal slurry samples were obtained in half hour intervals over a 2 hour operating period. One run was extended for 2-1/2 hours and one run with a 20 minute residence time was continued for only one hour. Samples were obtained from the longitudinal center of the reactor by means of a sample line and at the discharge from the reactor. Samples of the total bulk discharge from the reactor were obtained as well as samples of the dechlorinated bulk coal. The samples were analyzed by the CSMRI for sulfur forms which are listed in Table 11 and for proximate and ultimate analyses which are listed in Table 12.

FILTRATION-WASH

FILTRATION-WASHING of the coal slurry was conducted on the horizontal belt vacuum filter, generally at a water/coal of 3/1, with water at 21°C. The filtration-wash was generally accomplished the day following the chlorination.

DECHLORINATION

DECHLORINATION of the washed-dried coal was done at 400°C, atmospheric pressure, residence time of 55 minutes with nitrogen purge at 5 SCFH.

PSOC 282 COAL

Run 1-11/24/80 was conducted with a dry PSOC 282 coal feed of 2 kg/hour, water feed of 4 kg/hour, residence time of 87 minutes, chlorine feed rate of 3 SCFH, 70°C and atmospheric pressure (Table 11). The samples obtained at half hour intervals over the two hour operating period indicated a range of 25-32% desulfurization with pyritic sulfur removals of 19-33% and organic sulfur removals of 0-9%. Washing of the sulfate sulfur was in some cases poor. This was in most cases the fault of coal sample handling procedures and not the result of the horizontal belt vacuum filter-spray wash unit. If a correction is made for the residual sulfate sulfur, then the

Table 11. Continuous Flow Mini-Pilot Plant Experimental Data for Coal Desulfurization by Chlorinolysis

Run # and Date	PROCESS CONDITIONS	PROCESSED COAL	PROCESSED COAL ANALYSES(4)										
			Sample(1) Time	Chlorine	Organic Sulfur		Pyritic Sulfur		Sulfate Sulfur	Total Sulfur		Total Sulfur (Sulfate Free)	
					Res.(2)	Rem.(3)	Res.	Rem.	Res.	Res.	Rem.	Res.	Rem.
			(hr.)	(wt.%)	(wt.%)	(%)	(wt.%)	(%)	(wt.%)	(wt.%)	(%)	(wt.%)	(%)
PSOC-282, HVB, ILL. No. 6 Jefferson County, ILL., Orient No. 6 Mine, Washed; - 200 mesh Sulfur Forms (wt.%): Organic-S 0.75, Pyritic-S 0.43, Sufate-S 0.36, Total-S 1.54; Chlorine 0.47 (wt.%)													
1-11/24/80	Chlorination: Feed - Coal 2 kg/hr., water 4 kg/hr., chlorine 3 SCFH, Residence Time 87 min., Temp. 70°C, Pressure atm. Filtration-wash: Horizontal belt vacuum filter, water/coal-3/1, 21°C. Dechlorination: Coal feed 2 kg/hr., Temp. 400°C, Residence Time 55 Min., Pressure 3" water (gauge), Nitrogen Feed 5 SCFH.	Chlorinated	0 M(5)	4.16	0.70	7	0.33	23	0.07	1.11	28	1.04	32
			0 D(6)	4.16	0.68	9	0.35	19	0.08	1.12	27.3	1.04	32
			0.5 M	4.2	0.76	-1	0.29	33	0.07	1.13	26.6	1.06	31
			0.5 D	4.08	0.86	-15	0.45	-5	0.07	1.37	11	1.30	16
			1 M	4.25	0.76	-1	0.32	26	0.06	1.15	25	1.09	29
			1 D	4.26	0.71	5	0.32	26	0.06	1.1	29	1.04	32
			1.5 M	4.7	0.74	1	0.32	26	0.06	1.12	27	1.06	31
			1.5 D	4.33	0.78	-4	0.30	30	<0.05	1.09	29	1.09	29
			2 M	4.30	0.73	3	0.29	33	0.08	1.11	28	1.03	33
			2 D	4.22	0.74	1	0.31	28	<0.05	1.05	32	1.05	32
			Bulk	4.11	0.58	23	0.34	21	0.24	1.17	24	0.93	40
		Dechlorinated	Bulk	0.81	0.48	36	0.18	58	0.31	0.97	37	0.66	57
PSOC-276, HVA, Ohio No. 8, Harrison County, Ohio, Georgetown, No. 24 Mine; - 200 mesh Sulfur Forms (wt.%): Organic-S 1.17, Pyritic-S 2.63, Sufate-S 0.06, Total-S 3.87; Chlorine 0.09 (wt.%).													
3-12/11/80	Chlorination: Feed-Coal 1.5 kg/hr., water 3 kg/hr., chlorine 5.3 SCFH, Residence Time 120 Min., Temp 70°C, Pressure atm. Filtration-Wash: Horizontal belt vacuum filter, water/coal - 3/1, 21°C Dechlorination: Coal Feed 2 kg/hr., Temp. 400°C, Residence Time 55 Min., Pressure 3" water (gauge), Nitrogen Feed 5 SCFH.	Chlorinated	0 M	7.97	1.21	-3	1.06	60	0.17	2.44	37	2.27	41
			0 D	7.85	1.19	-2	0.86	67	0.16	2.21	43	2.05	47
			0.5 M	8.17	1.14	3	1.27	52	0.17	2.59	33	2.42	37
			0.5 D	8.22	1.20	-3	0.89	66	0.14	2.23	42	2.09	46
			1 M	8.26	1.18	-1	0.86	67	0.16	2.20	43	2.04	47
			1 D	8.38	1.20	-3	1.04	60	0.17	2.42	37	2.25	42
			1.5 M	7.82	1.16	1	1.18	55	0.22	2.56	34	2.34	40
			1.5 D	8.16	1.19	-2	0.76	71	0.18	2.13	45	1.95	50
			2 M	8.52	1.16	1	0.79	70	0.20	2.14	45	1.94	50
			2 D	10.8	1.17	0	0.77	71	0.20	2.14	45	1.94	50
			Bulk(7)	8.68	-	-	-	-	-	2.23	42	2.05	47
		Dechlorinated	Bulk	1.5	1.33	-14	0.58	80	<0.05	1.91	51	1.91	51

Table 11. (cont'd)

Run # and Date	PROCESS CONDITIONS	PROCESSED COAL	PROCESSED COAL ANALYSES(4)										
			Sample(1) Time	Chlorine	Organic Sulfur		Pyritic Sulfur		Sulfate Sulfur	Total Sulfur		Total Sulfur (Sulfate Free)	
			(hr.)	(wt.%)	Res.(2) (wt.%)	Rem.(3) (%)	Res. (wt.%)	Rem. (%)	Res. (wt.%)	Res. (wt.%)	Rem. (%)	Res. (wt.%)	Rem. (%)
2-12/1/80	Chlorination: Feed-Coal 2 kg/hr., water 4 kg/hr., chlorine 5.3 SCFH, Residence Time 87 Min., Temp. 70°C, Pressure atm. Filtration-wash: Horizontal belt vacuum filter, water/coal-3/1, 21°C. Dechlorination: Coal feed 2 kg/hr., Temp. 400°C, Residence Time 55 Min., Pressure 3" water (gauge), Nitrogen Feed 5 SCFH.	Chlorinated	0 M	4.14	1.02	13	0.98	63	0.27	2.27	41	2.00	48
			0 D	4.47	1.09	7	0.94	64	0.22	2.25	42	2.03	48
			1 M	2.87	1.0	15	1.06	60	0.31	2.37	39	2.06	47
			1 D	2.74	1.03	12	1.09	59	0.26	2.38	39	2.12	45
			1.5 M	2.78	1.45	-24	1.00	62	0.18	2.63	32	2.45	37
			1.5 D	2.55	1.14	3	1.12	57	0.27	2.52	35	2.25	42
			2 M	2.79	1.24	-6	1.17	56	<0.05	2.42	37	2.42	37
			2 D	2.68	0.84	28	1.26	52	0.22	2.32	40	2.10	46
			2.5 M	2.91	1.03	12	1.31	50	0.21	2.54	34	2.33	40
			2.5 D	2.83	1.30	-11	1.16	56	<0.05	2.46	36	2.46	36
			Bulk	3.37	1.13	3	1.09	59	<0.05	2.21	43	2.21	43
		Dechlorinated	Bulk	1.35	1.31	-12	0.6	77	<0.05	1.91	51	1.91	51
4-12/17-81	Chlorination: Feed-Coal 2.9 kg/hr, water 5.8 kg/hr., chlorine 10.6 SCFH, Residence Time 60 Min., Temp. 70°C, Pressure atm. Dechlorination: ABORTED	Chlorinated (not Dechlorinated)	0 M	4.79	1.19	-2	1.06	60	0.21	2.47	36	2.26	42
			0 D	4.95	1.16	1	1.09	59	0.24	2.49	36	2.25	42
			0.5 M	2.21	1.26	-8	1.33	49	0.22	2.81	27	2.59	33
			0.5 D	ABORTED									
5-12/18/80	Chlorination: Feed-Coal 2.9 kg/hr., water 5.8 kg/hr., chlorine 10.6 SCFH, Residence Time 60 Min., Temp. 70°C, Pressure atm. Filtration-wash: Horizontal belt vacuum filter, water/coal-3/1, 21°C. Dechlorination: Coal feed 2 kg/hr., Temp. 400°C, Residence Time 55 Min., Pressure 3" water (gauge), Nitrogen Feed 5 SCFH.	Chlorinated	0 M	2.13	1.21	-3	2.42	8	0.17	3.80	2	3.63	6
			0 D	1.61	1.14	3	3.07	-17	0.19	4.40	-14	4.21	-9
			0.5 M	4.97	1.24	-6	1.58	40	0.18	3.01	22	2.83	27
			0.5 D	4.78	1.19	-2	1.66	37	0.20	3.05	21	2.85	26
			1 M	6.71	1.19	-2	0.92	65	0.17	2.28	41	2.11	45
			1 D	6.60	1.13	3	1.21	54	0.17	2.53	35	2.36	39
			1.5 M	7.64	1.16	1	1.03	61	0.17	2.36	39	2.19	44
			1.5 D	7.90	1.11	5	1.05	60	0.20	2.36	39	2.16	44
			2 M	8.90	1.06	9	0.94	64	0.20	2.20	43	2.00	48
			2 D	9.14	1.27	-9	0.66	75	0.18	2.10	46	1.92	50
			Bulk(7)	6.0	-	-	-	-	-	2.51	35	2.32(8)	40
		Dechlorinated	Bulk	1.82	1.36	-16	1.47	44	<0.05	2.85	26	2.7	30

Table 11. (Cont'd)

Run # and Date	PROCESS CONDITIONS	PROCESSED COAL	PROCESSED COAL ANALYSES(4)										
			Sample(1) Time	Chlorine	Organic Sulfur		Pyritic Sulfur		Sulfate Sulfur	Total Sulfur		Total Sulfur (Sulfate Free)	
			(hr.)	(wt.%)	Res.(2) (wt.%)	Rem.(3) (%)	Res. (wt.%)	Rem. (%)	Res. (wt.%)	Res. (wt.%)	Rem. (%)	Res. (wt.%)	Rem. (%)
6-12/29/80	Chlorination: Feed-Coal 8.8 kg/hr, water 17.5 kg/hr., chlorine 31.4 SCFH, Residence Time 20 Min., Temp. 70°C, Pressure atm. Filtration-wash: Horizontal belt vacuum filter, water/coal-3/1, 21°C. Dechlorination: Coal feed 2 kg/hr.,Temp. 400°C, Residence Time 55 Min., Pressure 3" water (gauge), Nitrogen Feed 5 SCFH	Chlorinated	0 M	3.35	1.09	7	1.75	33	0.26	3.09	20	2.83	27
			0 D	3.72	1.18	-1	1.39	47	0.26	2.84	27	2.58	33
			0.5 M	3.89	1.12	4	1.26	52	0.24	2.62	32	2.38	39
			0.5 D	4.54	1.18	-1	1.08	59	0.23	2.49	36	2.26	42
			1 M	3.67	1.14	3	1.67	37	0.24	3.06	21	2.82	27
			1 D	4.10	1.15	2	1.50	43	0.23	2.87	26	2.64	32
			Bulk(7)	4.12	-	-	-	-	-	2.73	30	2.49	35
		Dechlorinated	Bulk	1.36	1.25	-7	1.34	48	<0.05	2.58	33	2.55	34
7-1/12/81	Chlorination: Feed-Coal 2 kg/hr., water 0.9 kg/hr., Methylchloroform 4 kg/hr., chlorine 7.2 SCFH, Residence Time 87 min., Temp. 21-60°C, Pressure atm. Filtration-wash: Horizontal belt vacuum filter, water/coal -3/1, 21°C Dechlorination: Coal Feed 2 kg/hr., Temp. 400°C, Residence Time 55 Min., Pressure 3" water (gauge), Nitrogen Feed 5 SCFH.	Chlorinated	0 M	10.2	1.05	10	0.47	82	0.20	1.71	56	1.51	61
			0 D	9.92	1.15	2	0.33	87	0.21	1.71	56	1.50	61
			0.5 M	10.6	1.10	6	0.40	85	0.18	1.67	57	1.49	61
			0.5 D	10.3	1.07	9	0.39	85	0.19	1.66	57	1.47	62
			1 M	10.0	1.04	11	0.38	86	0.20	1.62	58	1.42	63
			1 D	10.9	1.08	8	0.37	86	0.20	1.66	57	1.46	62
			1.5 M	9.86	0.81	31	0.55	79	0.22	1.59	59	1.37	65
			1.5 D	10.7	0.95	19	0.45	83	0.20	1.61	58	1.41	64
			2 M	10.6	0.88	25	0.44	83	0.21	1.53	60	1.32	66
			2 D	11.0	0.86	26	0.49	81	0.21	1.57	59	1.36	65
			Bulk	13.0	1.13	3	0.38	86	0.36	1.86	52	1.50	61
		Dechlorinated	Bulk	2.10	1.08	8	0.48	82	0.17	1.74	55	1.57	59

(1) Samples are collected during steady-state. Steady-state is defined as (30 min. + Residence Time) after start-up.

(2) Residual.

(3) Removal.

(4) Sulfur forms are dry and chlorine free basis, by alternate method.

(5) Samples are collected from the middle of the chlorinator.

(6) Samples are collected from the discharge end of the chlorinator.

(7) Bulk samples were not collected but represent integrated average of time sample.

(8) Not including time sample.

Table 12. Proximate and Ultimate Analyses[a] of Raw and Chlorinolysis Processed Coal (Mini-Pilot Plant)[b]

Components - (Wt.%)[c]	PSOC 276						PSOC 282	
	Raw	MPP[d] Run 2-12/1/80	MPP Run 3-12/11/80	MPP Run 5-12/18/80	MPP Run 6-12/29/80	MPP Run 7-1/12/81	Raw	MPP Run 1-11/24/80
Volatiles	37.2	20	23.4	23.5	24.6	24.5	33.8	24.2
Fixed Carbon	51.3	67.1	64.5	62.6	62.2	61.1	59.5	69.2
Ash	11.5	12.9	12.1	13.9	13.2	14.3	6.7	6.56
Moisture[g]	1.89	6.34	0.62	0.16	0.38	0.15	3.1	0.23
HHV[e], Btu/lb	12,755	12,273	11,963	11,735	12,078	11,363	13,092	12,967
Carbon	71.6	72.3	70.5	68.6	70.5	67.9	74.8	77.2
Hydrogen	5.67	3.78	3.74	3.75	4.12	3.36	4.82	4.02
Nitrogen	1.28	1.4	1.24	1.18	1.24	1.17	1.69	1.8
Sulfur	3.91	1.91	1.88	2.8	2.55	1.7	1.54	0.97
Chlorine	0.16	1.35	1.5	1.82	1.36	2.1	0.47	0.81
Oxygen [f]	5.87	6.25	9.02	7.92	7.0	9.44	10.0	8.54

a Reference Table 11.
b Process involves chlorination, filtration-wash, and dechlorination at 400°C.
c Dry basis
d Mini-pilot Plant.
e High heating value.
f By difference.
g As determined basis

desulfurization is increased to 29-33%. These sulfur forms analyses were obtained on the individual grab samples. A sample of the integrated bulk flow from the reactor for the 2 hour period indicated a low 24% desulfurization if correction was not made for the high residual sulfate content in the sample. If the desulfurization was based on complete sulfate removal, then the desulfurization is increased to 40%. Dechlorination of the bulk coal sample increased the desulfurization to 57%. No apparent explanation is indicated for the relatively poor showing of the grab samples and the relatively good showing of the chlorinated bulk and dechlorinated bulk samples. Samples obtained at the mid-section of the reactor and discharge end gave nearly identical desulfurization values indicating that the extension of residence time beyond 43 minutes (reactor midsection) was not meaningful.

PSOC 276 COAL

Six runs were conducted with PSOC 276 coal with one of the runs aborted, Table 11. Coal feed ranged from 1.5 kg coal per hour for a residence time of 120 minutes to 8.8 kg coal per hour for a residence time of 20 minutes. Pressure was atmospheric. Temperature was 70°C except for run 7 at 21-60°C; i.e., no preheat of the reactor. Chlorine feed rates were from 5.3 to 31.4 SCFH, corresponding to approximately the stoichiometric amounts of chlorine for oxidizing the coal sulfur to sulfate. Run 2 was at a 20% lower chlorine flow rate.

Run 3 at a residence time of 120 minutes showed a sulfur removal of 33-45% at the reactor mid section and 37-45% at the discharge. A chlorinated bulk sample was not obtained, but an integrated average of the grab samples indicated a average desulfurization of 42%. The sample washing of grab samples was relatively poor in taking out the sulfate sulfur which was in the range of 0.14-0.22 wt.%. If one assumes sulfate sulfur to be zero, the mid-section desulfurization is 37 to 50% and the discharge desulfurization to be 42 to 50%. The dechlorinated bulk sample indicated 51% desulfurization. The appearance was that the level of desulfurization increased from the beginning of the 2 hour run at 47% up to 50% at 1-1/2 and 2 hours at the reactor discharge (assuming zero sulfate). The change over this time period was even greater when looking at the reactor mid-section. Desulfurization increased from 37-41% at the start of the run to 50% at 2 hours. Organic sulfur removal was zero over the entire 2 hour period (corresponding to batch reactor results) and pyritic sulfur removal was 52-71%.

