JPL PUBLICATION 80-15

(NASA-CR-163152) COAL DESULFURIZATION BY LOW TEMPERATURE CHLORINOLYSIS, PHASE 2 Final Repo:t (Jct Propulsion Lab.) 146 p HC A07/MF A01

N80-24464

Unclas

G3/28 20945

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January 15, 1980

Prepared for

U.S. Department of Energy

Through an agreement with

National Aeronautics and Space Administration

by

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

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Coal Desulfurization by Low Temperature Chlorinolysis Phase II

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COAL DESULFURIZATION BY LOW TEMPERATURE CHLORINOLYSIS - PHASE II

ABSTRACT

Coal desulfurization by low temperature chlorinolysis was conducted by the Jet Propulsion Laboratory, California Institute of Technology. An engineering scale batch reactor system was constructed and operated for the evaluation of five high sulfur bituminous coals obtained from Kentucky, Ohio and Illinois. Forty-four test runs were conducted under conditions of 100 x 200 mesh coal, solvents - methylchloroform and water, 60-130°C, 0-60 psig, 45 to 90 minutes and gaseous chlorine flow rate of up to 24 SCFH. Sulfur removals demonstrated for the five coals were: maximum total sulfur removal of 45-66%, pyritic sulfur removals of 71-95% and organic sulfur removal of 46-89% (4 of 5 coals with methylchloroform) and 0-24% with water. In addition, an integrated continuous flow mini-pilot plant was designed and constructed for a nominal coal feed rate of 2 kilograms/hour which will be operated as part of the follow-on Phase III program. Equipment flow sheets and design drawings are included for both the batch and continuous flow mini-pilot plants.

PREFACE

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

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FOREWORD

This is the Final Report for Phase II of the Coal Desulfurization by Low Temperature Chlorinolysis project conducted by the Jet Propulsion Laboratory under DOE Interagency Agreement No. ET-77-I-01-9060 with NASA for the period October 1, 1978 through September 30, 1979. The reported work covers the design, construction and operation of a batch reactor system for testing of 5 coals at 2 kilograms per batch and the design and construction of a continuous flow mini-pilot plant for operation at 2 kilograms coal per hour. JPL Proposal No. 70-1222 describes the follow-on Phase III effort for continued operation of the batch reactor for testing of additional coals and operating conditions as well as the operation of the continuous flow mini-pilot plant.

The work described in this report involves the inventions on 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.

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INTRODUCTION

JPL initiated the development of the chlorination process for coal desulfurization in 1976 under an internally funded research program. The preliminary experimental work on Illinois No. 6 bituminous coal with a total sulfur content of 4.77 weight percent and approximately equal amounts of organic and pyritic sulfur demonstrated 70% organic sulfur reduction, 90% pyritic sulfur reduction and 76% total sulfur reduction (Ref. 1). Laboratory scale research sponsored by the U.S. Bureau of Mines and Department of Energy was then conducted on 12 bituminous, sub-bituminous and lignite coals obtained from eastern, midwestern and western states. Ten of the coal samples for the laboratory work were obtained from the Penn State Coal Bank and two from the Pittsburgh Mining Technology Center of DOE. The laboratory scale operation was conducted on 100 gram coal samples contained in a 500 ml stirred flask using methylchloroform, carbon tetrachloride and tetrachloroethylene solvents with addition of 30 to 70% water (dry coal basis) at atmospheric pressure and temperatures of 65 to 100°C. Coal was generally at -100 to +200 mesh with 2 parts of solvent to 1 part coal. Gaseous chlorine was injected into the coal slurry by means of a fritted glass diffuser. The laboratory results indicated that half of the coals had over 60% total sulfur removal, over 50% organic sulfur removal and over 70% pyritic sulfur removal. Trace element removals of 50 to 90% accompanied the coal desulfurization. An accompanying engineering cost analysis indicated an overall process cost of $13 to $19 per ton for PSOC 219 coal containing 2.56 weight percent of total sulfur. A detailed representation of the work is provided in References 2 and 3.

The Phase II program, reported here, is a follow-on to the laboratory scale activity. The Phase II program was designed to conduct batch reactor testing in bench-scale equipment capable of engineering scale-up and with provisions for operation above atmospheric pressure and at accompanying higher temperatures than employed in the laboratory scale operation. The scale of operation was also increased from the 100 gram laboratory scale to 2 kilograms of coal per batch. Operation at increased temperatures and pressures was thought to provide a means for increasing coal desulfurization levels above that obtained in the laboratory scale operation.

The highly corrosive nature of the coal slurry with attendant chlorine HCl and H_2SO_4 raised serious questions on the availability of suitable construction materials for the chlorination reactor. A consideration of exotic metals such as tantalum proved to be inordinately expensive. Consultation with Pennwalt Corporation and Stebbins Engineering and Manufacturing Co. decided JPL on the use of acid-resistant brick and mortar for reactor construction. Brick and mortar immersion tests conducted in Phase I under chlorination operating conditions provided a selection of brick and mortar suitable for reactor construction. Reactor designs were carried out by both Pennwalt Corporation and Stebbins Engineering and Manufacturing Co. for the Phase II program.

Looking ahead in the development of the coal desulfurization process, a decision was made to carry out a parallel effort to the batch reactor program for design and construction of a mini-pilot plant for continuous flow operation. The continuous flow reactor design has brought to the fore, as expected, a great many engineering considerations that are not encountered in the batch reactor operation. The mini-pilot plant has been designed, and constructed and is available for operation in the next phase of the program.

SUMMARY

This represents the Final Report for Coal Desulfurization by Low Temperature Chlorinolysis - Phase II conducted by the Jet Propulsion Laboratory, California Institute of Technology at Pasadena, California under DoE Interagency Agreement No. ET-79-I-01-9060 with NASA for the period October 1, 1978 to September 30, 1979.

The Phase II activity consisted of:

(1) design, construction and operation of an engineering scale batch reactor system for desulfurization of 2 kilograms of coal per batch ar

(2) design, construction and installation of a continuous flow mini- pilot plant for coal desulfurization at 2 kilograms per hour.

Engineering Scale Batch Reactor

The engineering scale batch reactor system was constructed to include an acid-resistant brick-lined reactor, reflux condenser, solvent recovery tank, gas holder, vacuum filter-spray wash and electrically heated rotary tube dechlorinator.

Forty-four test runs were conducted with five bituminous coals from Kentucky, Ohio, and Illinois. The batch reactor system provided a twenty fold scale-up to 2 kilograms of coal from the previous Phase I laboratory scale experiments of 100 grams. Chlorination conditions were expanded to include reaction temperatures from 60 to 130°C, pressures from 0 to 60 psig and increased chlorine flowrates to 24 SCFH. Additional chlorination condition changes included the added use of water in lieu of methylchloroform as a solvent and a reduction in total reaction time to 45 minutes with the corresponding decrease in total chlorine feed to the coal. A separate hydrolysis stage (used in laboratory scale experiments) following the chlorination was eliminated with substitution of a spray water wash of the coal filter cake to displace the mother liquor from the coal. Coal dechlorination was scaled up from the 2-4 gram sample contained in a 1-inch diameter quartz tube (Phase I) to a 5-inch diameter by 5-feet long, 304 S.S. rotary tube contained in a Lindberg electric furnace with capacity for two kilograms of coal, representing a 500-1000 fold scale-up.