Run 2 at a residence time of 87 minutes and at 80% of stoichiometric Cl_2 flow (for total sulfur oxidation to sulfate) was run for 2-1/2 hours. Sulfate sulfur remaining in the coal after sample washing was high, up to 0.31 wt.%. As a result, total desulfurization was 36-48% (assuming zero sulfate) and 32-41% (without a sulfate correction) for the grab samples. The bulk chlorinated sample gave 43% desulfurization. The bulk dechlorinated sample gave 51% desulfurization. Organic sulfur removal appeared to be significant in some of the grab samples, ranging from zero to 28%. The pyritic sulfur removal was 50 to 64%. The bulk samples showed essentially no organic sulfur removal and 59-77% pyritic sulfur removal with higher removal with dechlorination.

The overall result for run 2 was that the dechlorinated bulk sample gave identical desulfurization to that experienced in run 3 despite the shorter retention time and decreased chlorine flow rate.

Run 4 was aborted after a half-hour. Grab samples indicated a 33-42% desulfurization of the chlorinated coal with a residence time of 60 minutes and stoichiometric chlorine flow rate.

Run 5 at a residence time of 60 minutes and stoichiometric chlorine flow showed initially very poor results for the first half hour of run time. The desulfurization did increase to 44-50% at 1-1/2 to 2 hours run time. However, the bulk sample after dechlorination showed only a 26% desulfurization. The values for desulfurization at the reactor mid-section were very similar to those obtained at the discharge section. No credible explanation is available for the low desulfurization values at the start of the run or for the bulk dechlorinated sample except to suggest that the analytical results for these samples were incorrect or the sampling of the bulk sample was not representative. (These samples were grouped with a large number of samples sent to the CSMRI for analyses that represented an unusually large work load. Special provisions had to be made to get all of the samples analyzed in a relatively short time. (Analytical error under the circumstances is a possibility). Unfortunately, a chlorinated bulk sample was not obtained and the indicated bulk value is a calculated average from the grab samples. However, the calculated average, disregarding the first zero time sample at the discharge that gave a -9% desulfurization is still greater (40%) than the dechlorinated bulk sample showing 30% desulfurization.

Run 6 was operated at 8.8 kg of coal feed per hour for a residence time of 20 minutes with stoichiometric chlorine feed. The grab samples indicated a 27-39% desulfurization at the mid-section and a 32-42% desulfurization at the discharge of the reactor. The grab samples all had a substantial sulfate content indicating a poor washing of these samples. The calculated bulk sample of chlorinated coal gave 35% desulfurization and therefore indicated that the dechlorinated bulk sample at 33% desulfurization was probably low and not representative. The run was 1 hour in duration. The indication from this run is that a large part of the desulfurization occurs in 10 minutes or less. Organic sulfur removal values were scattered from 0 to 7% and pyritic sulfur removals were 33-59%.

Run 7 was made with methylchloroform solvent in lieu of water with an accompanying amount of water for hydrolysis, i.e., 0.45 water/coal. Residence time was 87 minutes with 2 kg coal feed per hour. No preheat was applied to the reactor and the temperature went from 21°C to 60°C with cooling water admitted to the cooling coil.

Phase II experimental data indicated that PSOC 276 coal was desulfurized with methylchloroform to a greater extent than with water whereas other coals had equivalent desulfurization results with water and methylchloroform. The desulfurization data with methylchloroform in this run was much more attractive than with the earlier runs with water. Total desulfurization was uniformly high at 61-66%. Organic sulfur removal varied considerably between grab samples with the range being 2-31%. Pyritic sulfur removal was 79-87%. The chlorinated bulk sample showed 61% desulfurization. The dechlorinated bulk sample was slightly lower at 59% desulfurization.

The sulfate content remained high after washing. If the sulfate is included in the residual coal sulfur, the desulfurization level drops by about 5%.

No appreciable difference existed between the mid-reactor and discharge samples. This suggests that the reaction was complete in half of the total reactor retention time or 43 minutes.

Generally, the mini-pilot plant runs gave results very similar to that obtained in the batch reactor. Some anomalous behavior exists with the desulfurization values. That includes run 1 with PSOC 282 coal in which the initial grab samples during the run showed abnormally low desulfurization and yet the dechlorinated bulk sample came up to a high 57% desulfurization. Also run 5 with PSOC 276 coal showed some low desulfurization values at the beginning of the run and with the dechlorinated bulk sample. However, the majority of results were comparable to that obtained in the batch reactor. The relatively high desulfurization with methylchloroform solvent relative to water using PSOC 276 coal suggests the relative attractiveness of the methylchloroform solvent for PSOC 276 coal. However, the Phase II batch work indicated that of the five bituminous cals tested, only PSOC 276 coal behaved in this fashion. Some of the low sulfur coals tested in this Phase III showed somewhat better results for desulfurization with methylchloroform than with water.

COAL PROXIMATE-ULTIMATE ANALYSES-MINI-PILOT PLANT

PSOC 282 Coal

Proximate and ultimate analyses for PSOC 282 coal are included (Table 12) for raw and chlorinolysis processed coal in mini-pilot plant run 1-11/24/80.

Volatiles were reduced by 28.4% with a 16.3% increase in fixed carbon while ash remained constant and heating value was reduced by 1%. Ultimate analyses indicated a 3.2% increase in carbon, a 16.6% decrease in hydrogen, a 6.5% increase in nitrogen, 37% decrease in sulfur, a 72% increase in chlorine and a 15% decrease in oxygen.

PSOC 276 Coal

Five runs were made with PSOC 276 coal, four with water as a solvent and run 7-1/11/81 with methylchloroform (Table 11). The notable difference between the water runs and methylchloroform run were that the methylchloroform run resulted in an increased loss of heating value as a result of an increased ash content, and decreased hydrogen content, as well as an increased oxygen content. Sulfur removal was also significantly greater with the methylchloroform run (Table 12).

The processed PSOC 276 coal relative to the raw coal showed: a substantial reduction in volatiles (37.2 wt.% vs. 20-24.5 wt.%); increase in fixed carbon (51.3 wt.% vs. 61.1-67.1 wt.%); increase in ash (11.5 wt.% vs. 12.1-14.3 wt.%); and decrease in heating value (12,755 vs. 11,1363-12,273 Btu/lb). Ultimate analyses indicated: a sightly changed fixed carbon (71.6 wt.% vs. 67.9-72.3 wt.%); decrease in hydrogen (5.67 wt.% vs. 3.36-4.12 wt.%); slight nitrogen change (1.28 vs. 1.18-1.4 wt.%); sulfur reduction (3.91 vs. 1.7-2.8 wt.%); substantial chlorine increase (0.16 wt.% vs. 1.135-2.1 wt.%); and oxygen increase (5.87 wt.% vs. 6.25-9.44 wt.%).

Although chlorine values are high in the processed coal, this reflects more of a need to improve the mechanics of the continuous flow dechlorination operation rather than an intrinsic characteristic of the dechlorination process. The greater desulfurization of PSOC 276 coal with methylchloroform was borne out in Phase II batch reactor tests and appears to be an intrinsic characteristic of the PSOC 276 coal with methylchloroform solvent in the chlorination process.

COAL BALANCE - MINI-PILOT PLANT

A coal material balance, Table 13, was conducted for five of the mini-pilot plant runs with one run on PSOC 282 coal and four runs with PSOC 276 coal. Operating conditions for the runs are indicated in Table 11. Run time was generally 2 to 2-1/2 hours in duration. The material balance was conducted in two parts. The first part included the coal accounting across the chlorination and filtration-wash. The second accounting was across the dechlorination.

Chlorination/Filtration-Wash

Coal feed to the reactor was measured over the period of the run with the calibrated dry coal screw feeder. Raw coal analyses for chlorine and sulfur provided a calculated coal feed rate less chlorine and sulfur content. Coal slurry samples were removed at half hour intervals during the course of the run. The weight of individual coal slurry samples was measured and the combined weight of samples was subtracted from the coal fed to obtain the weight of treated coal. The chlorine content of the coal slurry samples was based on the chlorine feed rate. The sulfur in the coal slurry was based on that of the raw coal. The only difference is that some of the sulfur is in solution as sulfate. A correction of the coal slurry samples for chlorine and sulfur provided a net weight of coal removed with sampling.
The bulk of the coal after chlorination was generally stored over night and then filtered and washed on the horizontal bed vacuum filter. The weight of coal from the filtration unit was based on the weight of the wet coal corrected for moisture content obtained by analyses on a "Ohaus" balance. Chlorine and sulfur content was obtained by CSMRI analyses of the chlorinated coal samples. The net weight of washed coal was obtained after correction for chlorine and sulfur content.

A coal accounting after chlorination, filtration and wash indicated a 93% recovery for PSOC 282 coal (run-1/11/24/80). Coal accounting for PSOC 276 coal was poor on runs 2-12/1/80 and 3-12/11/80 at 73-75% coal recovery. However, runs 5-12/18/80 and 2-1/12/81 showed a good recovery of 94-105%. The probable explanation for the runs with relatively poor accounting is that the calibration of the dry coal screw feeder was off the mark. Some slight losses of coal fines are present in the wash water but the amount appears to be negligible.

Dechlorination

The coal feed to the dechlorinator consisted of the recovered dried coal from the filtration-wash stage. The weight of dechlorinated coal was corrected for the chlorine and sulfur content, as determined by CSMRI analyses. The product coal recovery after dechlorination at 400°C for 55 minutes was 82% with PSOC 282 coal and 88-106% for PSOC 276 coal. A measurement of oil and tar content from the dechlorination stage amounted to 0.6% of the PSOC 282 coal and 0.2-13.7% of the PSOC 276 coal. The total accounting for PSOC 282 coal was 83%. The total accounting for the PSOC 276 coal was much better at 94-106%.

A conjecture is that the low dechlorination accounting for PSOC 282 coal is based on the occurence of a significant amount of low molecular weight gases that did not deposit in the oil and tar trap, whereas PSOC 276 coal had a greater fraction of oils and tars that were trapped.

Table 13. Coal Mass Balance - Continuous Flow Mini-Pilot Plant

RUN NO. AND DATE	RAW COAL FED TO REACTOR				SAMPLES REMOVED FROM REACTOR				CHLORINATED, FILTERED, WASHED, AND DRIED COAL				COAL ACCOUNTING			DECHLORINATED PRODUCT COAL (3)							
																RECOVERED COAL					OIL AND TAR		
	Coal (1) (g)	Chlorine (g)	Sulfur (g)	Coal-Cl_2-S (g)	Coal (2) (g)	Chlorine (g)	Sulfur (g)	Coal-Cl_2-S (g)	Coal (g)	Chlorine (g)	Sulfur (g)	Coal-Cl_2-S (g)	Coal- (g)	Recov. (%)	Input Coal (g)	Coal (g)	Chlorine (g)	Sulfur (g)	Coal-Cl_2-S (g)	Recov. (%)	Mass (g)	Recov. (%)	Total Recov. (%)
PSOC-282, HVB, Illinois, No. 6, Jefferson, Illinois (Orient No. 6 Mine, Washed)																							
1- 11/24/80	4248	20	65	4163	267.7	11.3	3.1	253	3832	159	45	3628	3881	93	3628	3012	24.4	29.2	2958	82	21	0.6	83
PSOC-276, HVA, Ohio No. 8, Harrison, Ohio (Georgetown No. 24 Mine)																							
2- 12/01/80	4777	4.3	184.9	4588	256	8.3	6.0	242	3366	(4) 113.4	(4) 74.4	3178	3434	75	3178	3500	47.3	66.8	3386	106	6	0.2	106
3- 12/11/80	2752	2.5	106.5	2643	189.7	16	4.4	169	1944	(4) 168.7	(4) 8.2	1767	1936	73	1767	1608	24.1	30.7	1553	88	111	6.3	94
5- 12/18/80	5201	4.7	201.3	4995	170	14.8	7.0	148	5763	(4) 345.8	(4) 167.1	5132	5250	105	5250	5125	93.3	146	4886	93	307	5.8	99
7- 01/12/81	3574	3.2	138.3	3433	231.3	25.8	3.9	201	3542	460.5	65.9	3016	3217	94	3016	2803	58.9	48.8	2695	89	412	13.7	103

(1) Dry weight of coal fed during steady-state.

(2) Includes dry weight of all samples collected furing an experimental run.

(3) Dechlorination temperature is 400°C.

(4) Percentage chlorine and sulfur content is integrated average of time samples. Reference Table 11.

COAL ANALYSES

LECO ACID-BASE VS. ESCHKA ANALYSES FOR TOTAL SULFUR

Leco acid-base analyses were conducted for total sulfur in the processed coal immediately after the conduct of laboratory, batch reactor and mini-pilot plant runs. More accurate and complete analyses conducted by the CSMRI normally took a matter of weeks because of delays in sample shipment, etc.

To provide a record of the accuracy of the Leco acid-base sulfur determination relative to the Eschka analyses performed by CSMRI, a tabulation of the data were made, Appendix B, Table B-1. Generally, good agreement was observed, although there are a significant number of instances in which poor agreement was noted, deviations greater than 0.2 wt.%. Thus, the Leco acid-base analysis for total sulfur should be considered to provide a good indication of total sulfur, but nevertheless, requiring confirmation by a more reliable analyses such as the Eschka method.

ASTM VS. ALTERNATE METHOD ANALYSES FOR PYRITIC SULFUR

The ASTM procedure provides for an "iron" determination to obtain the pyritic sulfur value (see Appendix B). The alternate method provides for a direct determination of sulfur from pyritic sulfur by barium sulfate precipitation (see Appendix B).

Attention was drawn to the inadequacy of the pyritic sulfur determination by an "iron" determination as a result of the Phase II experimental work. It was demonstrated in numerous runs that samples of coal slurry that were obtained as grab samples during the runs with methylchloroform gave progressively increased values of organic sulfur removal with increasing reaction time and relatively low values of pyritic sulfur removal. The organic sulfur value is obtained by difference between total sulfur and the sum of pyritic and sulfate sulfur. Thus, an error in the pyritic sulfur determination is translated into a reverse error in the organic sulfur value. The anomaly became evident when the value of organic sulfur removal did not persist when the coal-methylchloroform slurry was processed by water addition and distillation of the solvent from the slurry. The apparent explanation is that the "grab samples" were not processed adequately and the iron released from the pyrite remained with the coal and was not extracted by the methylchloroform to any great degree. With water, the iron was more soluble and this phenomenon did not exist as exemplified by the bulk samples of coal not exhibiting the "high" organic sulfur removal. Samples of coal that exhibited this phenomenon with methylchloroform were submitted to the CSMRI for analyses by the ASTM method and by the "alternate" procedure for direct sulfur determination by barium sulfate precipation in lieu of "iron" determination. The comparative results (Table 14) confirm the disparity, with the ASTM procedure indicating a high pyritic sulfur content and the "alternate" method indicating a low or zero value of pyritic sulfur. Unprocessed raw coal samples gave identical pyritic sulfur values by the two methods indicating that the problem was in processed coal. Water processing of the coal did not show this disparity in pyritic sulfur value.

Table 14. Comparative Pyritic Sulfur Determinations by "Sulfur" and "Iron" Measurements - Phase II Samples

Analytical Sample Number	Coal Sample (Run-Min)[4]	Coal PSOC Number	Sulfur Forms Analysis (wt.%)					Total
			Pyritic		Organic		Sulfate	
			ASTM	Alt.[3]	ASTM	Alt.[3]		
SP2[1]	Raw Coal	219	0.56	0.62	1.02	0.96	0.61	2.20
Phase II[2]	Raw Coal	219	0.73		0.81		0.60	2.15
SP3[1]	Raw Coal	282	0.64	0.63	0.88	0.89	0.16	1.68
Phase II[2]	Raw Coal	282	0.77		0.72		0.10	1.59
SP1[1]	21-90	282	0.32	0.63	0.36	0.66	0.14	0.82
Phase II[2]	21-90	282	0.69		0.13		0.17	1.00
SP4[1]	28-90	219	0.31	<0.01	0.34	0.65	0.12	0.78
Phase II[2]	28-90	219	0.79		0.00		0.17	0.96
SP5[1]	39-45	282	0.03	<0.01	0.45	0.48	<0.05	0.48
Phase II[2]	39-45	282	0.67		0.08		<0.05	0.75

Notes: 1 - Phase II samples of coal resubmitted to the Colorado School of Mines Research Institute for comparative analysis of pyritic sulfur by ASTM (Iron) determination and sulfur ($BaSO_4$ ppt) determination. Results received 04/18/80.

2 - Samples analysis by CSMRI during Phase II.

3 - Pyritic sulfur determination by "sulfur" determination. (Shows very little residual sulfur relative to iron determination for desulfurized samples. Raw coal samples unaffected.

4 - Represents Phase II Run No. and reaction time in minutes to identify sample.

In the current Phase III experimental work, grab samples of coal slurry obtained during the run were not analyzed. These were the samples that were troublesome when runs were with methylchloroform. However, the question persisted whether the ASTM procedure for pyritic sulfur would provide some bias with the fully processed bulk samples for runs with methlchloroform. Control samples, including raw coal and samples from runs with water were also submitted to the CSMRI for analyses and comparison of the two pyritic sulfur determination methods. The data are listed, Table 15.

Raw coal analyses (Table 15) are close together for pyritic sulfur by the two methods in 2 of the samples and within 0.16 wt.% in the third sample.

Bulk chlorinated coal samples for one water and three methylchloroform runs gave very close results for pyritic sulfur by the two methods (Table 15).

Bulk chlorinated and dechlorinated coal samples gave nearly identical pyritic sulfur results by the two methods irrespective of water or methylchloroform use in the runs (Table 15).

Bulk chlorinated coal with post-treatment by 10% NaOH using water as a solvent gave some differences in pyritic sulfur between the two methods, but less than 0.09% wt.% which is within the claimed experimental accuracy for the ASTM procedure (Table 15).

Bulk chlorinated, post-treated coal with 10% NaOH and dechlorinated gave very similar results for pyritic sulfur by the two methods. A comparison of pyritic sulfur values between the two methods for coal chlorinated in water, dechlorinated and then hydrodesulfurized gave identical pyritic sulfur values, with both values at less than 0.05 wt.% (Table 15).