Operation of the chlorinator was beset by severe corrosion-erosion problems of exposed stainless steel surfaces which were resolved by teflon cover of the metal surfaces. The acid-resistant brick and mortar construction of the chlorinator showed no attack whatsoever and appears to be totally suitable for this service. Gaseous chlorine injection into the coal slurry required some testing and development of diffuser elements to provide good chlorine dispersion without plugging with coal tar. Teflon tubing drilled with 1/32-inch holes for chlorine dispersion proved to be satisfactory. The complexity of the batch reactor operation with a continuous inflow of gaseous chlorine and rapid exothermic reaction provided some difficult control problems for maintaining pressure, temperature and chlorine flow rates at prescribed levels. As a consequence, a substantial number of the early runs were obtained at other than optimum or prescribed operating conditions for achieving maximum coal desulfurization. Improvements in operating procedures should reflect an overall improvement in desulfurization results.

For the five bituminous coals tested, maximum desulfurization levels achieved were 52-63% with methylchloroform and 45-66% with water, somewhat less than comparable laboratory scale tests. Pyritic sulfur removals were high at up to 71-95% with both methylchloroform and water. Four of the five coals showed high organic sulfur removals, up to 46-89% for individual coals with methylchloroform and up to 24% with water. Despite reduced organic sulfur removal with water, water shows considerable promise in achieving competitive total desulfurization levels to that achieved with methylchloroform, while affording a substantial process cost advantage over the methylchloroform.

High organic sulfur removal remains a distinctive characteristic of the chlorination process. Many competitive chemical coal cleaning processes remove only pyritic sulfur or at best 20% of the organic sulfur, thus limiting their potential for total sulfur removal. The high organic sulfur removal achieved in the chlorination process when combined with a high level of pyritic sulfur removal affords the promise of achieving sulfur compliance levels for high sulfur bituminous coals.

Thermal dechlorination was found to increase desulfurization by 4-11% over that obtained in the chlorination. A second stage of chlorination increased desulfurization by over 10% of that achieved in the single stage (i.e., before thermal declorination). Large coal particle sizes in the range of -1/8 inch to +100 mesh showed 5-26% lower desulfurization levels than -100 to +200 mesh particles.

Even smaller particle sizes may provide increased levels of desulfurization. Changes in conditions of temperature, pressure and chlorine flowrate were not found to be significant influences on the level of desulfurization. An apparent conclusion from the previous observations is that the chlorine concentration in solution (in either methylchloroform or water) under the chlorinator operating conditions is more than sufficient to sustain the desulfurization reaction, and that desulfurization is controlled by mass transfer and/or reaction kinetics within the coal particle rather than in the bulk slurry solution. A spray water wash of the coal vacuum filter cake was sufficient to consistently reduce the sulfate content in the coal to less than 0.05 wt. %.

Thermal dechlorination at 400°C and 30-60 minutes generally removed better than 90% of the residual chlorine in the coal. The objective is to consistently achieve a level of $\sim$ 0.1 wt.% residual chlorine, which has been achieved in some laboratory scale runs. Coal analyses of the raw and processed coal showed a reduction in volatile matter of 8-15 wt.%, a corresponding increase in fixed carbon, ash reduction of 1-4 wt.%, a relative increase in carbon of 3-6 wt.%, a hydrogen decrease of 1-2 wt.% and heating value losses in the range of 0-1200 B.t.u./lb. Trace elements arsenic and mercury showed substantial reductions of 50-60 and 80%, respectively. Elemental analyses of the ash in the five coals showed a reduction of 43-75% iron and 35-86% calcium after processing. Chlorinator gas analyses after chlorination showed only slight amounts of chlorinated hydrocarbons in the gas phase indicating only slight chlorine side reactions with the coal slurry which would lead to a loss of coal.

Material balances for 41 runs across the chlorination, solvent distillation and coal filtration - wash indicated a material accounting of raw coal of 100 $\pm$ 3%, organic coal fraction - 99.3 $\pm$ 3%, ash - 114%, sulfur - 94%, chlorine - 86%, methylchloroform - 83 $\pm$7%. The high organic coal fraction recovery demonstrates that no significant amount of coal is lost in the chlorinator from either chlorination or oxidation reactions of coal. The high ash recovery is attributed to the severe corrosion of exposed metal surfaces and material test coupons that occurred in the chlorinator and were recovered in solution. Chlorine and methylchloroform losses were largely attributed to sample taking and vapor losses from the system. Methylchloroform recovery was improved in the later stages of operation, up to 98%, by added cooling of the volatile solvent before discharge to the recovery tank to minimize vapor losses. Coal recovery across the dechlorinator was poor at 88 ±5%. Losses were largely mechanical handling losses in charging and removing coal from the dechlorinator. Attendant chlorine recoveries were between 91-95%.

Future work on the batch reactor under Phase III will investigate additional high sulfur coals and improved operating conditions including coal pretreatment as a means of improving coal desulfurization to achieve EPA compliance levels and to improve the understanding of mass transfer and chemical reaction limitations in the chlorination process for coal desulfurization. A parametric investigation will be conducted of the dechlorination process in order to achieve acceptable levels of dechlorination, namely residual chlorine levels of ∿ 0.1 wt.%.

Equipment descriptions, operating procedures, experimental data and test results follow in Part I - Bench-Scale Batch Reactor System for Coal Desulfurization by Chlorination.

Mini-Pilot Plant

The continuous flow mini-pilot plant has been designed and constructed to operate engineering scale equipment in integrated fashion at a nominal coal feed rate of 2 kilograms per hour. Operating conditions are 0-100 psig, 50-150^{o}C, gaseous chlorine flows in slight excess of stoichiometric requirements for coal desulfurization, solvent/coal ratios of 2/1 and -40 to +200 mesh coal feed. The chlorination unit is a pipeline type reactor constructed of acid resistant brick and mortar with design and fabrication by Stebbins Engineering and Manufacturing Co. Exposed metal surfaces will be protected by Teflon to resist the severe corrosion of stainless steel experienced in the batch reactor.

Major equipment components include: a dry coal storage hopper and screw feeder, solvent and water metering pumps, acid resistant brick-lined chlorinator equipped with a Chemineer agitator, flash distillation unit for solvent separation from the coal slurry, reflux condenser, solvent recovery tank, horizontal belt vacuum filter and water spray wash, electrically heated dechlorinator, product coal storage hopper and caustic scrubber for HCl off gases. Equipment specifications, drawings, and operating procedures are included in Part II - Continuous Flow Mini-Pilot Plant for Coal Desulfurization by Chlorination. Operation of the mini-pilot plant is scheduled as part of the follow-on Phase III program.

PART 1

BENCH-SCALE BATCH REACTOR SYSTEM FOR COAL DESULFURIZATION BY CHLORINATION

EQUIPMENT

Bench-Scale Batch Reactor System

The bench-scale batch reactor system is depicted, Figure 1a with Instrumentation and Controls in Figure 1b. 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 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-feet long rotary tube with a capacity of 2 kilograms of coal.