The conclusion of these comparative analyses is that both the ASTM and "alternate" pyritic sulfur determination procedures can be relied upon to give acceptably accurate analyses. The phenomenon exhibited in Phase II can be attributed to the use of methylchloroform and the sample processing procedure that did not allow extraction of the iron content from the coal sample despite adherence to the ASTM procedure.

BATCH REACTOR TAR

Tar samples were obtained from the bench-scale batch dechlorinator and analyzed by the CSMRI for proximate and ultimate analyses, Table 16. The attendant chlorination and dechlorination conditions are listed. The tar represented 3.4-4.4 wt.% of the coal feed to the dechlorinator. Sulfur values in the tar were 1.05-1.11 wt.%. Ash values were 2.03-5.85 wt.%. Hydrogen values were high at 6.45-7.52 wt.% with an attendant heating value of 11,935 -14,497 Btu/lb. Chlorine content was also high at 3.18-7.01 wt.%.

The conclusion is that the recovered tar has a high heating value including high hydrogen and volatiles content. But, the tar would have to be treated for sulfur and chlorine content before it could be used as a fuel.

Table 15. Comparison of ASTM and Alternate[c] Methods for Sulfur Forms Analyses of Processed Coals

Batch Run No.	Chlorination Solvent	Coal Type (PSOC No.)	SULFUR FORMS (wt.%)						Total Sulfur (wt.%)[d]
			ASTM METHOD			ALTERNATE METHOD			
			Organic	Pyritic	Sulfate	Organic	Pyritic	Sulfate	
			RAW COAL						
-	-	230	0.52	0.35	<0.05	0.36	0.51	<0.05	0.87
-	-	276	1.29	2.11	0.54	1.39	2.08	0.47	3.94
-	-	282	0.75	0.43	0.36	0.70	0.50	0.34	1.54
			BULK CHLORINATED COAL[b]						
5	Water	282	0.69	0.32	0.14	0.63	0.37	0.15	1.15
7	MC[a]	282	0.73	0.14	<0.05	0.67	0.20	<0.05	0.87
8	MC	282	0.71	0.12	<0.05	0.67	0.16	<0.05	0.83
10	MC	282	0.62	<0.05	<0.05	0.62	<0.05	<0.05	0.62
			BULK CHLORINATED-DECHLORINATED COAL[b]						
11	Water	230	0.33	0.13	<0.05	0.33	0.13	<0.05	0.46
48	Water	276	1.08	0.16	<0.05	1.11	0.13	<0.05	1.24
13	Water	282	0.63	0.22	<0.05	0.60	0.25	<0.05	0.85
14	Water	282	0.54	0.10	0.06	0.62	0.08	<0.05	0.70
17	Water	282	0.66	0.15	<0.05	0.62	0.19	<0.05	0.81
12	MC	230	0.37	0.09	<0.05	0.37	0.09	<0.05	0.46
10	MC	282	0.59	<0.05	<0.05	0.54	0.05	<0.05	0.59
15	MC	282	0.54	0.07	<0.05	0.54	0.07	<0.05	0.61
			BULK CHLORINATED-POST TREATED COAL[b]						
2	Water	282	0.62	0.11	<0.05	0.58	0.15	<0.05	0.73
13	Water	282	0.65	<0.05	<0.05	0.60	0.05	<0.05	0.65
22	None	282	0.74	0.05	0.09	0.64	0.14	0.10	0.88
			BULK CHLORINATED-POST TREATED-DECHLORINATED COAL[b]						
2	Water	282	0.53	0.16	<0.05	0.56	0.13	<0.05	0.69
4	Water	282	0.59	0.10	<0.05	0.61	0.08	<0.05	0.69
13	Water	282	0.73	<0.05	<0.05	0.65	0.08	<0.05	0.73
3	MC	282	0.78	0.20	<0.05	0.71	0.27	<0.05	0.98
22	None	282	0.39	0.26	0.29	0.55	0.09	0.30	0.94
			BULK CHLORINATED-DECHLORINATED-HYDRODESULFURIZED COAL[b]						
48	Water	276	1.06	<0.05	<0.05	1.06	<0.05	<0.05	1.06
49	Water	276	0.84	<0.05	0.19	0.84	<0.05	0.19	1.03

a. Methylchlorform

b. Reference Tables 3 and 4

c. Direct determination of pyritic sulfur by $BaSO_4$ precipitation in lieu of the iron determination.

d. Moisture and chlorine free basis

Table 16. Analyses of Batch Reactor Tar From Dechlorinator (PSOC-276, -325 Mesh)

ANALYSES/PROCESS CONDTIONS	Batch Run 49-01/08/81	Batch Run 57-01/16/81
Moisture[a]	Not Determined[b]	Not Determined[b]
Ash	5.85	2.03
Carbon	67.6	76.2
Hydrogen	6.45	7.52
Nitrogen	1.77	1.40
Sulfur	1.18	1.05
Chlorine	7.01	3.18
Oxygen (Difference)	10.1	8.6
Heating Value, Btu/lb	11,935[c]	14,497[c]
Wt. % of Tar Produced	3.4	4.4
Chlorination Conditions:		
Solvent	H_2O	H_2O
Time, Min.	60	60
Temperature, °C	70	70
Dechlorination Conditions:		
Time, Min.	60/60	60
Temperature, °C	500/700	500
Purge Gas, 5 SCFH	N_2/H_2	N_2

a. All analyses are on the As-Determined Basis, Wt. %.
b. Moisture by oven drying is not accurate for tars.
c. The heating value is depressed by an unknown quantity of moisture.

SUPPORTING RESEARCH STUDIES

IRON PYRITE DISSOLUTION IN CHLORINOLYSIS PROCESS

Iron Pyrite ground to 100 x 200 mesh and -325 mesh was put into water at 10 grams per liter with a gaseous chlorine feed rate of 0.3 standard liters per minutes. Samples were obtained at 15 minute intervals and analyzed for the conversion of FeS_2 to iron and sulfate in solution (Table 17).

The data indicate that the -325 mesh pyrite sample was 86% converted in 15 minutes, 95.9% converted in 30 minutes with 99.8% conversion in 45 minutes. The 100 x 200 mesh pyritic particles show a much slower conversion with only 33% conversion in 15 minutes, 52.5% conversion in 30 minutes, 75.5% conversion in 45 minutes, 92.2% in 60 minutes and 100% in 75 minutes.

The apparent conclusion is that particle size has a strong rate determining effect on pyrite dissolution which corresponds with the chlorinolysis data in which grinding a processed 100 x 200 mesh coal to -325 mesh coal had the effect of increasing desulfurization by an added 10-15%.

DECHLORINATION RESEARCH

Prof. Gavalas of the Caltech Chemical Engineering Department in conjunction with Dr. Mitsuo Oka conducted a research investigation into the dechlorination of chlorinated coal obtained in the desulfurization process.

A summary of their results is indicated in Appendix D. Their findings are that the residual chlorine in coal dechlorinated at 400°C, has a remaining chlorine composition of 35 5% HCl, 15 5% RCl and 50 5% as ArCl where RCL are alkyl chlorides and ArCl are aromatic chlorides. Sodium hydroxide solution and solvents were able to extract HCl and alkylchlorides. However, aromatic chlorides are inert toward NaOH solution and solvents and are only removed by thermal treatment at elevated temperatures.

COAL SULFUR CONTROL, INC., DESULFURIZATION PROCESS

Recent publicity about the Coal Sulfur Control, Inc., process for beneficiation and sulfur removal by means of a chlorine process suggested to DOE that a need existed to investigate this "new" coal cleaning process. A description of the process and attendant analysis is included in Appendix F. The results of a trip to Cincinnatti, Ohio, and analysis of the resulting raw and treated coal samples indicated that no new or novel technology was used. The process depended upon the normal ash reduction that can be obtained in a coal washing process with an accompanying sulfate sulfur removal by a water wash. "Gob Piles" of coal have been standing above ground for years and the pyritic sulfur that is normally present has been oxidized to sulfate which is easily removed by washing. The residual organic sulfur in the coal is not removed.

SUPPORTING COAL DESULFURIZATION RESEARCH

Auxiliary research work was conducted on: (1) electrolytic desulfurization via reactive intermediates, (2) chlorination using supercritical CO_2 as a reaction medium, and (3) solvent swelling of coal, followed by replacement of the swelling solvent with a solvent inert to chlorine and chlorination of the resultant mixture.

A summary of the work that was carried out is included, Appendix G.

Table 17. Kinetics of Iron Pyrite Dissolution Under Chlorinolysis Conditions
(water solvent, 70°C, atm pressure, intense stirring)

Iron Pyrite Mesh Size	Initial Pyrite Concentration in Water			Chlorination				Conversion	
	FeS_2 Solids (g/L)	Fe (g/L)	S as SO_4 (g/L)	Chlorine* Feedrate (SLPM)	Time (Min.)	Fe in Solution (g/L)	S as SO_4 Insulation (g/L)	% of Total Fe in Solution	% of Total S in Solution
-325	10	4.61	15.85	0.3	0	0	0	0	0
					15	3.96	13.7	86	86
					30	4.4	15.2	95.9	95.9
					45	4.6	15.8	99.8	99.7
					60	4.57	15.7	99.1	99.0
100-200	10	4.61	15.85	0.3	0	0	0	0	0
					15	1.54	4.87	33	31
					30	2.42	8.41	52.5	53
					45	3.48	12.2	75.5	77
					60	4.25	14.9	92.2	94
					75	4.69	16.1	101.7	101.6
					90	4.77	16.5	103.5	104.1

* During first fifteen minutes enough chlorine gas was injected to convert Fe and S in pyrite solids to Fe^{+++} and SO_4 respectively.

RESULTS AND CONCLUSIONS

Twenty-two bituminous, sub-bituminous and lignite coals representing 12 states from the East, Midwest, Southeast and West were treated by the chlorinolysis coal desulfurization process. The desulfurization results for the high sulfur coals (>1% sulfur) were: sulfur removal - total 45-60%, pyritic 80-90%, organic 0-30%. The desulfurization results for the low sulfur coals (<1% sulfur) were: sulfur removal - total 20-50%, pyritic 40-80%, organic 0-30%.

PRETREATMENT/POST-TREATMENT

Pretreatment and post-treatment of the coal relative to the chlorination process was investigated in order to obtain increased coal desulfurization. Coal treatment methods included: 2-10% NaOH in water at temperatures of 90°C to 290°C for sixty minutes; 1-10% Na_2CO_3 at 90°C; 9-40% HNO_3 at 95-100°C for 30-60 minutes; methanol and 50% methanol - 50% carbontetrachloride at 58-70°C for 60 minutes; 10% H_2SO_4 at 90°C for sixty minutes. Treatment was carried out on the bench-scale batch reactor at 2 kg of coal and on a laboratory-scale at 100 grams of coal. The more severe pretreatment with 9% NaOH at temperatures of 230°C for 60 minutes and 9-42% HNO_3 at 70-100°C for 30-60 minutes resulted in total sulfur reductions equivalent to those achieved by the chlorinolysis process alone. However, the inclusion of the chlorination after the severe pretreatment and high sulfur reduction in the pretreatment did not result in significant additional sulfur removal from the coal. The sulfur reduction in this type of severe treatment included essentially all the pyritic sulfur with some small amounts of the organic sulfur. However, the remaining organic sulfur appeared to be resistant to attack by any of the oxidizing or leaching agents tried. This proved to be true when 10% NaOH at 90-290°C was tried for 60 minutes on the chlorinated coal as well as trying 10% Na_2CO_3 at 230°C for sixty minutes. The inclusion of 9% NaOH and 10% Na_2CO_3 in the chlorination did not appear to alter the desulfurization to any great extent except perhaps to depress desulfurization slightly. However, the interpretation of the data is complicated to some extent by the apparent interfence of the NaOH solution with the Leco sulfur analyses. Anomalous results for total sulfur were present in some of the runs when NaOH had been used in the treatment of the coal. The use of methanol and 50% methanol - 50% carbontetrachloride either as a coal pretreatment or during chlorination gave low or moderate values of desulfurization.

DECHLORINATION STAGE

The use of the dechlorination stage with relatively high temperatures of 400°C and higher for obtaining increased desulfurization was suggested by the Phase II experimental work in which an added 5 to 10% desulfurization was obtained in the dechlorination stage at 400°C, 60 minutes with nitrogen. The use of temperatures from 400°C to 700°C with nitrogen for 60 minutes did not provide any increase in desulfurization above the 5-10% added desulfurization found in the Phase II work.

Some added benefit appeared to be obtained when low sulfur coals were processed by using a dechlorination temperature of 500°C in lieu of 400°C with nitrogen. Processing of the coal with nitrogen at 700°C provided no real increase in desulfurization over that obtained by the chlorinolysis process under optimum conditions and with dechlorinations at 400-500°C.

The addition of oxidizing gases to the dechlorination stage with nitrogen at 400°C, that included 1% NO_2, 1% SO_2, 5 and 21% O_2, had no effect on increasing the desulfurization.

The replacement of nitrogen with hydrogen and elevating the temperature from 400°C to 500-700°C had a very pronounced effect on increasing the desulfurization. Desulfurization was increased from a level of 60% with PSOC 276 and 282 coals as obtained in the chlorinolysis process to values of 80-90% at 700°C for 60 minutes. Six other low and high sulfur coals were tested and showed equally promising increases in sulfur removal with hydrogen treatment at 700°C when the chlorinolysis process by itself had shown relatively low desulfurization. Of the six coals, four coals were desulfurized by 77-80% with desulfurization for the other 2 coals being increased from 18-20% by the normal chlorinolysis process to 52-64%. The attendant residual sulfur levels for four of the six coals was in the range of 0.17-0.24 wt.%.

PROXIMATE/ULTIMATE ANALYSES

Sulfur forms, proximate and ultimate analyses are included for all twenty-two of the raw coals. A comparison of proximate and ultimate analyses with processed coals is included only for PSOC 276 and 282 coals. However, proximate and ultimate analyses are included for coals processed in the laboratory-scale, bench-scale and mini-pilot plant. Processing conditions include the normal chlorinolysis process of chlorination and dechlorination with nitrogen at 400 and 500°C as well as the treatment of both PSOC 276 and 282 coals with hydrogen at temperatures of 500 to 700°C.

Volatiles are substantially reduced by the chlorinolysis process, primarily as a result of the dechlorination treatment at 400-500°C, with the decrease in volatiles becoming greater with the increase in dechlorination temperature. There is an accompanying increase in fixed carbon that suggests that the decrease in volatiles is less a loss from the coal than the result of a polymerization of the coal structure to transfer volatiles to fixed carbon. Treatment with hydrogen at 600 and 700°C further decreases the coal volatiles but to a much greater extent at 700°C than at 600°C. Treatment of unchlorinated raw coal with hydrogen at 700°C provides a volatiles content equal to or slightly higher than that obtained for the chlorinated coal treated with hydrogen at 700°C.

Ash levels with chlorinolysis-processed coal drop somewhat as a result of the extraction of iron and trace metals from the coal in the chlorination and washing stage. This was shown in Phase II results and the current phase III batch results. The mini-pilot plant results with PSOC 276 show an increase in ash buildup. The dechlorination temperature was kept at 400°C, so large losses of organic coal are not a likely explanation. An inadequate wash of the coal as evidenced by the high residual sulfate in the product coal is a more likely explanation.

Ash buildup with increasingly severe treatment temperatures is evidenced. However, a coal balance based on ash content indicates that the chlorinated coal subjected to 700°C may lose as little as 10% of the coal whereas raw coal (not chlorinated) will lose as much as 30-40% of the coal.

Heating value of chlorinolysis processed coal (PSOC 276, 282) will change slightly, either increase or decrease from the raw coal value depending upon the relative changes of ash and hydrogen content. The hydrogen treated coal at 600-700°C willincrease sightly in heating value relative to the raw coal by the sharp reduction in oxygen content, up to 80-100%. Heating values of processed coal in the mini-pilot plant decreased from raw coal values in all runs with a average 6% decrease for PSOC 276 with water and a 11% decrease with methylchloroform. The larger decrease of PSOC 276 heating value with methylchloroform corresponded with the higher increase in ash concentration from 11.5 wt.% to 14.3 wt.%. The heating value of processed PSOC 282 coal dropped only slightly, less than 1%.

Ultimate analysis of the chlorinolysis processed coal showed substantial increases in carbon (10%) and decreases in hydrogen content of 37% with dechlorination at 500°C in the batch reactor. The mini-pilot plant dechlorinated coal at 400°C showed either a slight increase in carbon or more generally a slight reduction in carbon content for PSOC 276 coal. PSOC 282 coal showed a slight increase in carbon. The hydrogen content generaly decreased about 35% in the mini-pilot plant runs with PSOC 276 but the hydrogen decrease was only 17% with PSOC 282 coal. Treatment of the coal with hydrogen at 600-700°C substantially increased the carbon content over that obtained in the chlorinolysis process with accompanying further decreases in the hydrogen content and decreases in the oxygen content. With dechlorination at 400°C (mini-pilot plant) oxygen content of the chlorinolysis processed PSOC 276 coal increased, corresponding to the finding in Phase II work. PSOC 282 oxygen content decreased about 15%. However, with dechlorination at 500°C, the oxygen content of the chlorinolysis processed coal decreased. With hydrogen treatment at 600-700°C, the oxygen content of both PSOC 276 and 282 coals decreased further with the oxygen content approaching zero for PSOC 276 coal.

Nitrogen values for processed coal changed, increasing or decreasing by slight absolute amounts (0.2-0.3 wt.%) but with no apparent regularity with treatment except to indicate that perhaps chlorinolysis processing resulted in a slight increase in nitrogen content and that subsequent hydrogen treatment at 600-700°C resulted in a slight nitrogen decrease. Mini-pilot plant runs showed a mixture of increases and decreases in nitrogen among the PSOC 276 runs. PSOC 282 in the mini-pilot plant run showed an increase in nitrogen.

Chlorine values were relatively low when chlorinolysis processed coal was dechlorinated at 500°C. In the mini-pilot plant with dechlorination at 400°C, the chlorine values were high at 1.35-1.82 wt.% for PSOC276 coal and 0.81 wt.% for PSOC 282 coal. With hydrogen treatment at 600-700°C, chlorine values dropped to less than 0.1 wt.%, reducing the chlorine content to less than that in the raw coal.

MINI-PILOT PLANT

The mini-pilot plant was operated with PSOC 276 and 282 coals, -200 mesh for seven runs with operating times of 2 to 4-1/2 hours per run. The chlorination was operated with 1.5 to 8.8 kilograms of coal feed per hour using a solvent to coal ratio of 2 with retention times of 20 to 120 minutes. The coal was fed dry by a screw feeder with metering pumps providing the solvent feed. Operation was at atmospheric pressure, 21 to 70°C with gaseous chlorine feed of 3 to 31.4 SCFH (80-100% of stoichiometric feed for sulfur oxidation to sulfate).

The chlorinated coal slurry was discharged to a holding tank from which it was fed to a horizontal belt vacuum filter for filtration and spray washing at 2 kg coal per hour.

The filter cake was dried and fed to a continuous flow dechlorinator equipped with flights. Dechlorinator operation was at: 400°C, atm. pressure, nitrogen feed of 5 SCFH and coal feed of 2 kg/hour, residence time of 55 minutes.

The mini-pilot plant operation demonstrated that coal desulfurization results for the continuous flow chlorinator were in general agreement with those obtained in the batch reactor. However, there were a number of departures from batch reactor data. Residual sulfate sulfur values were significant in a majority of the coal samples indicating that both the grab samples of coal from the chlorinator were poorly washed and the filter cake wash on the horizontal belt vacuum filter was inadequate. The spray wash of the bulk coal during the filtration was observed to be poor and could be easily improved by operation at higher coal feed rates with thicker filter cakes. This would provide for a better and more efficient water spray.

Grab samples of coal slurry obtained during the run showed relatively low desulfurization values in some cases. However, in most instances the dechlorinated bulk coal sample indicated a coal desulfurization that was greater than the average of the individual grab samples. This is partly the result of the contribution that the dechlorination stage makes to the desulfurization process. With PSOC 282 coal, total desulfurization was 57% with an accompanying 36% organic sulfur removal and 58% pyritic sulfur removal. The relativity low pyritic sulfur removal and the relativity high organic sulfur removal is unusual and suggests an analytical error.

With PSOC 276 coal, runs with water showed a range of 33-51% desulfurization and with methylchloroform 59-61% desulfurization. Organic sulfur removals were approximately zero with pyritic sulfur removals of 44-82%. Individual grab samples during the run gave fluctuating sulfur form values among the samples.

Proximate and ultimate analyses for the six runs indicated that the dechlorination at 400°C in the mini-pilot plant dechlorinator provided less chlorine removals from the product coal then dechlorination at 500°C. Additionaly, mini-pilot plant coal volatiles reduction, fixed carbon increases, and hydrogen reduction were not as great at 400°C as they were at 500°C.

Ash levels increased rather than decreased, perhaps as a result of poor coal washing. Oxygen levels increased for PSOC 276 coal, but decreased for PSOC 282 coal.

COAL MASS BALANCES

Coal mass balances across the batch reactor chlorination, and filtration-wash showed generally good accounting, within 97-103%. Coal mass balances across the batch dechlorinator showed accountings of 77-98% with an average of 85-90%.

Mass balances on the mini-pilot plant were somewhat inferior to those obtained in the batch reactor across the chlorination, filtration-wash at 73-105%. However, mass balances were better across the mini-pilot plant dechlorinator at 82-106% than across the bench-scale dechlorinator.

REFERENCES

1. Kalvinskas, John J., et al, Final Report Coal Desulfurization by Low Temperature Chlorinolysis, Phase II, JPL Publication 80-15, January 15, 1980.

2. Kalvinskas, John J., et al, Final Report for Phase I-Coal Desulfurization by Low Temperature Chlorinolysis, JPL Publication 78-8, November 23, 1977.

3. Annual Book of ASTM Standards, Part 26, American Society for Testing and Materials, Philadephia, Pennsylvania, 1980.

APPENDICES

APPENDIX A

LABORATORY-SCALE EXPERIMENTAL PROCEDURE

A-I. PROCEDURE FOR PRETREATMENT, CHLORINATION, AND POST-TREATMENT IN LABORATORY GLASSWARE

1. Equipment: 500 ml reaction flask, turbine impeller, a single coarse fitted glass diffuser to disperse chlorine, a variable reflux condenser, trap, and scrubber. The glassware system was properly assembled according to the Figure 1.

2. Determine the moisture content of the feed coal.

3. Charge 100 grams of dry coal into the reaction flask.

4. Start heating the water bath.

5. Pour appropriate amount of solvent into the reaction flask. Homogenize the slurry by moving the stirrer shaft by hand before using the air drive. Adjust the stirring speed to avoid splattering.

6. Start timer and the chlorine flow after the target temperature is reached (slurry, not bath).

7. Check the temperature and chlorine flowrate every few minutes. Keep the chlorine pressure in the rotameter section below 2 psig or adjust the apparent flowrate accordingly.

8. Withdraw appropriate amounts of coal slurry time samples from the reaction flask.

9. Filter slurry samples in a 7 cm Buchner funnel and set aside a filtrate sample. If the solvent is immiscible with water, wash with that solvent until the effluent is mostly clear, before water washing (water/coal 2, at 25°C).

10. At the end of the experimental run, shut-off the stirrer, heater, and chlorine flow simultaneously.

11. Within three minutes, disconnect feed lines, and the variable reflux head from the reactor flask.

12. Filter the reaction flask contents in an 18.5 cm Buchner funnel. Two parts of water per part of dry coal was used to wash cake. Dry the coal cake overnight in an oven at 70° to 100°C before dechlorination.

A-II. PROCEDURE FOR DECHLORINATION AND HYDRODESULFURIZATION IN THE QUARTZ TUBE-FURNACE

1. Equipment: Quartz tube (1"ID x 36"long), coal holding tube, electric furnace, oil and tar trap, and scrubber. Assemble dechlorination system according to the Figure 2.

2. Place thermocouple with quartz tube and preheat both quartz tube and furnace to 400°C under nitrogen at a flowrate of 20-90 cc/min. Start tube rotation at about 2 RPM.

3. Prepare the ice bath for the tar trap flask and refill the water in the scrubber.

4. Determine the moisture content of the feed chlorinated coal.

5. Weigh two grams of coal into the coal holding tube. Four grams is the reasonable maximum if large quantities are required.

6. After both quartz tube and furnace are stabilized at 400°C, perform following steps:

   (a) turn off rotation.
   (b) remove thermocouple along with rubber stopper.
   (c) place coal holding tube into the quartz tube.
   (d) reinstall thermocouple.
   (e) start tube rotation.
   (f) maintain nitrogen flow for dechlorination experiments. For hydrodesulfurization experiments, use hydrogen gas at a prescribed flowrate.

7. After one hour, turn-off electric heater and cool quartz tube contents to 150°C under nitrogen blanket.

8. Remove coal from holding tube and weigh it before transferring into a half-ounce vial.

9. Obtain scrubber samples for analysis.

10. Remove and weigh oil and tar sample from the trap.

APPENDIX B

ANALYTICAL PROCEDURES

B-I. ALTERNATE METHOD TO DETERMINE FORMS OF SULFUR IN COAL

The pyritic sulfur content in the coal is determined by oxidation of pyrite to ferric sulfate and subsequent gravimetric analysis of barium sulfate precipitate, rather than by atomic absorption determination of iron as described in the ASTM method.

1. Reagents.

   a. Bromine water: Reagent grade bromine is added to distilled H_2O until a saturated solution is obtained. The bromine saturated water is decanted off to make reagent b.

   b. Bromine/HCl solution: Add 250 ml of concentrated HCl to 250 ml of water and to this add 500 ml of saturated bromine water, mix well.

   c. Barium chloride solution: 10% (w/v) in H_2O.

   d. HCl solution for SO_4 sulfur determination: HCl/H_2O (2/3).

   e. HNO_3 solution for pyritic sulfur determination: HNO_3/H_2O (1/7).

2. Procedure

   a. 1.00xx grams of coal is weighed into a 250 ml beaker, 50 ml of HCl (2/3) is added and the sample is refluxed for 1/2 - 3/4 hour.

   b. The solution is cooled, filtered through 11 cm #40 Whatman filter paper and washed with hot, distilled H_2O. The filtrate and washings are collected in a 400 ml beaker and the filter paper and residue are placed in the original beaker.

   c. The filtrate from b is adjusted to a methyl orange endpoint (pH 3-4), if necessary, and heated to boiling. $BaCl_2$ is added slowly with stirring. The solution is allowed to sit for 1 hour at this temperature and then removed from the hot plate and allowed to sit overnight. The $BaSO_4$ is collected in 11 cm #42 Whatman filter paper and washed with hot distilled H_2O. The filter paper is then ignited off and the $BaSO_4$ ignited to 900°C for 1/2 hour, cooled and then weighed.

$$\textbf{(AD) \% Sulfate Sulfur} = \frac{\textbf{BaSO}_4\textbf{ weight x 13.74}}{\textbf{sample weight}}$$

d. The filter paper and residue from b is placed in the original 250 ml beaker, macerated with a glass stirring rod, and 50 ml of HNO_3 (1/7) are added and refluxed for 1/2 - 3/4 hour.

e. The solution is filtered through 15 cm #40 Whatman filter paper and washed with hot, distilled H_2O. The filtrate and washings are collected in a 400 ml beaker, adjusted to methyl organ endpoint (if necessary) and 10 ml of bromine water/HCl solution added. The solution is boiled until clear or until a methyl orange endpoint is obtained (no Br_2 consuming the indicator). $BaCl_2$ is added and the procedure is followed as in C.

$$\text{(AD) pyritic sulfur \%} = \frac{BaSO_4 \text{ weight} \times 13.74}{\text{sample weight}}$$

Note 1: The $BaSO_4$ solutions are washed with hot, dilute HCl (1/25) if there is an appreciable iron discoloration noted.

B-II. ANALYTICAL PROCEDURE TO DETERMINE THE FORMS OF SULFUR IN COAL (ASTM METHOD)

1. Summary of Method

a. Sulfate sulfur is determined by extracting a weighed sample for coal with dilute hydrochloric acid followed by precipitation with barium chloride ($BaCl_2$) and weighing as barium sulfate ($BaSO_4$). Sulfate sulfur is soluble in dilute hydrochloric acid; pyritic and organic forms of sulfur are insoluble.

b. Pyritic sulfur is determined by extracting a weighed sample of coal with dilute nitric acid followed by titrimetric or atomic absorption determination of iron in the extract as a measure of pyritic sulfur. Extraction of pyritic sulfur from coal with dilute nitric acids involves oxidation of ferrous iron to ferric and sulfide sulfur to sulfate, both of which are soluble in nitric acid. Because the extraction dissolves sulfate and pyritic sulfur plus a small amount of organic sulfur, the dissolved sulfur is not a reliable measure of pyritic sulfur. Consequently, it is obtained by determining the amount of iron combined in the pyritic form, which is equal to the difference between nitric acid and hydrochloric acid-soluble iron. However, there are certain limitations to the use of the sulfate sulfur residue for determination of pyritic sulfur in coal: if pyritic iron is high, the large sample required for determination of small amounts of sulfate sulfur will contain large quantities of iron and may require dilution; the determination of pyritic iron cannot be carried out until both extractions of sulfur have been completed.

c. Organic sulfur is determined by substracting the sum of sulfate sulfur and pyritic sulfur from the total sulfur as determined in accordance with ASTM Method D-3177 (Eschka Method).

2. Reagents

a. Barium Chloride Solution (100 g/litre) - Dissolve 100 g of barium chloride ($BaCL_2 \quad 2H_2O$) in water and dilute to 1 litre.

b. Hydrochloric Acid (2 + 3) - Mix 2 volumes of concentrated HCl (sp.gr. 1.19 with 23 volumes of water.

c. Hydrochloric Acid (1 + 23) - Mix 1 volume of concentrated HCl (sp. gr. 1.19) with 23 volumes of water.

d. Nitric Acid (1 + 7) - Mix 1 volume of concentrated nitric acid (HNO_3, sp. gr. 1.42) with 7 volumes of water.

3. Procedure

a. Sulfate Sulfur

(i) Extraction of Sulfate Sulfur - Weigh to the nearest 0.1 mg about 5 g of thoroughly mixed air-dried coal which as been ground to pass a No. 60 (250- m) sieve, transfer to a 250-ml Erlenmeyer flask, and add 50 ml of HCl (2 + 3). Fit the cold-finger condenser into the neck of the flask, place on the hot plate, and boil for 30 min. Rinse the cold-finger condenser into a flask with HCl (1 + 23) and filter through a medium-texture double acid-washed filter paper into a 400-ml beaker. Transfer the residue to the filter, wash six times with HCl (1 + 23) using a total of about 35 ml, and determine sulfate sulfur in the filtrate as described in (ii) and (iii). The residual coal may be retained for the determination of pyritic sulfur. Discard the residual coal if a separate sample is used for the pyritic sulfur determination.

(ii) Removal of Iron - To the filtrate from (i) add 10 ml of saturated bromine water, cover with a watch glass, and boil for 5 min to ensure that all iron is in the ferric state and to expel excess bromine. Precipitate iron by slowly adding NH_4OH (sp gr 0.90) until a slight excess is present, then add 5 ml more, constantly stirring to coagulate the yellowish brown ferric hydroxide precipitate. Place the covered beaker on the hot plant and boil for 1 min. Filter off the iron precipitate using an ashless, medium-texture filter paper, collecting the filtrate in a 600-ml beaker. Wash the precipitate several times with hot water to which has been added a trace of NH_4Cl and NH_4OH. Retain the filtrate, with washings for determination of sulfur, and the precipitate, with the original beaker, for the determination of nonpyritic iron when a separate sample is used for the determination of pyritic sulfur. If a separate sample is not used, the precipitate may be discarded.

(iii) Final Determination of Sulfate Sulfur - Neutralize the filtrate from (ii) with concentrated HCl (sp gr 1.19) and add an excess of about 1 ml, employing methyl organge as indicator. Heat the solution to boiling and add dropwise, with stirring, 10 ml of the $BaCl_2$ solution. Continue boiling for 15 min and allow to stand for 2 hr. just below boiling. Filter through an ashless paper and wash with hot water until silver nitrate ($AgNO_3$) solution shows no precipitate with 1 drop of the filtrate. Place the wet fiter containing the precipitate of barium sulfate ($BaSO_4$) in a weighed platinum, porcelain, silica, or refractory crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering. Smoke the paper off gradually and at no time allow it to burn with flame. After the paper is practically consumed, raise the temperature to approximately 925°C and heat to constant weight. The value so obtained, corrected for the blank (see (iv)) represents the sulfate sulfur of the coal.

(iv) Make a blank determination following the same procedure and using the same amounts of all reagents as described in (i), (ii), and (iii).

b. Pyritic Sulfur

(i) Transfer the sample obtained from the HCl extraction of sulfate sulfur to a 250-ml Erlenmeyer flask and add 50 ml of HNO_3 (1 + 7). Fit a cold-finger condenser in the neck of the flask, and either boil for 30 min. or let stand overnight at room temperature. Rinse the cold-finger condenser with HNO_3 (1 + 7), filter the contents of the flask through a medium-texture, double acid-washed filter paper, and wash six times with the HNO_3 (1 + 7), collecting the filtrate and washings in a 600-ml beaker. Discard the residual coal on the filter paper and retain the filtrate for determination of iron which is a measure of pyritic sulfur.

(ii) Alternative Method for Determination of Iron by Atomic Absorption - Dilute the filtrate obtained in (i) to 200 ml with water. Transfer a 50-ml aliquot of this solution to a 100-ml volumetric flask and add 10 ml of lanthanum solution (weight of sample may be varied to eliminate aliquot). Dilute to volume with water. Prepare a standard by combining 10 ml of 1000 ppm iron solution and 10 ml of lanthanum solution in a 100-ml volumetric flask and diluting to volume with water. Prepare a blank solution by combining 30 ml of HNO_3 (1 + 7) and 10 ml of lanthanum solution in a 100-ml volumetric flask and diluting to volume with water. Determine absorbances of the blank solution, the standard, and the sample at 372 nm using an air-acetylene flame.

Note 1: The wavelength of 376 nm is chosen for the determination to provide a less sensitive line and wider linear range for the iron absorbance. Linearity exists with concentration in this range for the iron absorbance. Linearity in this range of iron concentration should be checked for each individual instrumental setup and appropriate dilutions made if necessary. Alternatively, the 248.3 nm line may be used.

Note 2: If concentration mode is used and unknown is bracketed, a blank
4. is unncessary.

Calculation

a. Sulfate Sulfur - Calculate the percentage of sulfate sulfur as follows:

Sulfate sulfur, % = [(A - B) x 13.735]/W

where:

A = grams of $BaSO_4$ precipitated,
B = grams of $BaSO_4$ in the blank, and
W = grams of sample used for sulfate sulfur determination.

b. Calculate the percentage of sulfur when the iron determination is made by atomic absorption as follows:

From absorbance:

$$\text{Pyritic sulfur, \%} \quad \frac{C-A}{B-A} = \frac{4.58}{W}$$

where:

A = absorbance of blank,
B = absorbance of standard,
C = absorbance of sample, and
W = weight of sample extracted as selected for sulfate or pyrite sulfur determination.

If the values higher than 5 % pyritic sulfur are obtained, a new sample solution should be prepared from the 20 ml of the filtrate (b (i)) and 10 ml of lanthanum solution, diluted to 100 ml the value obatained on this solution x 2.5 = percent pyritic sulfur.

c. Organic Sulfur - The percentage of organic sulfur is obtained by subtracting the sum of the percentages of sulfate and pyritic sulfur from the percentage of total sulfur as determined by the Eschka method.

5. Precision

a. Repeatability - Results of consecutive determinations carried out on the same sample in the same laboratory by the same operator using the same apparatus should not differ more than the following:

Sulfate sulfur	0.02
Pyritic sulfur, under 2 %	0.05
Pyritic sulfur, 2 % or more	0.10

b. Reproducibility - The means of results of duplicate determinations carried out by different laboratories on representative samples taken from the same bulk sample after the last stage of reduction should not differ more than the following:

Sulfate sulfur	0.04
Pyritic sulfur, under 2 %	0.30
Pyritic sulfur, 2 % or more	0.40

B-III. MODIFIED LECO PROCEDURE FOR TOTAL SULFUR AND CHLORINE DETERMINATION IN COAL

Summary of the Method

A 0.2 g of coal sample is burned at 1300°-1350°C (2370°-2460°F) in a resistance tube furnace. The sulfur dioxide, sulfur trioxide, and chlorine formed are absorbed in a hydrogen peroxide solution, producing sulfuric and hydrochloric acids. The total acid content is determined by titration with sodium hydroxide. The titrated solution was further treated with mercuric oxycyanide (Hg(OH)CN) to provide correction for hydrochloric acid from the total acid content.