Reactor

The batch reactor is depicted, Figure 2a with the condenser, Figure 2B and gas holder, Figure 2c. 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 (Ref. 2). 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 reactor head is removable and consists of a 150 pound, 18-inch blank pipe flange drilled to accommodate a centrally mounted agitator unit and port openings for

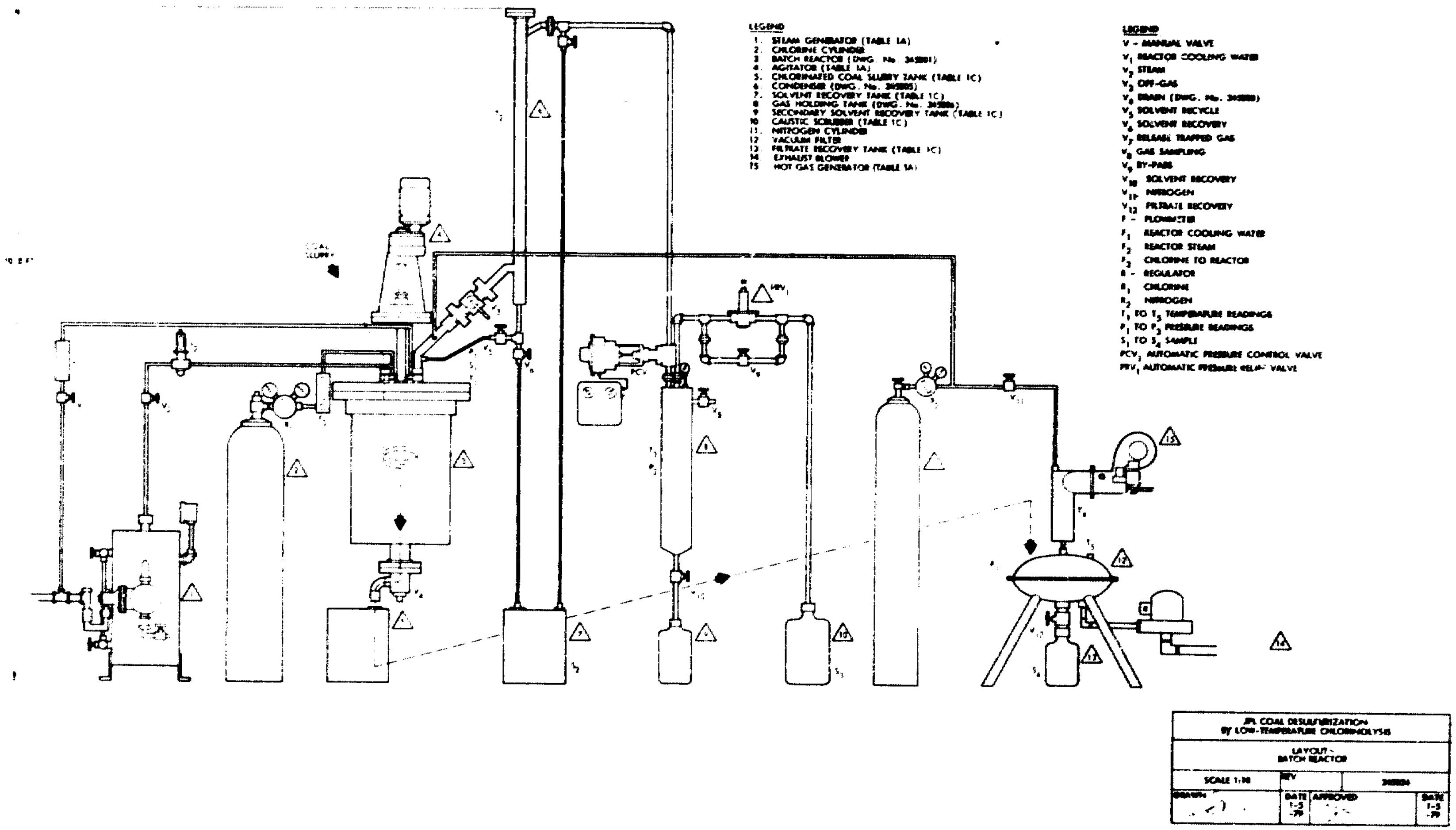


Figure 1a. Bench-Scale Batch Reactor System

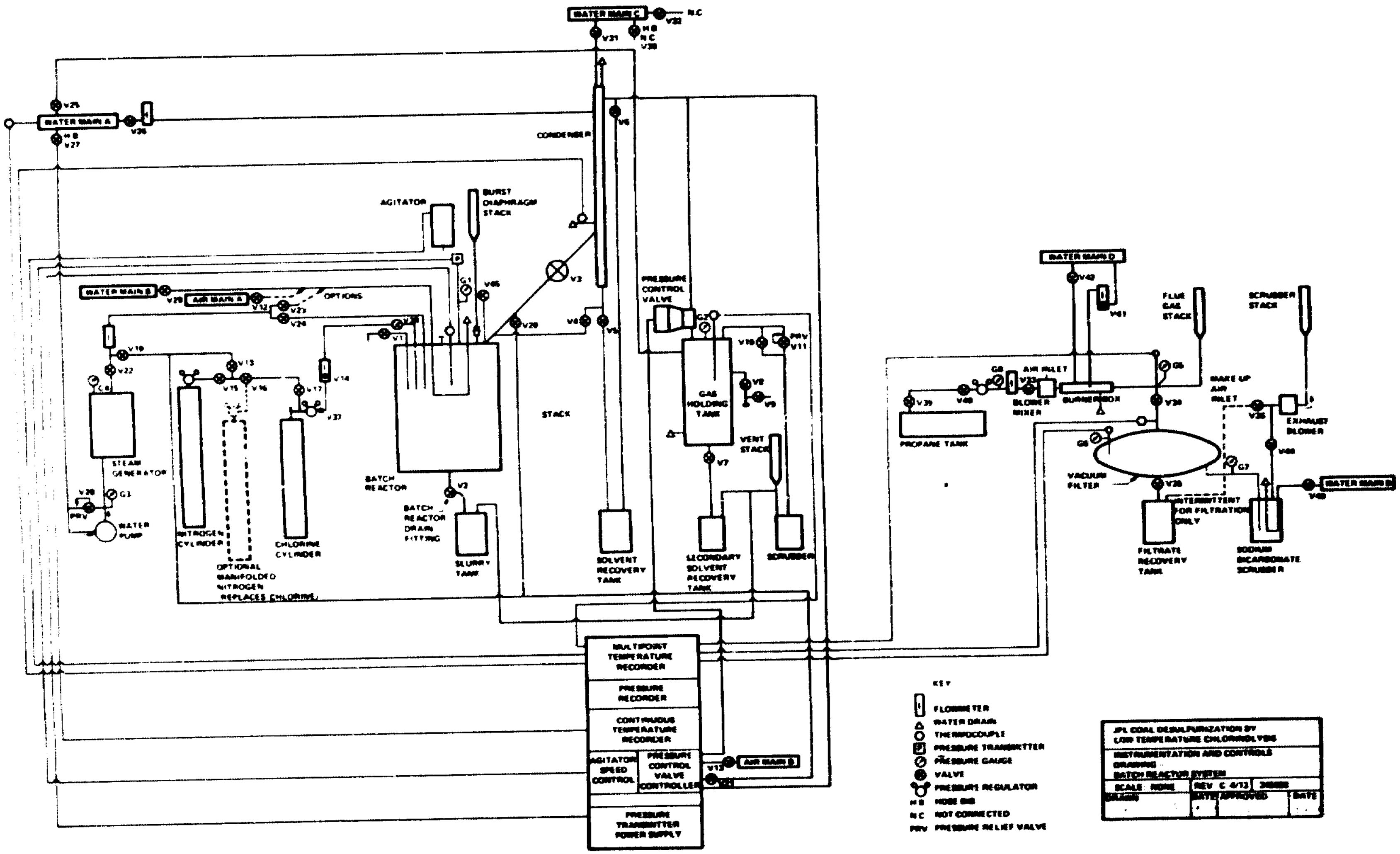
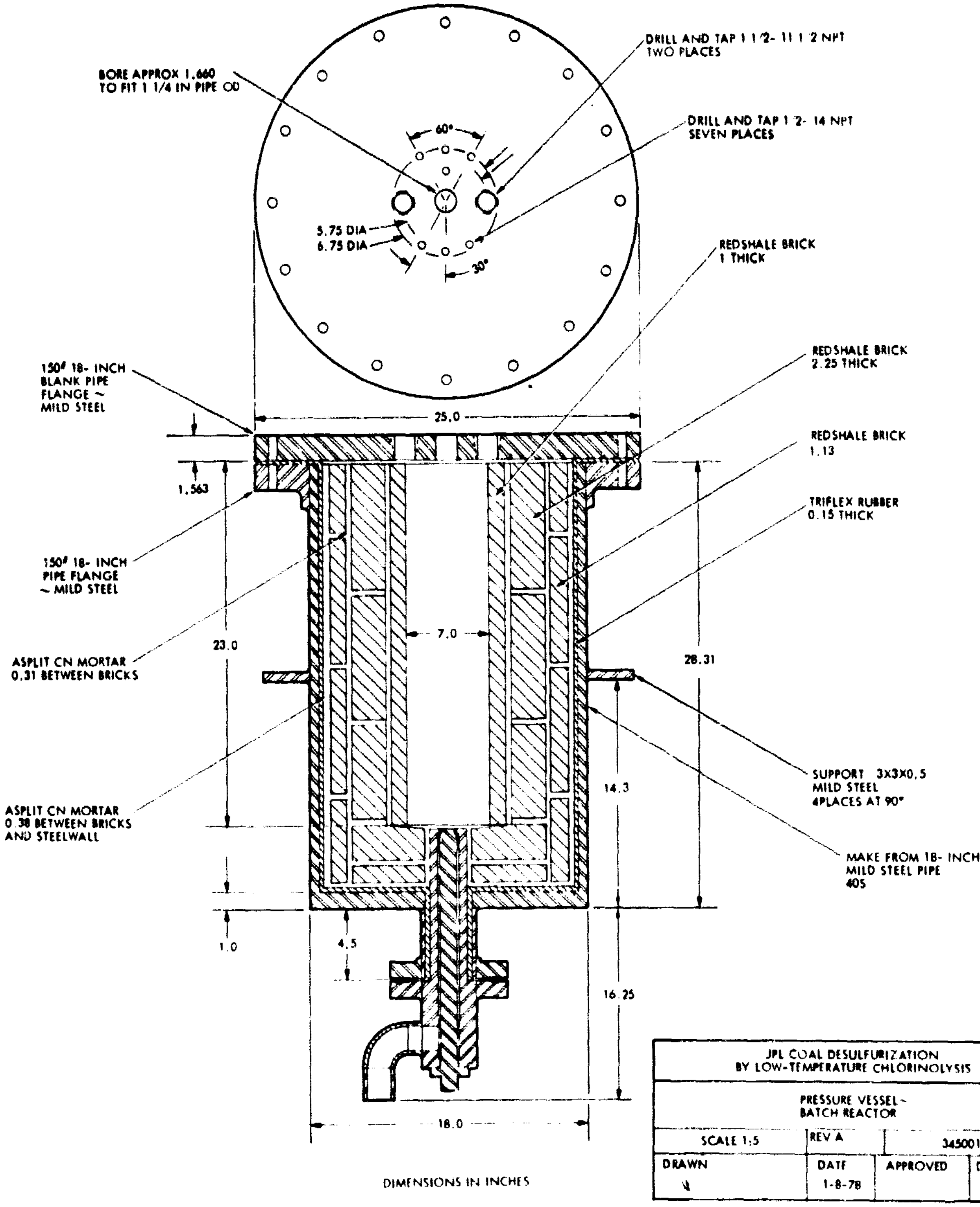


Figure 1b. Instrumentation and Controls -- Batch Reactor System



JPL COAL DESULFURIZATION BY LOW-TEMPERATURE CHLORINOLYSIS			
PRESSURE VESSEL ~ BATCH REACTOR			
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Figure 2a. Bench-Scale Batch Reactor