Reagents

0.05 N Sodium Hydroxide Standard solution
0.01 N Sulfuric acid standard solution, or prepare by dilution from 0.1 N standard solution

Mercuric Oxycyanide Solution (Hg(OH)CN). Dissolve 0.25g of $HgOHg(CN)_2$ powder in 20 ml distilled water per portion of this reagent. Prepare one portion per sample boat plus four portions for blanks, for each set of samples. Discard this solution if it is not used in 2 or 3 days, into the titration waste container.

NOTE: Mercuric oxycyanide powder is a highly poisonous substance and will explode when touched with a flame or by percussion.

Hydrogen Peroxide 1% Solution. Dilute 100 ml of 30% H_2O_2 with distilled water to 3 liters. Discard this solution down a laboratory sink if it is not used after 2 or 3 days.

Methyl Purple Indicator Solution

Apparatus

Use LECO Model No. 534-500 total sulfur analyzer equipped with a Model No. 571-500 two tube 1.5 KW resistance furnace and a Model No. 517-200 manually operated acid-base titrator.

Procedure

A. Startup

1. Preheat resistance furnace to a temperature of 2460°F (1350°C).

2. Prepare the hydrogen peroxide and mercuric oxycyanide solutions.

3. Place the oxygen baffle in the combustion tube, fill the titration vessel with hydrogen peroxide solution, and adjust the oxygen flow to 1 liter/min.

4. Fill precleaned back-titration burettes with fresh sulfuric acid and sodium hydroxide solutions.

5. Make sure that there is sufficient capacity in the titration waste container to handle the day's wastes.

B. Sample Analysis Sequence

1. Weigh about 0.2 g of sample to the nearest 0.1 mg and spread it in a clay combustion boat.

2. Fill the titration vessel half-full with the hydrogen peroxide solution. Add 10 drops of methyl purple indicator solution and adjust the pH with dilute sulfuric acid (0.01N) until the green color turns gray or else reaches the green-gray transition.

3. Put the boat in the combustion tube so that the center of the boat is four inches from the center of the hot zone and replace the oxygen baffle.

4. After 1-1/2 minutes, push the boat to the center of the hot zone, removing the oxygen baffle only as long as necessary to quickly perform the operation.

5. After about seven minutes of combustion (5-1/2 minutes with the boat in the hot zone), titrate with 0.05 N sodium hydroxide solution until the purple color fades, just short of the endpoint.

6. After 8 minutes of combustion (6-1/2 minutes with the boat in the hot zone) disconnect the rubber hose from the ceramic combustion tube and rinse the rubber hose and the bubbler with distilled water into the titration vessel three times.

7. Reconnect the rubber hose to the combustion tube and complete the sodium hydroxide titration.

8. Add 20 ml of mercuric oxycyanide solution to the titration vessel.

9. Titrate the liberated hydroxyl ion with dilute (0.01N) sulfuric acid.

10. Drain and rinse the titration vessel and remove the boat from the combustion tube.

C. Shutdown

1. For each set of samples, run a dilute sulfuric acid (0.01N) blank in triplicate on the mercuric oxycyanide solution.

2. Reduce the furnace temperature to 1500°F.

Calculation

S = wt.% sulfur in coal, as-determined basis.
A = units of 0.05N sodium hydroxide used (LECO burette "%" units).
B = ml of 0.01 N sulfuric acid used in full determination. C = ml of 0.01 N sulfuric acid used in blank determination for the mercuric oxycyanide solution.
W = sample size in grams.
Cl = wt.% chlorine in coal, as-determined basis.
R = 1.133, if no standards are run with the sample set.

otherwise $\dfrac{\text{known sulfur content of the standard coal}}{\text{average sulfur content by titration of three standard samples}}$

$$S = R \times \frac{0.5}{W} \left[A - \frac{(B-C)}{31.28}\right]$$

$$Cl = \left(\frac{B-C}{W}\right) \times 0.0355$$

Table B1. Leco Acid-Base Analyses versus Eschka Analyses* For Total Sulfur

Run No.	Total Sulfur by Leco[b] (wt.%)[a]	Total Sulfur by Eschka (wt.%)[a]	Total Sulfur Difference (Leco - Eschka) (wt.%)
		RAW COAL	
** B4	1.97	1.54	0.43
B5	1.46	"	-0.08
B14	1.42	"	-0.12
B17	1.48	"	-0.06
B18	1.43	"	-0.11
B19	1.56	"	0.02
B24	1.43	"	-0.11
*** L2	1.56	"	0.02
L3	1.47	"	-0.07
L7	1.64	"	0.1
L9	1.31	"	-0.23
L10	1.43	"	-0.11
L17	0.92	"	-0.62
B11	0.69	0.87	-0.18
B12	0.67	"	-0.2
B26	3.66	3.87	-0.21
B27	0.32	0.47	-0.15
B28	0.69	0.68	0.01
B33	0.63	"	-0.05
B34	0.64	"	-0.04
B29	0.99	1.03	-0.04
B30	0.56	0.87	-0.31
B35	0.79	"	-0.08
B32	2.44	2.15	0.29
L21	0.45	0.56	-0.11
		RAW COAL/HYDRODESULFURIZED	
L42	0.48	0.57	-0.09
L46	2.68	2.43	0.25
		PRETREATED COAL	
B2	1.13	1.22	-0.09
B3	1.1	1.17	-0.07
B4	1.87	1.94	-0.07
B17	1.34	1.39	-0.05
		CHLORINATED/POST-TREATED COAL	
B2	0.63	0.73	-0.1
B3	0.82	0.92	-0.1
B4	1.5	0.92	0.6
B13	0.51	0.56	-0.14
B16	0.88 (0.74)	0.91 (0.79)	-0.03 (-0.05)
B22	0.72	0.88	-0.16
B26	1.32	1.52	-0.2
L31	1.43	0.72	0.71

Table B1. Leco Acid-Base Analyses versus Eschka Analyses* For Total Sulfur

(continued)

Run No.	Total Sulfur by Leco[b] (wt.%)[a]	Total Sulfur by Eschka (wt.%)[a]	Total Sulfur Difference (Leco - Eschka) (wt.%)
CHLORINATED/DECHLORATED COAL (cont'd)			
B38	1.72	1.58	0.14
L29	3.11	2.78	0.33
MPP2	2.04	1.94	0.10
MPP3	2.04	1.91	0.13
L22	1.10	0.77	0.33
L26	0.94	0.63	0.31
L30	0.63	0.61	0.02
CHLORINATED/DECHLORINATED/HYDRODESULFURIZED COAL			
L24	0.76	0.61	0.15
L33	0.69	0.58	0.11
L38	0.22	0.29	-0.07
L39	0.64	0.60	0.04
L40	0.45	0.43	0.02
L41	0.36	0.32	0.04
L43	0.81	0.81	0.0
L44	1.24	1.22	0.02
L45	1.13	1.21	-0.08
L47	1.03	0.99	0.04
L48	0.53	0.55	-0.02
L49	0.78	0.78	0.0

* Colorado School of Mines Research Institute Analyses
** Batch Reactor Experiments
*** Laboratory glassware experiments
**** Mini-Pilot Plant experiments

a. Dry and chlorine free basis
b. Sulfur combusted and preoxidized to $SO_4^=$, Cl^- interface corrected with Hg(CN)OH reagent, resistance furnace method.
c. Coal was dechlorinated at 400, 450 and 500°C before analysis

APPENDIX C

OPERATING PROCEDURE FOR BENCH-SCALE BATCH REACTOR SYSTEM

C-I. OPERATING PROCEDURE FOR CHLORINATOR, FLASH DISTILLATION, AND FILTRATION WASH

I. INTRODUCTION

This standard operating procedure outlines the conditions required for the safe operation of the batch chlorinator and filtration system (Figure 5).

II. OPERATING RULES AND CONDITIONS

Operation of the batch chlorinator and filtration system will be permitted only under the following rules and conditions.

Prior to beginning an experimental run, the following steps must be completed.

1. Make sure all fittings in the batch chlorinator and filtration system are securely fastened.
2. Make sure entire system is completely leak free.
3. A complete description of an experimental run should be available to the operator.
4. Excess chlorine gas should be scrubbed with sodium hydroxide solution.

III. PERSONNEL SAFETY

Personnel operating the batch chlorinator and filtration system should be equipped with:

1. Protective garments such as lab coat and rubber gloves.
2. Eye protection glasses
3. Proper type respiratory equipment such as scott air pack for toxic gases and coal dust.
4. Fire extinguishing equipment should be available in operating condition including water shower.

IV. EQUIPMENT SAFETY

A. CHLORINE CYLINDER

1. Chlorine cylinder and chlorine gas line should be heated to 70 to 80°F.
2. Do not exceed chlorine gas cylinder temperature above 100°F.
3. Do not allow liquid chlorine into batch reactor. Liquid chlorine and coal mixture is explosive.

B. BATCH REACTOR

1. Make sure pressure rupture disc is installed.
2. Do not exceed pressure above 100 psig.
3. Do not exceed temperature above 150°C.

V. EMERGENCY PROCEDURE

1. Leaks detected during a pressure test.

    a. In the drain valve V2.
    Abort the run. Repair the seal.

    b. In flanges and connections.
    Try to close by tightening the connections and screws on flanges. Pressure test again. If leaks still persist, abort the run and repair the seals.

    c. In valves.
    Abort the run. Repair or replace the valve.

2. During the run.

    a. Heating of the charge.

        1. Steam generator failure.
        Abort the run. Repair.

        2. Excessive pressure develops inside the system.

            a) Slow down the steam rate
            b) Abort the run. Stop the steam flow.

    b. During the chlorine addition.

        1. Temperature rises beyond the prescribed limits.

            a) Turn on cooling water to the reactor.
            b) Slow down the rate of chlorine addition.
            c) Close the chlorine tank valve and other chlorine line valves.

        2. Pressure rises beyond the prescribed limits.

        Relieve the pressure by opening valves V3, back pressure regulators by-pass valves V34 and V10. If line filters are plugged, use alternate vent line. Gases will be vented via scrubber. Other safety feature is burst diaphragm which is set to open at 142 psig and release the gases to the atmosphere via venting stack. When either burst diaphragm breaks or pressure relief valve opens stop the flow of chlorine instantly (i.e., close the chlorine tank valve first and then the remaining chlorine valve lines. Vacate the building.

3. Chlorine leaks to outside atmosphere develop.

   a) If small and easily repairable (e.g. by tightening of flange screws or fitting) repair immediately.
   b) When sizeable, stop chlorine flow and try to release the pressure inside the reactor by venting through a scrubber.

VI. OPERATING PROCEDURE

A. START-UP

1. Weigh the slurry tank and both solvent recovery tanks and connect the slurry tank and secondary solvent recovery tank back to the system.

2. Primary solvent recovery tank must not be connected to the equipment at any time except during solvent distillation which has to be conducted at atmospheric pressure only. Close valves V45 and V6.

3. Fill the scrubber with 10 liters of 2N sodium hydroxide solution.

4. Close the drain plug (V2) in the reactor. Make sure that O-ring is seating properly.

5. Close all valves in the system. Note: If pressure check is to be conducted above 80 psig, pressure relief valve has to be readjusted to open at higher pressure.

6. Turn on recorders in the instrument panel.

7. Conduct the pressure check for leaks.

   - Turn on the pressure recorder.
   - Adjust the back pressure valves (V33 and V11) to close at expected operating pressure.
   - Pressurize the reactor with nitrogen via chlorine line. Open the nitrogen tank valve V1, adjust the regulator to 30 psi above expected operating pressure. Open valves V15, V16, V17, V37, V14, and V38.
   - Let the pressure in the reactor equilibrate with the nitrogen pressure. Close the valve V38. Observe the pressure drop inside the reactor over a period of 10 minutes on pressure recorder.
   - Check for leaks around the reactor gasket, drain valve and connections in chlorine line with a soap solution.
   - Open slowly valve V3. Check to see if the pressure in the gas holding tank rises noticeably. If it does, back pressure regulator is open (not sealing). Correct if necessary. Check for leaks in other places by the procedure outlined above.

- Open valve V8 and V9 and check if any flow of gas occurs. This would reveal a small leak in the back pressure regulator V33 and V34.

- Make certain that back pressure regulators V33 and V11 are adjusted to open at 2 to 3 psig higher than the test pressure during pressure check!!
- Close valves V8 and V9. Open the back pressure regulator by-pass V34. Check for leaks in valves V7 to V11 and in connections.
- Close the nitrogen tank valve and valves V15, 16, 17, 37, 14, and 38.
- Slowly release the pressure from the equipment via valve 10.

8. Disconnect the burst diaphragm stack next to the reactor lid and use the port to fill the reactor with 2 kg of ground coal (as is or moistened with water) followed by the required amount of solvent. Weigh coal and solvent to 1 gram on Ohaus balance. Establish moisture content with Ohaus moisture balance. Coal should be 2 kg on dry basis.

9. Close the opening and reconnect the burst diaphragm stack.

10. Purge the equipment with nitrogen at 2-5 psig for 5 to 10 minutes. Open nitrogen tank valve and adjust the regulator. Open slowly valves V15, V16, V37, V14, and V38. Gases will exit via scrubber. Adjust the flow so that bubbling in the scrubber is not too vigorous.

11. Close nitrogen tank valve and valves V15, V16, V37, V14 and V38. Let the pressure equilibrate with outside.

12. Close valves V34 and V10.

13. Make sure you have already adjusted the back pressure regulators 2 to 3 psig above the test pressure.

14. Open valve V4.

15. Turn on the agitator to prescribed stirring rate.

16. Turn on the cooling water to the condenser and gas holding tank. Adjust the flow so that drain doesn't overflow. Cooling water to the condenser comes from the water main A via valve V26 (outer coil), and water main C via valve V31. Cooling water for gas holding tanks comes from water main A via valve V25.

17. Turn on the fans.

B. CHLORINATION

1. Open the steam valves (V22 and V23) and adjust the steam flow so that operating temperature inside the reactor is reached within 20 to 30 min. Then readjust to keep the temperature close to the operating plan. Use indirect steam heating.

2. Vent excess pressure from the reactor by opening back pressure regulators or valves V10 and V34. If line filter is plugged use alternate vent line.

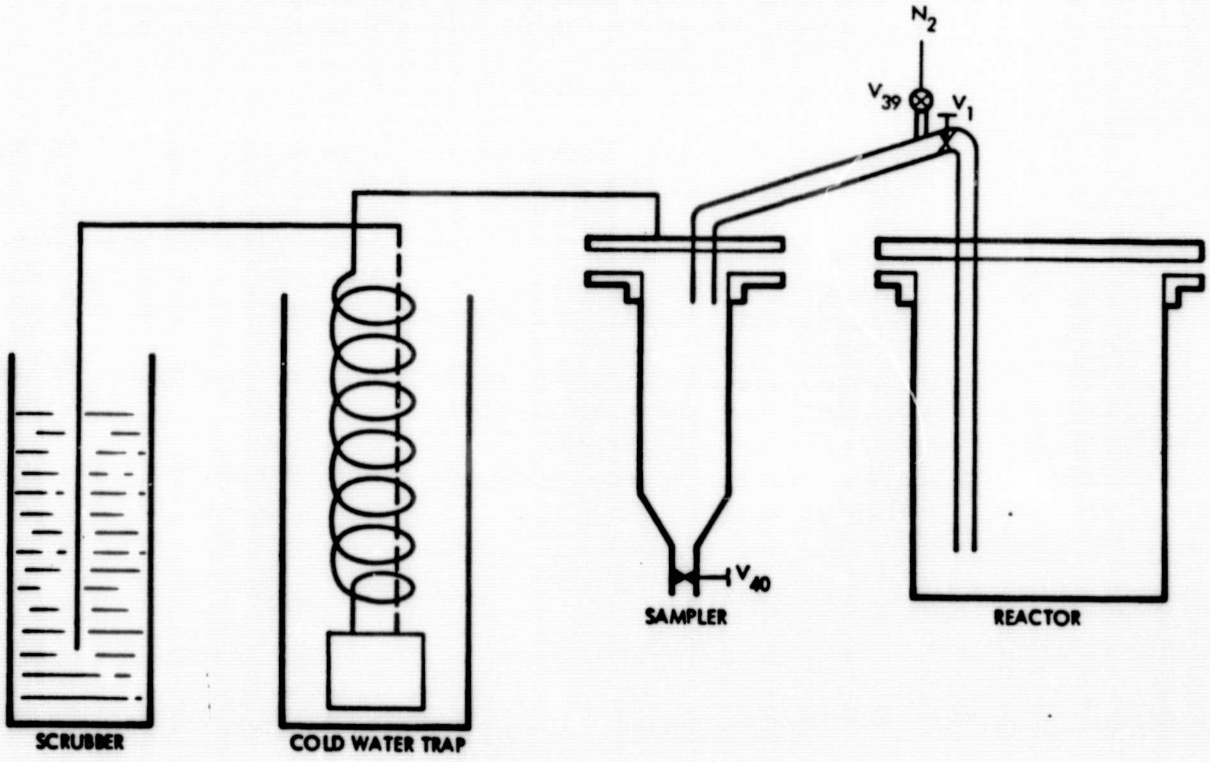
3. Close the steam valves V22 and V23.

4. Open valves V3.

5. Start the flow of chlorine. Open the chlorine tank valve. Adjust the pressure output of the chlorine regulator. Open and adjust valves V37, V14, V38 to reach a prescribed chlorine flow.

6. Keep the temperature at the prescribed operating level. Since the reaction of chlorine with coal is exothermic, cooling should be required at the beginning of the reaction. Close the steam flow (valves V22 and V23). Open and adjust water valve V29 so that enough cooling action is obtained to keep the temperature in prescribed limits. During the later stages of the reaction heating may be required again. This can be accomplished by opening valves V22 and V23. At that point turn off the cooling water (valve V29) to the reactor.

7. At prescribed time intervals withdraw samples of coal slurry by opening the valve V1 in the sampling line. Obtain 50 gram samples as a minimum. Use following procedure:



- Fill scrubber with 2N sodium hydroxide solution.
- Place cooling coil in ice water trap.
- Open valve V_1 to collect sample at prescribed time intervals.
- Open valve V_{39} to purge the system.
- Open valve V_{40} to collect sample in a beaker
- Clean sampler with fresh water.
- Weigh solvent in the trap at the end of the run.