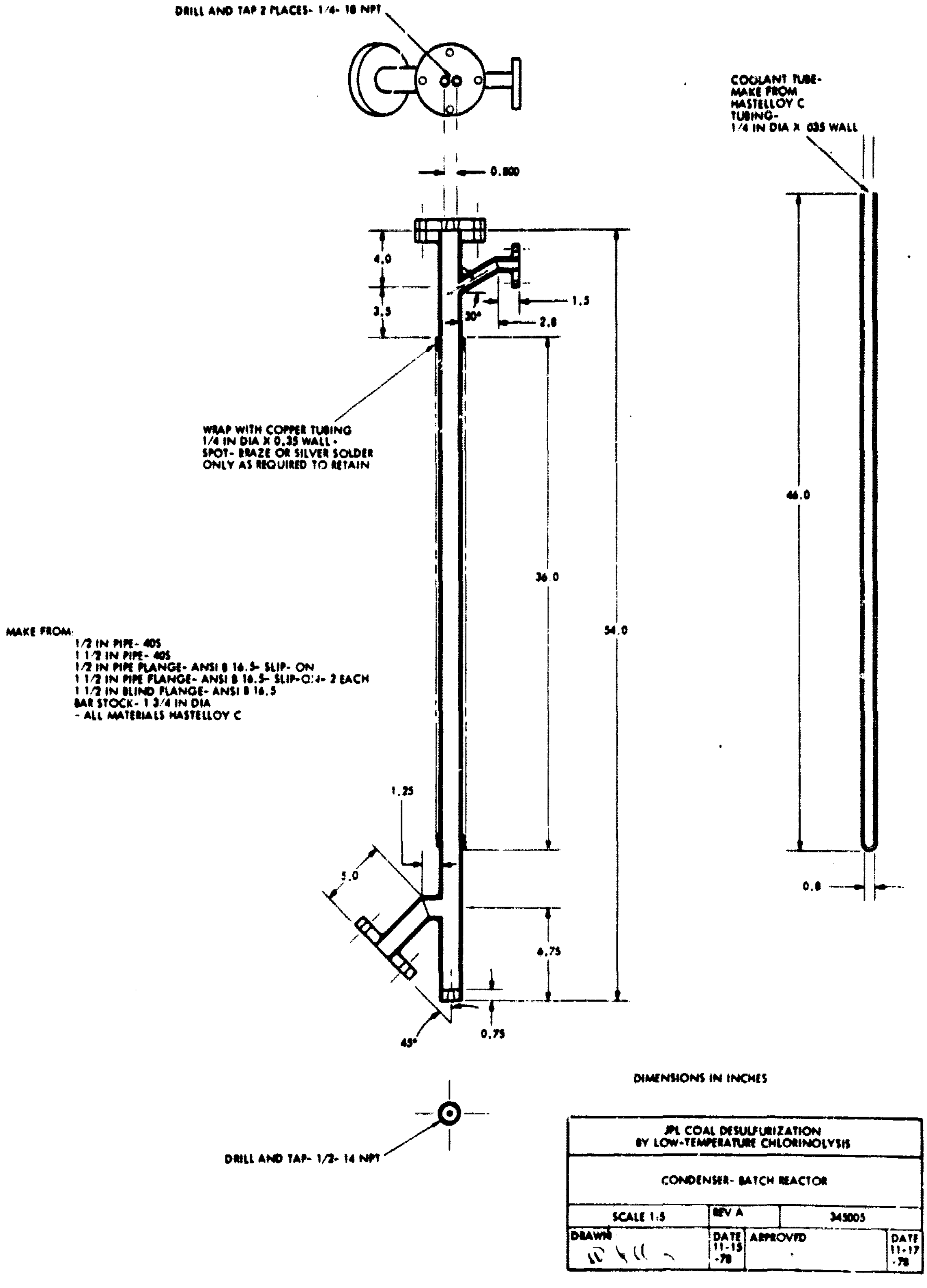

Figure 2b. Condenser – Batch Reactor

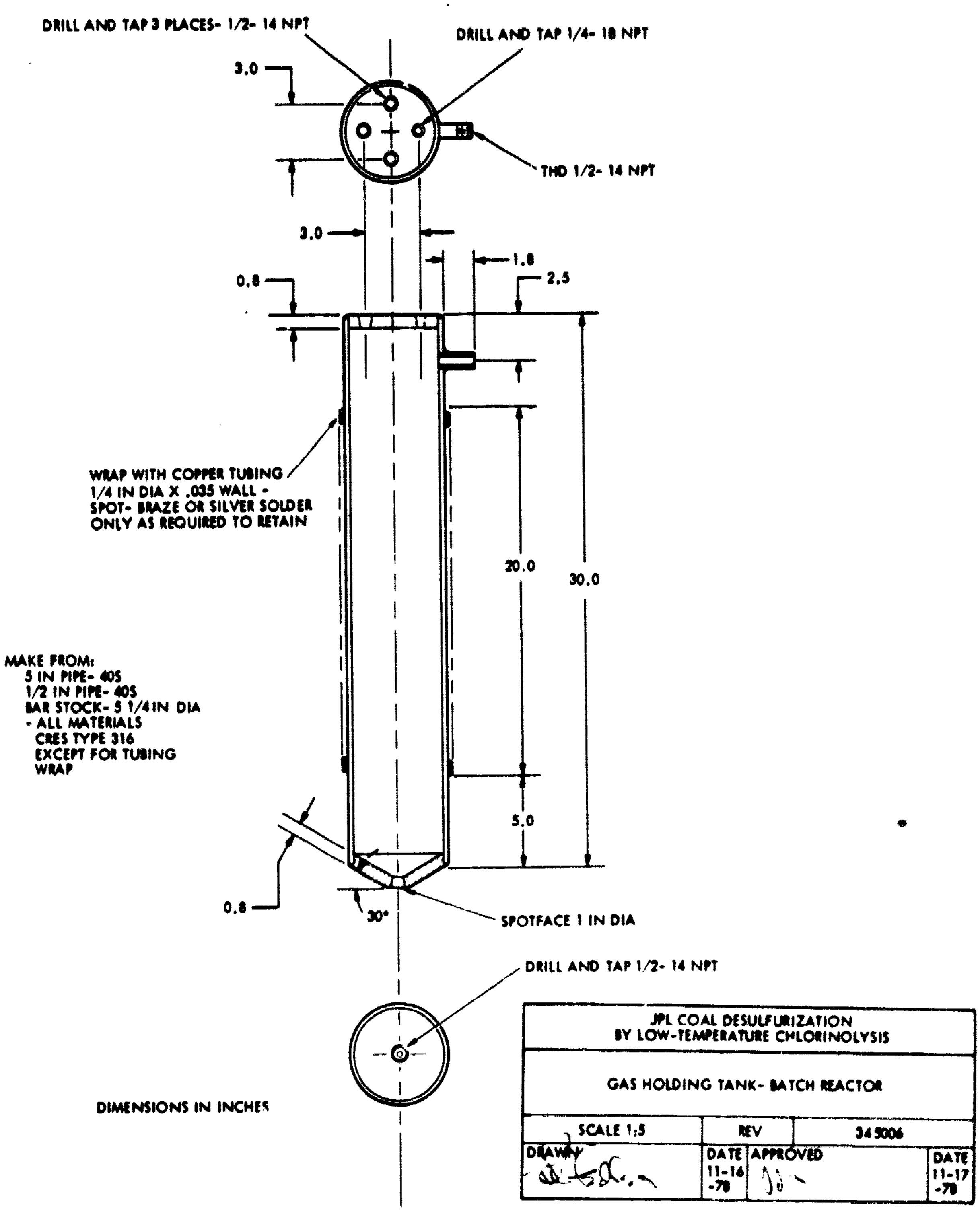

Figure 2c. Gas Holding Tank – Batch Reactor

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 11/2 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 live steam injection. The cooling water coil consists of 3 to 6 turns of 1/4-inch 316 stainless steel tubing on a 6-inch diameter circle. An outer cover of teflon tubing was provided to protect the tubing from the highly corrosive environment. Direct live steam injection was provided for reactor preheat by a Hot Shot Model No. MB-6L steam generator, 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 hot water immersion heating and monitored by a Linde Model F-M 4311-6 flowmeter with a range of 0.42 to 61.5 SCFH. Chlorine dispersion into the coal slurry was done initially by means of a 1/4-inch, 316 stainless steel tube discharge to the side and beneath the turbine impeller. Chlorine dispersion appeared to be inadequate by means of the 1/4-inch tube and was changed after Run 7 to a standard laboratory fritted glass diffuser. Mechanical problems of attachment, plugging and the fragile nature of the glass diffuser necessitated a change. Teflon tubing drilled with 20, 1/74 to 1/16-inch diameter holes was tried for the diffuser. A nominal size of 1/32-inch diameter holes in the Teflon provided a satisfactory compromise between diffuser plugging and chlorine dispersion. Coal slurry sampling was by means of a 1/2-inch, 316 stainless steel tube located to the side and near the reactor bottom. Pressure was continuously monitored by a Hewlett-Packard Model No. 1144 G pressure transmitter and 7100B pen recorder with a range of 0 to 120 psig. A dial pressure gauge (Series 2550, 3-D Instruments) provides direct readings, 0 to 150 psig with an accuracy of ±0.25 percent. A pressure rupture disc, aluminum coated with teflon for rupture pressures of 150 psig of +10 percent -5 percent at 70°F was obtained from Fike Metal Products, Model No. 1/2-30SB. Temperatures were monitored by iron-constantan (Type J) thermocouples with a Leeds and Northrup Speedomax multipoint recorder. Pressure was controlled at 0 to 100 psig by a Fisher Type 513 actuator on a design B valve body made of Hastelloy C-276 connected to a Fisher Type 4150 pressure controller and Fisher Type 67 pressure reducing regulator. A standard nitrogen gas cylinder and regulator provided 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 1) designed to accommodate 2 kilograms of coal was fabricated from a 2:1 elliptical tank head, 18-inch diameter, 12 gauge, 300 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, 304 stainless steel wire filtration screen. A exhaust fan provided vacuum filtration at 20 to 30-inches water vacuum. A manually applied spray water wash was provided. The wash water and filtrate were recovered in a filtrate recovery tank. Provisions for adapting the vacuum filter for drying and dechlorination by direct hot gas steam injection were unsatisfactory.

Dechlorination Unit

The dechlorination unit, Figure 3, was constructed from a Lindberg Model 58331 tube furnace sized for a 5-inch diameter by 5-foot long tube that could accommodate 2 kilograms of coal. The furnace is designed for operation at 100 to 1100°C with a three zone temperature control for 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 RPM. Nitrogen at 30 SCFH and 0.5 psig is 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.

Corrosion Problems

The prospect of chlorination conditions in the reactor being highly corrosive and erosive were anticipated. For this reason, an acid resistant brick lined reactor construction was undertaken with the consultation of both the Pennwalt Corporation and Stebbins Engineering and Manufacturing Company. Pennwalt Corporation provided the batch reactor design specifications under which Thorpe Engineering Co. (Pennwalt's West Coast Fabricating Co.) constructed the reactor. As a part of the reactor design, there was a need to have port openings for a drain, thermocouple with an Inconel metal sheath, stainless steel cooling coil, stainless steel sampling tube, gaseous chlorine injection tube, as well as a stainless steel agitator and impeller for the coal slurry. On the basis of published

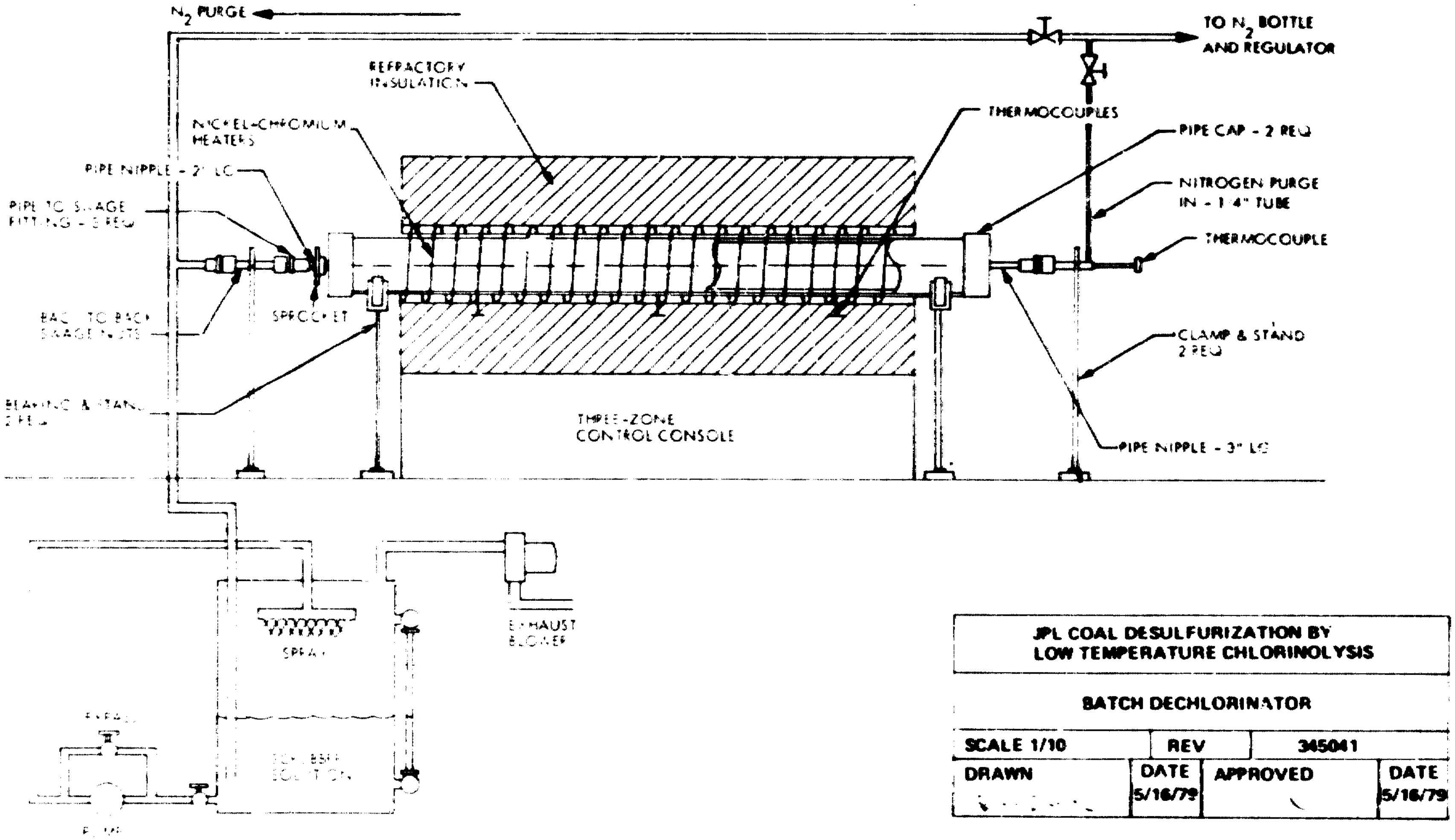

Figure 3. Bench-Scale Batch Dechlorinator

corrosion rate data with HCl, chlorine, H_2SO_4 and metal salts, Hastelloy B metal was obtained for the agitator shaft and turbine impeller with 316 stainless steel for the expendable injection lines, cooling coil, etc. Corrosion rates have proved to be much more severe than anticipated with corrosion as high as 4 mils during a one-hour chlorination run for the Hastelloy B shaft. Maintenance requirements for replacing cooling coils, thermocouples, inlet tubing has been high, requiring the reactor to be opened up after each run and necessary equipment replacements made. A covering of exposed metal with Teflon tubing and graphoil tape has been effective in eliminating the rapid destruction of cooling coils, thermocouples and injection lines. The acid resistant brick lined construction for the reactor has held up extremely well, showing no visible attack of either the brick or mortar. The brick is red shale brick with an Asplit CN mortar. For commercial equipment, material design solutions should be possible by seeking protective coatings for metal surfaces or using construction materials that can withstand the corrosion and erosion better than the stainless steel currently used. An investigation was conducted to see if refractory oxide coatings and plastic coatings could be deposited on the exposed metal surfaces as a means of alleviating the corrosion and erosion problems. Table 1 includes corrosion rate data and results on the various materials and coupons tested. The carbon steel coupons, plasma spray coated with zirconium oxide (containing 4-1/2% calcium oxide stabilizer as calcium) and 99.9% pure aluminum oxide, were obtained from the Wall Colmonoy Corp., Santa Fe Springs, CA. In a few hours of exposure, both zirconium oxide and aluminum oxide coupons were fractured at the edges due to heavy corrosion attack. Photographs of the coupons after exposure are shown in Figure 4.