8. At the end of prescribed reaction time shut off the chlorine flow (cylinder valve and valve V14, V37, V38). Purge the chlorine line with nitrogen.

9. Gases in the gas holding tank can be sampled during or at the end of chlorination by attaching a gas sampling cylinder to the end of tubing next to valve V9 and opening valves V8 and V9. Alternately, flex line next to the valve V20 can be disconnected and gas sampling cylinder can be attached at this point. Gas sample can be obtained by opening valve V20.

10. After the chlorine flow was turned off, the pressure in the system has to be equilibrated with atmospheric pressure by venting via a scrubber. Open valves V34 and V10. Valve V10 should be adjusted so that gas flow through the scrubber is not too vigorous.

11. Prepare for solvent distillation.

C. SOLVENT DISTILLATION

1. Pressure is reduced to ambient and maintained at 1 atm throughout the distillation.

2. Add 4 kg of distilled water to the coal-methylchloroform water slurry. Attach the plastic tubing hose leading from compression sprayer to the end of tubing next to the valve V45. Pressurize the sprayer with hand pump and open valve V45.

3. Close valve V45. Disconnect the compression sprayer.

4. Reconnect the line between solvent recovery tank along with solvent trap and valve V5.

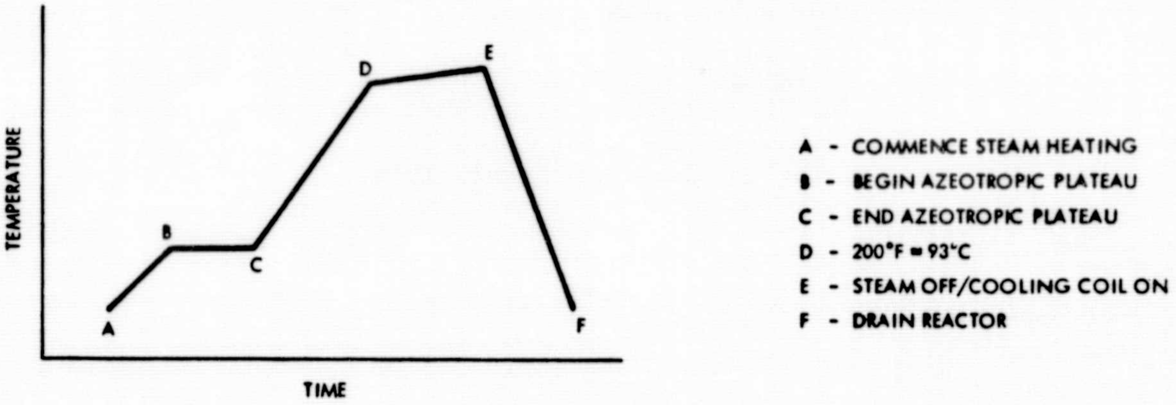
5. The slurry is heated by indirect steam (145°C) injection at a rate of 1400-2000 g/hr (usually 2000 g/hr) until the free water-methylchloroform azeotrope has distilled at 65°C.

6. The temperature in the reactor should be maintained between 90-100°C for about 30 minutes.

7. Allow reactor to cool with the aid of a cooling water coil to 70°C or below.

8. Weigh solvent in both solvent recovery tank and cold water trap.

9. Temperature time profile.



The entire distillation, A-F, required about 170 min, if it started at the usual initial temperature of 46°C. The azeotropic distillation, B-C, took 20 min when it was observed. The cooling time, E-F, ranged from 20 to 40 min. The slurry was easily handled at the drain temperature, usually 48°-68°C, but was as low as 24°C.

D. SHUT-DOWN (Batch Chlorinator)

1. Close the steam flow (valves V22, V23, and V23).

2. Turn on cooling water inside the reactor (open valve V29).

3. Cool the reactor within 20-30 min. to room temperature.

4. Purge the system with nitrogen at no more than 2 psig for 5 to 10 minutes. Vent the nitrogen and other gases through the scrubber.

5. Open sampling valve V1 and disconnect the burst diaphragm stack.

6. Open the drain valve V2 and drain the reactor to slurry tank. While draining turn the agitator slowly down and when the reactor is almost empty, shut it completely. Never let the agitator rotate when stirrer blades are not immersed in the liquid. Vibrations may bend the shaft.

7. Shut down the steam generator. On every second or third run, perform a blowdown.

8. Turn off recorders on instrument panel. Record time, date and run number on recorder chart.

9. Wash the reactor with water via diaphragm stack port. Collect the wash. Do not mix coal in wash water with the new slurry.

10. Prepare for filtration of coal slurry.

E. FILTRATION

1. Clean and weigh the filtrate recovery tank and reinstall it.

2. Clean and reinstall the empty sodium hydroxide scrubber tank.

3. Open V35 and V36 fully.

4. Make sure that the connections and plumbing leading to the filtrate recovery tank and the scrubber stack are tight to a few psi vacuum or pressure.

5. Properly place filter cloth on the top of the coarse mesh support screen.

6. Place filter paper on the top of the filter cloth.

7. Turn on the exhaust blower. Pour the slurry onto filter cloth while closing V36 to the extent necessary to remove water from the coal slurry.

8. When the standing water is gone, sprinkle on, or pour continuously, or pour in batches, 4 liters of water through the coal cake. If the wash water is applied in batches, use at least two.

9. Maintain suction until the cake is dry, but no longer than 20 minutes.

10. Remove cake from filter cloth.

11. Obtain weight and moisture content of cake.

12. Prepare for dechlorination.

F. EQUIPMENT MAINTENANCE NOTES

1. Check the level of grease in the stuffing box of the agitator very often (every run or every second run). If needed add more grease.
2. Never let the agitator turn when blades are not immersed in the liquid. Shaft can bend due to vibrations.
3. Steam generator should have a blowdown for every twenty four hours of operation.

C-II. OPERATING PROCEDURE FOR DECHLORINATOR

I. INTRODUCTION

This standard operating procedure outlines the conditions required for the safe operation of the batch reactor-dechlorinator system (Figure 10).

II. OPERATING RULES AND CONDITIONS

1. Batch reactor-dechlorinator system should be operated in oxygen free environment to avoid possible coal combustion and explosion.
2. All hot surfaces should be properly insulated.
3. System should be leak free.
4. Hydrochloric acid vapor should be scrubbed with sodium hydroxide solution.
5. A complete description of an experimental run should be available to the operator prior to starting the dechlorination operation.

III. PERSONNEL SAFETY

Personnel operating the batch reactor-dechlorinator system should be equipped with:

1. Protective garments such as lab coat and asbestos gloves.
2. Eye protection glasses.
3. Proper type respiratory equipment such as scott air pack for toxic gases and coal dust.
4. Fire extinguishing equipment should be available in operating condition. Water shower available.

IV. EMERGENCY PROCEDURES

1. Controls on the furnace may malfunction and furnace can overheat. Check periodically the control lights, to see if they go ON and OFF. Also, look periodically into the furnace tube. If it starts glowing in any section, check the controls and shut the furnace off.
2. Maintain the nitrogen flow through the pipe while loading and unloading hot coal. Otherwise the coal may catch on fire or explode.

4. Maintain the nitrogen flow through the pipe at all times while the coal is being dechlorinated. Failure to do so may cause fire and/or explosion.

4. In case of fire, use nitrogen flow and/or CO_2 fire extinguisher to smother it. Shut the furnace off.

5. Hot coal which is unloaded from the furnace may also catch on fire while stored in the cartridge. Put the fire down with CO_2 fire extinguisher.

VI. OPERATING PROCEDURE

A. PREPARE THE SCRUBBER

1. Disconnect the recirculating scrubber tank from the system at the two unions, flush with the tank lid.

2. Remove the tank on its dolly to the outside of Building 88.

3. Drain and rinse the tank and the recirculating system, the pump, bypass line, and drain line.

4. Mix 470 g (1.03 lb.) of sodium hydroxide (NaOH) into 23 liters (6.08 gallons) of tap water in the tank. All the powder should dissolve.

5. Retain a sample of about 100 ml of this solution for titration.

6. Close the tank and reinstall it.

B. PREPARE OIL AND TAR TRAP

1. Disconnect oil and tar trap from the system.

2. Clean trap with acetone.

3. Reinstall the trap in the system.

4. Place bucket full of ice cold water underneath the trap.

SET-UP

1. Remove coal containment cartridge from the furnace tube.

2. Install a blank flange at the south end of the furnace tube.

C. PREHEAT

1. Adjust the furnace temperature set points at 400°C.

2. Turn on the furnace at the main breaker.

3. Wait for the furance to equilibrate. The outside surface of furnace tube should reach 400°C within 20 minutes, but temperature uniformity may require about one hour. The heating coils will start to cycle off and on when the outside surface of furnace tube reaches the set temperature.

4. Turn on the tube rotation motor and set the speed to "20" (4 rpm) about 10 minutes before the coal is to be loaded.

D. COAL LOADING-PROVISIONAL PROCEDURE

1. Determine the moisture content of coal before use.

2. Turn on the exhaust system before loading the coal.

3. Be aware of the possible hazards of this operation. They are:

   a. The coal may catch fire.
   b. The coal may evolve a stifling cloud of HCl or vapors within a few seconds of making contact with the hot tube.
   c. A cloud of coal may billow out of the tube due to convection.

4. Pack the coal into the containment cartridge.

5. Start the nitrogen flowing at 10 SCFH.

6. Stop the furnace tube from turning.

7. Insert the coal containment cartridge into the tube furnace and close the flange.

8. Turn on the multipoint recorder. Set the chart speed on slow.

E. DECHLORINATION

1. Turn on the scrubber tank recirculation pump. Make sure its bypass valve is closed at least partially.

2. Restart the furnace rotation. Aim for 4 rpm (setting 20).

F. COOLING AND DISCHARGE

1. 60 minutes after the coal was inserted, shut off the furnace at the main console breaker.

2. Shut off the scrubber recirculating pump. However, maintain the nitrogen flow.

3. Let the tube cool for 30 min and record the time. Stop the rotation.

4. Shut off the temperature recorder.

5. Remove the coal containment cartridge from the furnace.

6. Cool the coal to room temperature while maintaining the nitrogen flow.

7. Shut off the nitrogen flow to the cartridge.
8. Collect dechlorinated coal in the stainless steel beaker.
9. Remove the scrubber tank from the system. Measure the solution volume and take a sample of about 250 ml for titration.
10. Drain the scrubber tank system and rinse it.
11. Disconnect oil and tar trap from the system.
12. Dissolve oil and tar in 50 cc of acetone.
13. Clean oil and tar trap with acetone and reinstall it.

C-III. OPERATING PROCEDURE FOR HYDRODESULFURIZER

I. INTRODUCTION

This standard operating procedure outlines the conditions required for the safe operation of the batch reactor-dechlorinator and hydrodesulfurization system located in the building 88. The operating rules and conditions, and personnel safety instructions outlined in the standard operating procedure No. C-II for the batch reactor-dechlorinator system also apply to the operation of the hydrodesulfurization system (Figure 12).

II. EQUIPMENT AND PERSONNEL SAFETY

1. Before feeding hydrogen in the dechlorinator, make sure that the following tasks have been performed.

   - Hydrogen cylinder, nitrogen cylinder, all control valves, and pressure gauge have been installed outside the building.
   - System is completely leak free. Check it by flowing nitrogen at 3" of positive water pressure.
   - Preheat dechlorinator to specified temperature under nitrogen blanket.

2. All personnel should stay outside the building while hydrodesulfurizing the coal.

III. EMERGENCY PROCEDURES

1. During dechlorination under nitrogen follow standard operating procedure No. C-II.

2. In case of fire during hydrodesulfurization of coal, immediately turn off hydrogen supply valve V_2 and open valve V_1 to feed nitrogen into the system. Wait for 2-3 minutes in order to purge the system with nitrogen. Put the fire down with CO_2 fire extinguisher. Call fire department if situation is out of control.

3. If filter in oil and tar trap is plugged, open valve V_3 to by-pass it.

IV. OPERATING PROCEDURE

1. Dechlorinate coal in nitrogen environment between temperature 400 to 500°C according to standard operating procedure No. C-II for batch reactor-dechorinator. Conduct tasks A to # described under operating procedure.

2. After coal is dechlorinated, increase temperature to from 500 to 700°C while maintaining the nitrogen flow through the dechlorinator.

3. Open valve V_4 and close valve V_5.
4. Turn off exhaust blower.
5. Make sure that dechlorinator is operating at 2 to 3" of positive water pressure.
6. Open valve V_2 to supply hydrogen at 2 to 5 SCFH as specified for the experiment.
7. Close valve V_1.
8. Hydrodesulfurize coal for 1 hr.
9. After hydrodesulfurization is completed, open valve V_1 and close V_2.
10. Completely purge the system with nitrogen for 5 minutes.
11. Follow same cooling and coal discharge procedure described in standard operating procedure No. C-II.

APPENDIX D

OPERATING PROCEDURE FOR CONTINUOUS FLOW MINI-PILOT PLANT

D-I. OPERATING PROCEDURE FOR CHLORINATOR, DISTILLATION, AND FILTRATION-WASH

I. INTRODUCTION

This standard operating procedure outlines the conditions required for the safe operation of the continuous flow mini-pilot plant chlorinator, distillation unit, and horizontal belt vacuum filter (Figures 26, 27).

II. OPERATING RULES AND CONDITIONS

Operation of the continuous flow mini-pilot plant will be under the following rules and conditions.

1. Make sure all fittings in the continuous flow mini-pilot plant are securely fastened prior to beginning an experimental run.
2. Make sure entire system is completely leak free.
3. A complete description of an experimental run should be available to the operator.
4. Excess chlorine gas should be scrubbed with sodium hydroxide solution.
5. Acid containing wastewater should be neutralized with caustic soda before discharge.
6. Personnel working on the mini-pilot plant should follow the safety procedure.

III. PERSONNEL SAFETY

Personnel operating the chlorinator and filtration system should be equipped with:

1. Protective garments such as lab coat and rubber gloves.
2. Eye protection glasses.
3. Proper type respiratory equipment such as scott air pack for toxic gases and coal dust.
4. Fire extinguishing equipment shuld be available in operating condition including water shower.

IV. EQUIPMENT SAFETY

A. Chlorine Cylinder

1. Chlorine cylinder and chlorine gas line should be heated to 70 to 80°F.
2. Do not allow liquid chlorine gas cylinder temperature above 80°F
3. Do not allow liquid chlorine into the reactor. Liquid chlorine and coal mixture is explosive.

B. Continuous Flow Reactor

1. Make sure pressure rupture disc in installed.
2. Do not exceed 100 psig pressure.
3. Do not exceed 150°C temperature.
4. Make sure far end of the reactor agitator shaft is supported by a teflon bushing.
5. Make sure that no carbon steel surface is exposed to the corrosive slurry and wet chlorine.

C. Dry Coal Feeder

1. Make sure coal slurry does not get into the coal feeder hopper.

V. EMERGENCY PROCEDURE

A. Leaks Detected During An Experimental Run

1. In flanges and connections: Try to close by tightening the connections and bolts on flanges. If leaks still persists, abort the run and repair.
2. In valves: Abort the run. Repair or replace the valve.
3. Caused by the corrosion of equipment: Abort the run and repair.

B. Failure to Heat Charge During An Experimental Run

1. Steam generator failure

   - Continue the experimental run only if required temperature can be maintained due to heat released by sulfur and chlorine reaction and solvent distillation is not required. Otherwise abort the run and repair.
   - If solvent distillation is required, abort the run and repair.

C. Overflow During An Experimental Run

1. Check water, solvent, and coal feed rate.

2. Check the rate of slurry discharge. It should be the same as the feed rate. Adjust feed and discharge rate. Discharge excess slurry and continue the run.

3. Abort the run only if slurry gets into the condenser and solvent distillation is required.

D. Chlorine Addition During An Experimental Run

1. Temperature rises beyond the prescribed limits.

   - Turn on cooling water to the reactor
   - Check rate of chlorine addition. Adjust it only if it is higher than required.
   - Turn off steam supply to the reactor.

2. Pressure rises beyond the prescribed limits

   - If caused by the plugging of the line filter, open valve V_{13} and relieve excess pressure via scrubber.
   - If caused by malfunction in back pressure regultor valve V_{14}, open valve V_{13} and relieve excess pressure via scrubber.
   - In case carbon diaphragm burst open due to excess pressure or corrosion, the chlorine gas will be released to the atmosphere via venting stack. Immediately close the chlorine tank valve; turn off water and solvent feed pumps; turn off dry coal feeder and steam generator; leave both slurry valves wide open. Vacate the building.

E. Failure to Feed Dry Coal During An Experimental Run

1. Caused by the backflow of the slurry into the coal feed hopper, abort the run and repair.

2. If feeder screw is jammed, abort the run and repair.

I. OPERATING PROCEDURE

A. Preparation

1. Make sure cooling/heating coil is properly wrapped with graphoil tape and installed in the reactor.

2. Make sure sampling line is cleaned and properly installed in the reactor.

3. Make sure agitator shaft is properly supported by the teflon bushing located at the discharge end flange, impellers and shaft are properly covered with graphoil tape, and impellers are not hitting either cooling coil or sampling line.

4. Close both feed and discharge end flanges.

5. Connect water feed line, solvent feed line, steam feed line, inlet cooling water line, dry coal feed line, instrumentation, and burst diaphragm at the feed end flange.

6. Connect discharge pipe to the distillation unit, sampling ine to the sampler, outlet cooling water to drain, and thermocouple at the discharge end flange.

7. Fill the scrubber with 10 liters of 4N sodium hydroxide solution and install it.

8. Clean and install slurry receiving and solvent recovery tanks.

9. Fill coal feed hopper with coal and close the flange.

10. Fill water feed tanks 1 and 2 with water and solvent feed tank with solvent only if experiment requires.

11. Adjust back pressure regulator valve V_{14} at 3-4 psig. higher than the experimental pressure.

12. Steam Generator

    - Close valve V_2.
    - Open valves V_{30} and V_1.
    - Turn on feed water pump if reactor pressure is above 50 psig.
    - Turn on steam generator.