Table 1. Chlorinator Corrosion Data on Test Materials

Process Environment: Coal, Methylchloroform, Water, Chlorine, Hydrochloric Acid, and Sulfuric Acid at 65-130°C

Material	Exposure Time (Hours)	Corrosion Rate (Mils/hour)	Remarks
Hastelloy B Agitator Shaft and Impeller	62	4 mils/hr. (35,000 mils/yr.)	Unsatisfactory
Hastelloy C-276 Coupon	6	2.2 mils/hr (19,500 mils/yr)	Unsatisfactory
Zirconium Oxide[a] Plasma Coating*	8	-	Fractured at the edges
Aluminum Oxide[a] Plasma Coating*	2	-	Fractured at the edges
Phenolic Resin Coating*[b] (Plasite - 3066)	2	-	Destroyed
Phenolic Epoxy Coating*[b]	2	-	Destroyed
Vinyl Ester Resin*[b] (Plasite - 4005)	2	-	Destroyed
Polyvinyl Chloride*[b]	2	-	Destroyed
Garolite-Phenolic Resin with Linen Base*	40	-	Destroyed
Teflon (Impeller, Cooling Coil, etc.)	74	-	Excellent
Graphoil Tape**	70	-	Excellent

*Carbon steel coupons
**Tape on Agitator Shaft

[a]Provided by Wall Colmonoy Corp., Santa Fe Springs, CA.
[b]Provided by Metal Protection Co., Cudahy, CA.

Figure 4. Test Material Coupons after Exposure to Chlorinator Operating Conditions

The corrosion tests were also performed on the phenolic resin, phenolic epoxy, vinyl ester resin, and PVC coated coupons obtained from the Metal Protection Company, Cudahy, Ca. All of these coupons were completely destroyed in the chlorinator environment (see Figure 4). Corrosion problems have not been exhibited in the dry dechlorinator environment.

Mechanical Changes

Chlorine injection into the reactor was originally designed to be through a 1/4-inch diameter, 316 SS tube located to the side and beneath the turbine impeller in the reactor. This was altered to improve the transfer of gaseous chlorine into solution by use of standard laboratory fritted glass cylinders. This was changed to Teflon tubing drilled with hole sizes ranging from 1/16 to 1/74-inch diameter, with a final choice of 1/32-inch diameter holes. A tabulation of run numbers with chlorine diffuser types is provided, Table 2. Extensive corrosion of the exposed stainless steel in the reactor drain plug necessitated a Teflon plug closure of the bottom drain after Run 20. The bottom drain was used to remove the coal slurry after completion of the batch reactor processing during the first 20 runs. After run 20 and through run 44 the coal slurry was removed through the sampling line that extended within 1/4-inch of the reactor bottom. The dead volume amounted to 456 milliliters. With corrosion of the sampling line, the proximity of the sampling line to the reactor bottom was decreased, increasing the dead volume. In the worst case, up to 2000 milliliters of dead volume was obtained. The sampling line was replaced every one to four runs. The coal slurry in the dead space was adequately removed by addition of a water rinse of the reactor. The first thermocouple failure was during run 6. Thermocouples were replaced before runs 7, 13 and 17. After run 6, a thin Teflon covering provided thermocouple protection although dulling the response. Cooling coils were rapidly corroded and had to be replaced every 2 to 3 runs. Starting with

Table 2. Chlorine Diffuser Type

Run No's	Diffuser Type*
1-7	1/4-inch diameter 316 S.S. tube
8	one coarse fritted glass cylinder (12 mm dia. x 22 mm)
9-13	two coarse fritted glass cylinders (12 mm dia. x 22 mm)
14-16	two extra coarse fritted glass cylinders (12 mm dia. x 22 mm)
17-19	one coarse and one extra coarse fritted glass cylinder
20	1/4 x 1/2-inch Teflon tube with 880 1/74-inch holes
21	1/4 x 1/2-inch Teflon tube with 32 1/16-inch holes
22-44	1/4 x 1/2-inch Teflon tube with 40 1/32-inch holes

*Installed beneath and to the side of impeller.

run 10, a Teflon covering provided protection for the 316 SS coil, although reducing the temperature control effectiveness. A Teflon impeller replaced the Hastelloy B impeller starting with run 8. The metal impeller was almost totally corroded away in the first seven runs. The Hastelloy B impeller shaft immersed in the coal slurry was reduced from one to three quarters of an inch in the first 33 runs. A graphoil wrap of the immersed shaft during the last 11 runs provided shaft protection and held up satisfactorily.

OPERATING PROCEDURE

Chlorination

The reactor was leak tested under nitrogen pressure, purged with nitrogen and charged with two kilograms of coal (-100 to +200 mesh, weight corrected for coal moisture) and four kilograms of solvent (either methylchloroform or water). In most runs, the reactor off-gas valve to the reflux condenser was closed with injected chlorine confined to the coal slurry and ullage space in the reactor. Agitation was set in the first few runs at 275 RPM based on Chemineer design standards. With the majority of runs agitation was set at 565 RPM, the maximum agitator speed. Direct steam injection provided reactor preheat to the desired operating temperature in 20 to 30 minutes. Chlorine flow was then initiated to the reactor 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. Temperature control was aggravated by the use of a Teflon tube cover on the cooling coil. Corrosion and erosion of exposed metal surfaces in the reactor was extremely severe. A Teflon cover was used to protect the cooling coil, thermocouple, chlorine injection tube and sampling tube. Coal slurry samples were obtained at 15, 30, 45 and in some cases 90 minutes. Samples were approximately 100 grams obtained close to the wall and near the reactor bottom. Stirring was sufficiently intense to insure a representative coal slurry sample.

Chlorine injection was initially through a 1/4-inch stainless steel tube located to the side and near the reactor bottom, beneath the turbine impeller. With high chlorine flow rates (>20 SCFH) and poor chlorine diffuser injection, there was a rapid reactor pressurization, i.e., 20-30 psig in 5 minutes. A reduced chlorine flow rate (10 SCFH) and good chlorine diffuser injection provided relatively little reactor pressurization (i.e., <5 psig) in 30 to 45 minutes until the coal slurry was apparently saturated with chlorine. At that point, rapid reactor pressurization occurred unless chlorine flow was stopped or sharply reduced. In some runs, chlorine flow rates had to be substantially reduced from initial values at the start of the reaction in order to avoid over pressurization with a closed reactor system. In some cases a continuous vent of off-gas, i.e., chlorine, was maintained to allow continued chlorine injection into the coal slurry. With fritted glass diffusers, problems were experienced with diffuser plugging by coal tar after 20 to 30 minutes of reaction time. This problem was also encountered when a Teflon diffuser tube was used with hole sizes less than 1/32-inch. Chlorine dispersion into the coal slurry was also found to be improved by increasing agitator speed from the initial setting of 275 RPM to 565 RPM. A detailed operating procedure is described in Appendix A, Table A-1.

Hydrolysis-Solvent Recovery

After chlorination, reactor pressure was reduced by venting reactor gases through the reflux condenser, 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 since water was present from the steam condensate in reactor preheat and coal moisture. 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. To provide comparable reactor operating conditions between methylchloroform and water runs, some water solvent runs were made with the coal slurry held in the reactor for one hour at temperatures of 65 to 100°C after the chlorination. Thus, if additional reaction or leaching of the coal was possible during the additional holdup time, this would be indicated by comparing analytical results of the processed bulk samples and samples withdrawn prior to the holdup period. A detailed operating procedure is described in Appendix A, Table A-2.