13. Turn on pressure recorder.

14. Conduct the pressure check for leaks.

    - Make sure back pressure regulator valve V_{14} is already adjusted to open at 3-4 psig. higher than the expected operating pressure.
    - Make sure all valves are closed except for valves V_{30} and V_1 which are installed to feed water to steam generator.
    - Turn on coal feeder and make sure entire line connecting to the reactor is filled with the coal. Do not keep on feeding coal to the reactor. Turn off coal feeder.
    - Pressurize coal feeder at the expected operating pressure by opening nitrogen tank valve and V_3.
    - Pressurize coal feeder at the expected operting pressure by opening nitrogen tank valve and V_3.
    - After coal feeder is pressurize close valve V_3 and nitrogen tank valve.
    - Pressurize reactor, flash distillation unit, condenser, and solvent recovery tank with nitrogen via chlorine line at expected operating pressure. Open nitrogen tank valve V_5, V_6, V_7, and V_8.
    - Let the pressure in the system equilibrate with nitrogen pressure. Close the valve V_4. Observe the pressure drop inside the reactor over a period of 10 minutes on pressure recorder.
    - Check for leaks around flanges, fittings and valves with a soap solution.
    - After pressure check for leaks is completed, slowly open valve V_{13} to depressurize the system.

15. Turn on cooling water to condenser by opening valves V_{16} and V_{17}.

16. Turn on exhaust fans.

B. Mini-Pilot Plant Start-up

1. For experimental runs using water as a solvent.

    - Open valve V_{30} and V_{18} and fill entire reactor with water (Figure 27).

2. For experimental runs using methylchloroform as a solvent.

    - Open valves V_{29} and V_{15} and turn on the metering pump. Fill entire reactor and also flash distillation unit with methylchloroform to the point where slurry level controller is installed (Figure 26).

3. Pressurize reactor, flash distillation unit, condenser, and solvent recovery tank at specified operating pressure by either nitrogen or if required by chlorine gas.

   - Open tank valve.
   - Open valve V_9 and V_{10}.
   - After system is pressurized close valve V_{10}.
   - Release any trapped air inside the reactor by opening vent line valve V_{11}.
   - Close valve V_{11}.

4. Turn on both agitators for reactor and distillation unit.

5. Turn on temperature and pressure recorders.

C. Chlorination and Distillation

1. Water feed.

   Make adjustment to obtain required flow rate.

   - Open valves V_{27} and V_{14}.
   - Turn on the pump.

2. Methylchloroform (solvent) feed.

   Make adjustment to obtain required flow rate.

   - Open valves V_{29} and V_{15}.
   - Turn on the pump.

3. Steam injection to maintain required temperature.

   - For direct steam injection open valves V_2, V_{24}, V_{22}.
   - For indirect steam injection through cooling coil open valves V_2, V_{24}, and V_{21}.

4. Coal Feed.

   - Make feed rate adjustments.
   - Turn on the coal feeder.

5. Chlorine Feed.

   - Open tank valve.
   - Open valves V_5, V_7, and V_8.
   - Adjust chlorine flowrate as specified.
   - If line filter installed after mass flow controller is plugged, open valve V_6.

6. If cooling is required to maintain specified temperature.

   - Close valves V_{24} and V_{22}.
   - Open valves V_{23} and V_{21}.

7. Distillation (required only when methylchloroform is used).

   - Inject steam at a specified flow rate by opening valve V_{25}.
   - Open valves V_{28} and V_{26} and turn on pump No. 2 to inject water at a flow rate equal to the methylchloroform feed rate.
   - Make sure valves V_{16} and V_{17} are open to supply cooling water to the condenser.

8. Slurry Discharge

   - Calculate time frequency of opening and closing of slurry valves by the following procedure.

$$\frac{\text{Holding volume between two slurry valves}}{\text{Volumetric flow rate of slurry}}$$

   - Preprogrammed timer so that discharge rate is same as the slurry feed rate.
   - Slurry collected in the slurry receiving tank before steady-state should not be mixed with the slurry collected after steady-state is achieved.
   - Make sure outlet gases from slurry receiving tank goes through the scrubber, and valve V_{20} is open.

9. Continuously operate mini-pilot plant for at least three hours after steady-state is achieved.

10. Open valve V_{12} every 30 minutes to collect 150 cc of samples in a sampler.

D. <u>Mini-Pilot Plant Shut-Down</u>

1. Install new slurry receiving tank. Do not mix slurry collected during steady-state in the slurry collected during shut-down. Turn off coal feeder.

2. Close valves V_8 and V_5 to stop flow of chlorine.

3. Close valves V_{14} and V_{15} and immediately turn off water feed pump 1 and solvent feed pump. Close valves V_{27} and V_{29}.

4. Turn off cooling water and steam injection by closing valves V_{21}, V_{22}, V_{23}, and V_{24}.

5. Slowly open valve V_{13} to depressurized the system.

6. Allow slurry in the reactor and distillation unit to drain via slurry valves.

7. Turn off water feed pump to distillation unit. Close valve V_{28} and V_{26}.

8. Turn off steam injection by closing valves V_{25} and V_2.

9. Open valves V_{22}, V_{23} and V_{30} to clean the reactor and distillation unit with fresh water.

10. Turn off steam generator and water feed pump.

11. Turn off both agitators.

12. Close valve V_{30}.

13. Purge chlorine line with nitrogen by opening valves V_4, V_5, and V_8.

14. Collect solvent from solvent recovery tank by opening valve V_{31}.

15. Filter slurry collected during steady-state on a horizontal belt filter.

E. FILTRATION

1. Clean and install filtrate recovery tank.

2. Fill caustic solution tank with 10 liters of 5 N sodium hydroxide solution.

3. Pump processed slurry collected during steady-state from slurry tank to the vacuum filter slurry feeder.

4. Turn on the agitator to keep coal in suspension in vacuum filter slurry feeder.

5. Turn on the vacuum pump.

6. Feed slurry at a specified flow rate. If coal feed rate is 2 kg/hr. the slurry feed rate will be 6 kg/hr.

7. Turn on wash water at a specified flow rate. If coal feed rate is 2 kg/hr, the wash water flow rate will be 4 kg/hr.

8. Filtrate will be collected in the vacuum receiving tank. A filtrate level control is installed in the vacuum receiving tank to turn off and on filtrate pump in order to transfer filtrate from vacuum receiving tank to the wastewater tank.

9. Turn on the agitator installed in the wastewater tank.

10. Collect filtrate in the wastewater tank till entire batch of slurry is filtered.

11. Collect filtrate sample for analysis.

12. Determine total volume of filtrate.

13. Transfer sodium hydroxide solution from caustic solution tank to wastewater tank to neutralize filtrate. Check acidity of the filtrate by litmus paper.

14. After wastewater is neutralized, discharge it into the sewer.

15. Collect washed cake in a pan discharged from the top left hand side of the vacuum filter belt.

16. Weigh entire batch of wet cake.

17. Dry this cake overnight in a 160°F oven.

18. Weigh entire batch of dry cake.

19. Use this dry cake for dechlorination.

20. Clean vacuum filter system and turn it off.

F. EQUIPMENT MAINTENANCE NOTES

1. Check the level of grease in the stuffing box of the agitator very often (every run or every second run). If needed add more grease.

2. Never let the agitator turn when blades are not immersed in the liquid. Shaft can bend due to vibrations.

3. Steam generator should have a blowndown for every twenty four hours of operation.

D-II. OPERATING PROCEDURE FOR DECHLORINATOR

I. INTRODUCTION

This standard operating procedure outlines the conditions required for the safe operation of the continuous flow mini-pilot plant dechlorinator (Figure 21).

II. OPERATING RULES AND CONDITIONS

1. Continuous flow mini-pilot plant dechlorinator should be operated in oxygen free environment to avoid possible coal combustion and explosion.

2. All hot surfaces should be properly insulated.

3. System should be leak free.

4. Hydrochloric acid vapor should be scrubbed with sodium hydroxide solution.

5. A complete description of an experimental run should be available to the operator prior to starting the dechlorination operation.

III. PERSONNEL SAFETY

Personnel operating the continuous flow mini-pilot plant dechlorinator should be equipped with:

1. Protective garments such as lab coat and asbestos gloves.

2. Eye protection glasses.

3. Proper type respiratory equipment such as scott air pack for toxic gases and coal dust.

4. Fire extinguishing equipment should be available in operating condition. Water shower is available.

IV. EQUIPMENT SAFETY

1. Before feeding coal in the hot dechlorinator, make sure that system is purged with nitrogen.

2. Do not heat dechlorinator above 500°C.

V. EMERGENCY PROCEDURES

1. Controls on the furnace may malfunction and furnace can overheat. Check periodically the control lights, to see if they go ON and OFF and also temperature recorder.

2. Maintain the nitrogen flow through the pipe and product coal storage drain at all time while the coal is being dechlorinated. Failure to do so may cause fire and/or explosion.

3. In case of fire, use nitrogen flow and/or CO_2 fire extinguisher to smother it. Shut the furnace off.

VI. OPERATING PROCEDURE

A. Prepare Scrubber

1. Disconnect the recirculating scrubber tank from the system at the two unions flush with the tank lid.
2. Remove the tank on its dolly from the tank lid.
3. Drain and rinse the tank and the recirculating system: the pump, bypass line, and drain line.
4. Mix 470g (1.03 lb.) of sodium hydroxide (NaOH) into 23 liters (6.08 gallons) of tap water in the tank. All the powder should dissolve.
5. Retain a sample of about 100 ml of this solution for titration.
6. Close the tank and reinstall it.

B. Prepare Oil and Tar Trap

1. Disconnect oil and tar trap from the system.
2. Clean trap with acetone.
3. Reinstall the trap in the system.
4. Place bucket full of ice cold water underneath the trap.

C. Set-Up

1. Make sure coal feeder, dechlorinator tube, and product coal collection drum have no left over coal from the previous run.
2. Install product coal collection drum.
3. Make sure angle of flights and tube rotation is adjusted to give specified retention time.

D. Preheat

1. Adjust the furnace temperature set points at 400°C.
2. Turn on the furnace at the main breaker.

3. Wait for the furnace to equilibrate. The outside surface of furnace tube should reach 400°C within 20 minutes, but temperature uniformity may require about one hour. The heating coils will start to cycle off and on when the outside surface of furnace tube is reach the set temperature.

4. Turn on the tube rotation motor and set the speed to desired rpm about 10 minutes before the coal is to be fed.

E. Coal Feeder

1. Determine the moisture content of coal before use.

2. Turn on exhaust system before feeding the coal.

3. Start the nitrogen flowing though coal feeder, dechlorinator tube, and product coal collection drum.

4. Turn on the cooling water through coal feeder discharge tube.

5. Turn on the multipoint temperature recorder. Set the chart speed on slow.

6. Start feeding the coal at required rate.

F. Dechlorination

1. Turn on the scrubber tank recirculation pump.

2. Turn on the exhaust system to allow HCl vapor to pass through the scrubber.

3. Make sure hot product coal is collected and cooled in the collection drum which is continuously purged with the nitrogen.

G. Cooling and Discharge

1. After entire batch of coal is dechlorinated, shut off the furnace at the main console breaker.

2. Shut off the scrubber recirculating pump. However, maintain the nitrogen flow.

3. Allow dechlorinator tube to cool. Stop tube rotation.

4. Allow coal in the collection drum to cool while maintaining the nitrogen flow.

5. Shut off the nitrogen flow.

6. Collect dechlorinated product coal, weigh, and store.
7. Remove the scrubber tank from the system. Measure the solution volume and take a sample of about 250 ml for titration.
8. Drain the scrubber tank system and rinse it.
9. Disconnect oil and tar trap from the system.
10. Dissolve oil and tar in 50 cc of acetone.
11. Clean oil and tar trap with acetone and reinstall it.

APPENDIX E

Distribution of Chlorine in Dechlorinated Coal

Mitsuo Oka

July 3, 1980

A series of experiments were performed showing that the residual chlorine (about 1%) in the dechlorinated coal is distributed among three forms of chlorides, HCl, alkyl chlorides (RCl) and aromatic chlorides (ArCl). The percent distribution for these three chlorides is estimated as follows:

HCl	35	5%
RCl	15	5%
ArCl	50	5%

No evidence was found for the presence of Cl_2 or the excess of inorganic chlorides in the dechlorinated coals as a result of chlorinolysis.

1. Treatment with water at room temperature eliminates up to 30% of the chlorine (as HCl) and at reflux temperature eliminates up to 40% of the chlorine (Runs 1-5). This result could indicate that the difference of 10% is due to hydrolysis of RCl under the higher temperature. The remaining 60% of the chlorine is attributed to ArCl. In the water treatment (Runs 2, 4-7), a semi-quantitative analysis of HCl was carried out by the AgCl gravimetric method. The results obtained appear to contain a fair amount of HCl. A similar conclusion can be drawn from the NaOH experiments which indicated 35% HCl, 15% RCl and 50% ArCl (Runs 8-11), assuming that NaOH eliminates HCl at room temperature and hydrolyzes RCl at the higher temperatures. About 67% of the chlorine in the chlorinated coal was removed by NaOH (Run 12), indicating 33% ArCl as compared to 50% in the dechlorinated coal.

2. The THF-H_2O system provided additional support for the conclusions of the first paragraph, i.e., 35% of HCl and 65% RCl and ArCl (Runs 13-16). In the THF-H_2 extraction, about 0.5% of organic material was extracted from the dechlorinated coal and 14% from the chlorinated coal (Runs 17-19). The THF extracts of dechlorinated and chlorinted coal showed an increase in chlorine percentage from 1.02 to 2.50 or from 9.91 to 19.5 respectively, which suggests that THF extracted more chlorinated compounds in both the dechlorinated and chlorinated coals. The HCI, extracted from the dechlorinated coal with THF, was removed during the evaporation of the THF under vacuum. Thus, the HCl does not remain in the THF extracts. Several control tests were carried out to verify the loss of HCl from the THF solutions.

3. The results from MeOH treatment (Runs 20-22) may be explained in terms of partial extraction of HCl since the extraction time was considerably shorter, 5-15 minutes.

4. It is shown from the pyrolysis experiments (Runs 23 and 24) that the 50% of the chlorine which was inert toward H_2O, NaOH or THF, must be a form of ArCl, because it finally decomposed by pyrolysis at 600°C to release HCl, therefore no more residual chlorine was present in the coal. A positive test for HCl was actually observed in the pyrolysis experiments. Although most experiments were performed for a period of 5 hours, a period of 2 hours seemed to be sufficient.

Table E-1

Results of Chlorine Analysis for Dechlorinated and Chlorinated Coals

Run	Coals	Treatment	% Cl(orig)[a]	% Cl (after treatment)[b]
1	dechlorinated	H_2O, r.t., 5 hrs.	1.29	0.93
2	dechlorinated	H_2O, r.t., 5 hrs.	1.29	1.03 (0.11)[c]
3	dechlorinated	H_2O, reflux 5 hrs.	1.29	0.80
4	dechlorinated	H_2O, reflux 5 hrs.	1.29	0.88 (0.19)[c]
5	dechlorinated	H_2O, reflux 5 hrs.	1.29	0.88 (0.20)[c]
6	chlorinated	H_2O, r.t., 5 hrs.	9.91	7.56 (0.87)[c]
7	chlorinated	H_2O, reflux 5 hrs.	9.91	(1.68)[c]
8	dechlorinated	10% NaOH, r.t. 2 hrs.	1.29	0.85
9.	dechlorinated	10% NaOH, 65°C 2 hrs.	1.29	0.69
10	dechlorinated	10% NaOH, 60°C 5 hrs.	1.29	0.66
11	dechlorinated	10% NaOH, reflux 3 hrs.	1.29	0.66
12	chlorinated	10% NaOH, reflux 3 hrs.	9.91	3.25
13	dechlorinated	THF-H_2O(20% H_2O) 50°C, 5 hrs.	1.03	0.66
14	dechlorinated	THF-H_2O(20% H2O) 50°C, 2 hrs.	1.29	0.98
15	dechlorinated	THF-H_2O(40% H_2O) 50°C, 5 hrs.	1.03	0.69

16	dechlorinated	100% THF, reflux, 2 hrs.	1.03		0.71
17	THF extract from dechlorinated coal	reflux, 2 hrs. % extract 0.5%	1.03		2.31
18	THF extract from dechlorinated coal	reflux, 2 hrs. % extract 0.5%	1.03		2.69
19	THF extract from chlorinated coal	reflux, 2 hrs. % extract 14%	9.91		19.5
20	dechlorinated	MeOH wash	0.98		0.88
21	dechlorinated	MeOH wash	1.29		1.04
22	chlorinated	MeOh wash	1.8		1.58
23	dechlorinated	Phyrolysis 600°C, 1 hr.	1.29		0.18[d]
24	dechlorinated	Phyrolysis 600°C, 1 hr.	1.29		0.10[d]

[a] As received from JPL

[b] Analyzed at CSMRI

[c] Analysis of Cl^- from AgCl precipitate

[d] Analysis at Cal Poly indicated that these values are indistingushable from the background, 0%.

APPENDIX F

Analysis and Laboratory Simulation of Coal Sulfur Control, Inc. Process for Coal Desulfurization

The Coal Sulfur Control, Inc. process is described in detail in Reference 1. The process consists of (1) a reactor stage in which a water solution of 0.5 wt.% chlorine is mixed with an equal weight of coal and agitated in an open vessel at 70°F for 25 minutes and (2) the coal slurry is then pumped to a water washer-separator unit in which upwelled water is rising at the rate of 4 inches/minute and the coal slurry is being pumped to the top of the washer-separator. The coal falls through the upwelled water and debris, soil and fine ash particles are carried up with the upwelled water and across a weir to be discharged. (3) the washed coal is discharged from the washer separator, is dumped into a Moyno pump feed hopper for feed to a solid bowl centrifuge. The coal is discharged in a relative dry state, 10-20% moisture, in the centrifuge coal product.

A laboratory simulation of the process in glassware was conducted by JPL. The laboratory equipment schematic of the process is shown in Figure F-1.

The results of laboratory experiments simulating the Coal Sulfur Control, Inc. process with Coals PSOC 282, 219 and a sample of the Dugger, Indiana gob pile coal are included in Table F-1. The indication is that a 10-20% coal desulfurization occurs in the product coal with a small amount of dirt and ash being carried out in the overflow water from the washer-separator. No substantial amount of coal desulfurization was noted in these experiments.

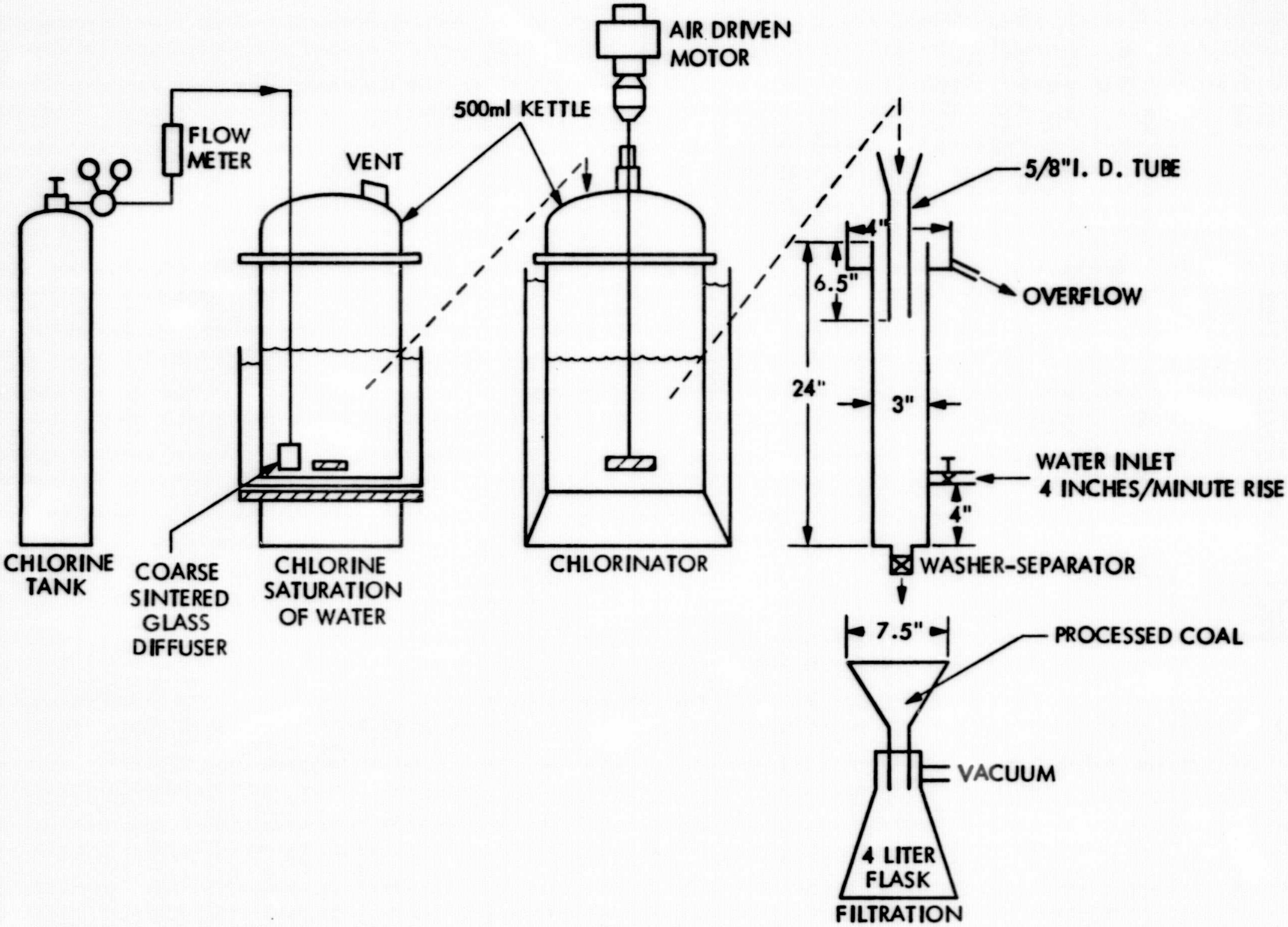


Figure F1. JPL Simulation of Development Energy Group, Inc. Process to Desulfurize and Deash "Gob" Pile Coal

Table F-1. JPL LABORATORY SIMULATION OF COAL SULFUR CONTROL, INC. PROCESS FOR COAL DESULFURIZATION

Run	Coal PSOC No.	Dry Coal Feed[a, b] (Grams)	Chlorine Water Feed		Water Overflow		Cost Slurry Prod.		Raw Coal		Solids Overflow		Product Coal		Sulfur Removal (%)
			(Grams)	Chlorine (wt.%)	Water (Grams)	Solids (Grams)	Water (Grams)	Coal (Grams)	S wt.%	Cl wt.%	S wt.%	Cl Wt.%	S wt.%	Cl wt.%	
1	282	143	150	0.4	6198	2.1	3663	132	1.57	0.13	1.15	0.47	1.42	0.19	10
2	219	144	150	0.53	5953	3.1	3294	138	1.89	0.01	1.6	0.47	1.51	0.36	20
3	Dugger, Ind. Gob Pile Coal	40	50	0.54	-	2.5	-	34	1.77	0.0	0.82	0.18	1.42	0.07	20

a - Wet weight coal is 150 grams except Dugger coal is 50 grams (PSOC 282 coal moisture is 4.7 wt.%, PSOC 219 coal moisture is 3.7 wt.%, Dugger coal is 20 wt.% moisture).

b - Mesh size PSOC 282 is 16x100 mesh, PSOC 219 coal is 100x200 mesh.

Analysis of Coal Samples Obtained from Coal Sulfur Control, Inc. Demonstration of Coal Desulfurization Process on June 24, 1980 (Gob Pile Coal Obtained from Dugger, Indiana)

Samples of the Dugger, Indiana Gob Pile Coal, product coal obtained from the centrifuge and overflow solids from the washer-separator were obtained during the demonstration of the Coal Sulfur Control, Inc. process described in detail in Reference 1. The raw coal and centrifuge product coal were analyzed by JPL and DOE for total sulfur. The JPL analysis was carried out with a Leco acid-base unit. A more extensive analysis was carried out by the Colorado School of Mines Research Institute Analytical Services laboratory. The analyses included sulfur forms, proximate, ultimate and ash composition for the raw and product coals and the overflow solids from the washer-separator unit. The data are recorded in Tables F-2 and F-3.

The total sulfur analysis of the raw and product coal by DOE, JPL and CSMRI indicated a total sulfur content in the raw coal of 1.78-1.77 wt.% and in the product coal of 1.60-1.84 wt.%, indicating no total desulfurization. The sulfur forms analysis by the CSMRI indicated that the raw coal had a 0.64 wt.% sulfate content and the product coal had a 0.26 wt.% sulfate content, indicating a substantial sulfate reduction due to the washing process, as would be expected. The organic sulfur content however, increases from 1.05 wt.% in the raw coal to 1.54 wt.% in the product coal. This is a consequence of the ash reduction from 27.6% in the raw coal to 9.32 wt.% in the product coal. The proximate and ultimate analyses of the raw and product coal reflect the decrease in ash of the product coal relative to the raw coal. Analysis of the ash between the raw and product coals, Table F-3, shows no substantial difference in composition. The ash composition is reported as the oxides as a convenient means of reporting and does not reflect that the oxides exist as represented. The pyritic sulfur content is less than 0.05 wt.% in both the raw and product coal. This reflects the aging and air oxidation of the pyrites to the sulfate which can be easiy washed out by dilute hydrochoric acid.

In summary, the Coal Sulfur Control, Inc. process appears to be a coal washing process that promotes deashing and sulfate sulfur removal as would be expected from a washing process. With gob piles of coal that have been standing for years it would be expected that the majority of pyritic sulfur was converted to sulfate sulfur and could be removed by an acid wash.

Table F-2. Analysis of Raw Coal, Product Coal and Waste Solids Overflow from Coal Sulfur Control, Inc. Demonstration (June 24, 1980) (Gob Pile Coal obtained from Dugger, Indiana).

Sample	Sulfur Forms						Proximate (wt.%)				Ultimate (wt.%, dry basis)					
	Sulfate (wt.%)	Pyritic (wt.%)	Organic (wt.%)	Total CSMRI (wt.%)	Total JPL wt.%	Total DOE Wt.%	Moisture (wt.%)	Dry Basis Vol-atiles	Dry Basis Fixed Carb.	Dry Basis Ash	C	H	S	N	CL	O (by diff)
Raw Coal	0.64	0.05	1.05	1.74	1.77	1.68	18.6	27.8	44.6	27.6	54.0	3.46	1.74	0.80	<0.1	12.3
Product Coal	0.26	<0.05	1.54	1.80	1.84	1.60	19.4	34.8	55.9	9.32	70.1	4.71	1.80	1.24	0.21	12.6
Waste Solids Overflow	-	-	-	-	-	-	33.5	21.1	34.1	44.8	38.5	2.26	1.07	-	0.93	-

Table F-3. ASH ANALYSIS - GOB PILE COAL, DUGGER, INDIANA (REPORTED AS OXIDES)

Sample	Ash Composition (wt.%)									
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	TiO_2	SO_3
Raw Coal	62.1	20.9	5.33	1.66	0.56	0.47	2.47	0.10	1.15	2.41
Product Coal	61.8	23.3	4.7	0.40	0.61	0.36	2.82	0.14	1.34	0.43

APPENDIX G

SUPPORTING COAL DESULFURIZATION RESEARCH

BY

DR. WILLIAM MUELLER

SEPTEMBER 22, 1980

The following is a report on work done on coal to date. Three things have been tried in connection with coal desulfurization. These are: 1) electrolytic desulfurization via reactive intermediates; 2) chlorination using supercritical CO_2 as a reaction medium; and 3) solvent swelling of coal, followed by replacement of the swelling solvent with a solvent inert to chlorine, and chlorination of the resultant mixture. These experiments were tried to determine whether electrolytic oxidation, a well-established industrial process, might provide an advantage over other processes in removal of sulfur from coal, and also to see whether supercritical fluid media or solvent swelling would provide better access to reactive sites in the coal structure. These experiments are detailed below.

Electrolysis of Coal Suspensions

Since chlorine is made by electrolysis of sodium chloride, it was decided to generate chlorine or other oxidizing species directly from electricity, thereby avoiding the need to produce and subsequently consume chlorine. Persulfate salts are also produced commercially via electrolysis, and the possibility of using persulfate generated in situ was briefly examined. Finally, the use of sodium methoxide in methanol was investigated. Methanol is reported to swell coal, and anodic oxidation of methoxide produces methoxyl radical, which can react analogously to chlorine radical in a number of addition reactins. Methoxyl radical might be expected to dimerize on the electrode, however the dimethyl peroxide thus formed would be expected to be reactive toward sulfur atoms.

The experimental apparatus consisted of a glass beaker with a platinum foil anode and stainless steel cathode, a magnetic stirrer, and a rectifier. The following experiments were performed:

1) PSOC 276 coal (60g) was suspended in 1000ml of a solution of 10 wt% NaCl in water. The mixture was electrolyzed at room temperature for 6 hours at a voltage of 4 volts and a current density of about 0.25 amps/in^2. Production of chlorine was tested with starch-iodide reagent. At first chlorine was taken up rapidly; the experiment was run until a excess of chlorine persisted for 1 hour. The pH under these conditions was initially neutral and became slowly alkaline as reaction proceeded. At these conditions of pH, little or no corrosion towards steel would be expected. The coal was filtered, washed with 6N HCL, and dried in vacuum and then at 80°C for 20 hours. Net recovery was 56.7g (Sample No. 346-2-20A).

2) The above experiment was repeated at 60-70°C at 6.0V and about 0.7 amps/in^2 for 20 hours to exhaustively chlorinate the coal. After washing and drying as above, 54g of coal (90%) were recovered (Sample No. 346-2-20D).

3) PSOC 276 coal (60g) was electrolyzed in 50% aqueous ammonium bisulfate (300ml) at 4V and 0.25 amps/in^2 for 20 hours. After washing and drying, 55.9g were recovered.

4) Same as 2) above except the mixture was not heated, and the pH was set at 9.5-10 with sodium carbonate. Under these conditions the chlorine produced is converted to hypochlorite. Hypochlorite is not as relative with carbon compounds as chlorine, and would be expected to show increased selectivity toward sulfur (Sample No. 346-2-20E).

5) PSOC 276 coal (60g) was suspended in a solution made by adding metallic sodium (35g) to methanol (300ml). Electrolysis was for 20 hours at 6V and 0.7 amps/in^2. (Sample No. 346-2-20C).

Analytical results are tabulated below.

Analytical Results for Electrolyzed PSOC 276 Coal

Process	Sample	Total	Organic S	Pyritic S	Sulfate S	Approx S Removed,% of initial S
	Untreated	3.87	1.17	2.63	0.06	--
1	346-2-20A	3.09	1.28	1.81	<0.05	20
3	346-2-20B	3.62	1.40	2.22	<0.05	6
5	346-2-20C	3.06	1.12	1.94	<0.05	20
2	346-2-20D	2.33	1.37	0.96	<0.05	40
4	346-2-20E	3.03	1.53	1.50	<0.05	20

The results basically show various degrees of removal of pyritic sulfur. The variation in organic sulfur content, 40%, is within the variation found for analysis of a single sample. Lowest total sulfur is found for 346-2-20D, the only sample chlorinated at elevated temperatures. This result is essentialy the same as that found for chlorination of coal in water at 60°C using chlorine from an external source. Processes 4 and 5 may result in 40% or more S removal if the temperature is increased.

Chlorination Using Supercritical CO_2 as Reaction Medium

Experimental apparatus consisted of an Autoclave Engineers Magnedrive Autoclave of about 300ml. capacity and 10,000 psi working pressure capability, and an Aminco high pressure (10,000 psi normal) compressor. The autoclave was provided with a gauge and inlet and outlet valves. Experiments were conducted at about 35-40°C and 8-10K psi.

The procedure was as follows:

Twenty grams of powdered coal were placed in a fine mesh stainless steel basket, which was then placed in the autoclave. The autoclave was sealed and a high purity chlorine was added to the desired pressure through the bleed valve. The bleed valve was closed and carbon dioxide was pumped into the autoclave via the inlet valve until the internal pressure was about 10K psi. (Critical point constants for CO_2 are 31°C and 1073 psi). Reaction was allowed to proceed for about 1 hour, the pressure was reduced to atmospheric by opening the bleed valve. The product was removed, heated for an hour with 10% sodium carbonate to hydrolyze any active chlorine, washed with distilled water, and dried.

Sample descriptions are as follows:

1) PSOC 219 coal, 100-200 mesh, treated with SCF CO_2, no chlorine.
2) Same as 1), treated with a mixture of SCF CO_2 and 20g 1,1,1-trichlorethane.
3) PSOC 219 treated with 0.9g Cl_2 in SCF CO_2.
4) Same as 3), treated with 1.9g Cl_2 in SCF CO_2.
5) Same as 3), treated with 3.2g Cl_2 in SCF CO_2.

During the workup, it was noticed that considerable colored matter was extracted from sample 5. Leco total sulfur analyses are tabulated below.

Total Sulfur Content of Samples Treated with SCF CO_2

Sample	Sample Post Treatment	% S	%Cl
1	none	2.66	0.18
1	Pyrolyzed @ 400°C	2.34	0.06
2	none	2.02	0.14
2	Dechlorinated @ 400°C	1.06	0.08
2	"	1.01	0.03
3	"	1.01	0.44
4	"	1.28	0.40
5	"	1.12	0.28

Examination of the table reveals some interesting results. Samples 2, 3, 4, and 5 have essentially the same sulfur content, however the chlorine content of chlorinated samples is higher than for unchlorinated, despite similar sulfur contents. It appears that a simple physical process, i.e., extraction of coal with trichloroethane in SCF CO_2, can remove 60% of the coal sulfur content. Mole ratios of Cl:S for samples 3, 4, and 5 are 1.6, 3.4 and 5.7 respectively. The effect of washing with dilute sodium carbonate has not been examined. The data may serve to indicate the importance of the physical state of the coal to any chemical treatment.

Solvent Swelling and Subsequent Chlorination

PSOC 219 coal (20g, 100-200 mesh) was suspended in dimethylsulfoxide (DMSO, 50ml). The temperature increased slightly, and after a few minutes a semisolid gel was formed. Additional DMSO (50ml) was added; the entire volume did not gel, and the gel volume was about twice the dry volume of the original coal. 1,1,1-Trichloroethane was added in 25ml increments at intervals of at least 4 hours until the solvent ratio was DMSO:MeCCL$_3$, 25:75. At this point the coal was filtered, immediately covered with pure MeCCL$_3$, and allowed to stand overnight. The mixture was filtered, again immediately covered with fresh MeCCL$_3$, and equilibrated for 18 hours. The swollen coal volume remained at about twice the original. MeCCL$_3$ does not appreciably swell coal, however by use of this solvent exchange technique it is possible to obtain coal swollen by a solvent that is inert to chlorine.

The swollen coal was placed in a 3-neck flask equipped with reflux condenser, chlorine sparge tube, and sample removal port. The mixture was heated to reflux (74°C), chlorine was added at a rate such that excess was present, and samples were removed at periodic intervals.

Results are tabulated below:

Chlorination of Swollen Coal Samples#

Time (min.)	% S	% Cl
0	1.95	0.51
0 dechlorinated	2.32	0.66
10	2.32	1.14
10 dechlorinated	2.41	1.09
20 dechlorinated	1.93	1.55
30	1.99*	2.90
30 dechlorinated	5.09*	3.94
60	4.10	2.71
60 dechlorinated	4.10*	1.72

Untreated PSOC 219 coal contains 2.15% sulfur and 0.12% Cl.

* The indicator color became very pale, though the colors didn't change hue, while the sample burned.

These results appear anomalous in that no desulfurization occurs, and in fact an increase in sulfur content is shown by some samples. This being so, these results probably do not merit serious consideration in the absence of further verification.

Conclusions

It is possible to chlorinate coal under conditions approximating those used to produce chlorine. Possible advantages of such a process versus chlorination by previously produced chlorine include not having to handle chlorine, noncorrosive reaction conditions, use of byproduct caustic to hydrolyze S-Cl bonds and remove HCl, and production of byproduct hydrogen which might be added to the coal. If chlorination appears to be a viable method for sulfur removal, a process variation of this type may be worth investigation.

The indicated 60% removal of sulfur from PSOC 219 coal using supercritical CO$_2$ and MeCCL$_3$ needs to be confirmed. Results of the coal swelling experiment need further confirmation before any interpretation is warranted.