Vacuum Filtration - Spray Wash

The coal-water slurry was added to the batch vacuum filtration unit, Figure 1. An exhaust blower provided 20 to 30 inches of water column vacuum. A water spray manually applied provided a displacement water wash of the filter cake with water/coal addition at 2/1. The detailed operating procedure is described in Appendix A, Table A-3.

Drying-Dechlorination

Coal samples were removed from the vacuum filter and dried in a vacuum oven overnight at 100°C. A majority of sulfur analyses were performed on the dried but undechlorinated coal samples. Some sulfur form analyses were performed in duplicate on dechlorinated and undechlorinated samples. Analytical results indicate that dechlorination at 400°C provides an added 4-11% total sulfur removal over the undechlorinated samples. Since the dechlorinator was not available until late in the program, a majority of chlorinated, washed, dried coals were stored for up to 3 months in closed glass containers before dechlorination.

Dechlorination of the coal was obtained in a Lindberg furnance equipped with a rotary 5-inch diameter by 5-foot long tube (Figure 3). The furnace and tube were preheated to the operating temperature of 400°C, flushed with nitrogen and charged with up to 2 kilograms of coal. Approximately 30 minutes were required to heat the coal charge to 400°C while maintaining a nitrogen purge of 30 SCFH. The coal was then held at 400°C for an additional 30 to 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 A, Table A-4.

Analyses

The major portion of coal analyses including sulfur forms (pyritic, sulfate and total sulfur), ultimate analyses, proximate analyses and trace element analyses of both raw and treated coal samples were contracted to the Colorado School of Mines Research Institute. The Colorado School of Mines Research Institute uses the Eschka method for total sulfur analyses and ASTM approved procedures for pyritic and sulfate sulfur with organic sulfur determined by difference. A majority of coal samples were sent to the Colorado School of Mines Research Institute. In addition, three duplicate coal samples were sent to: Galbraith Laboratories, Knoxville, Tennessee; Standard Laboratories, Charleston, West Virginia; and the DOE Coal Analysis Laboratory at the Pittsburg Mining Technology Center.

A Leco acid-base analyzer was used at JPL to provide immediate total sulfur analyses after completion of each test run. Because of potential chlorine interference, 2-4 gram samples of the chlorinated coal were first dechlorinated in a laboratory unit before Leco sulfur analyses.

Water filtrate solutions from the chlorinator and vacuum filter were analyzed for sulfates, chlorides, iron and trace elements.

Gas samples from the chlorinator at the completion of two chlorinations, one with methylchloroform solvent and one with water as a solvent, were analyzed by mass spectroscopy.

COALS

Selection

The five (5) coals selected for the bench-scale batch reactor tests are listed in Table 3 with attendant analyses for sulfur forms, proximate analyses, ultimate analyses, ash elemental analyses, and trace elements. They are bituminous coals obtained from Ohio, Illinois and Kentucky and were selected for testing by JPL and the DOE Pittsburgh Mining Technology Center. Five tons each of PSOC 276 and PSOC 282 coals were obtained directly from the Georgetown #24 and Orient No. 6 mines, respectively. Approximately 100 pounds of Island Creek Coal were obtained from the Pittsburg Mining Technology Center. The remaining coals PSOC 219 and PSOC 026 were obtained from the Penn State coal bank and are representative of the coals tested in the Phase I Laboratory test program.

Raw Coal Analyses

All of the analyses of the raw coals listed were obtained from the Colorado School of Mines Research Institute. In most instances, the analyses were substantially different from the Penn State Coal bank analyses for these coals.

Sulfur forms analyses were generally conducted for raw coal samples used in each test run, Table 3. The standard deviation was calculated for each of the sulfur forms analyses for each of the coals and represents the discrepancy between runs of sulfur forms that can be attributed to a combination of non-uniformity in coal

Table 3. Selected Raw Coals A
(Dench-Scale Batch Chlorination Process fo

ERDA PSOC Number	Seam, County, State (Mine, Mesh Size)	Rank	Run No.	Sulfur Forms (wt. %)[a] Organic	Pyritic	Sulfate	Total	Proximate Analysis (wt. %)[a] Volatile Matter	Ash	Fixed Carbon	Heating Value (BTU/lb)[a]	Moisture[b]	Ultimate Analysis (wt. % C	H	S	N	Cl
276[e]	Ohio No. 8, Harrison, Ohio (Georgetown #24 Mine, 100-200 mesh)	Bit, HVA	1	1.03	2.86	<0.05	3.89										0.17
			3	1.17	2.69	<0.05	3.86	37.2	10.9	51.8	12,822	1.99	71.4	5.51	3.86	1.06	0.31
			5	1.10	2.83	<0.05	3.93										0.31
			6	1.07	2.76	<0.05	3.83										0.16
			7	1.20	2.46	0.11	3.78										0.04
			9	1.28	2.51	0.11	3.90	37.6	11.2	51.2	12,986	2.20	72.0	5.36	3.90	1.40	0.09
			10	1.38	2.44	<0.05	3.82										0.16
			12	1.29	2.75	<0.05	4.12										0.13
			13	0.89	2.77	0.14	3.80										0.11
			14	1.08	2.75	0.13	3.96	36.7	12.4	50.9	12,457	1.48	71.3	6.14	3.96	1.37	0.13
			16	1.42	2.13	0.12	3.67										0.15
			Average[h]	1.17	2.63	0.06	3.87	37.2	11.5	51.3	12,755	1.89	71.6	5.67	3.91	1.28	0.16
			Std. Dev.	±0.16	±0.22	±0.06	±0.08	±0.5	±0.8	±0.5	±271	±0.37	±0.4	±0.41	±0.05	±0.19	±0.08
282[e]	Ill. No. 6, Jefferson, Ill. (Orient No. 6 Mine, Washed[f], 100-200 mesh)	Bit, HVB	15	0.78	0.82	0.05	1.65	34.7	7.21	58.1	13,280	5.37	76.3	5.05	1.65	1.71	0.48
			17	0.58	0.79	0.07	1.44										0.47
			20	0.76	0.73	0.08	1.57	36.8	6.37	56.8	13,341	4.06	74.6	5.69	1.57	1.74	0.51
			21	0.74	0.78	0.10	1.62	35.5	6.78	57.7	13,346	4.76	75.1	5.30	1.62	1.68	0.48
			22														
			23	0.75	0.77	0.10	1.62										0.53
			24	0.71	0.80	0.10	1.62										0.50
			25	0.78	0.79	0.09	1.66										0.55
			35	0.74	0.75	0.14	1.63										0.45
			36	0.68	0.75	0.12	1.56										0.53
			38	0.70	0.73	0.13	1.55										0.55
			Average[h]	0.72	0.77	0.10	1.59	35.7	6.79	57.5	13,322	4.73	75.3	5.35	1.61	1.71	0.50
			Std. Dev.	±0.06	±0.03	±0.03	±0.07	±1.1	±0.42	±0.7	±37	±0.66	±0.9	±0.32	±0.04	±0.03	±0.04
282[e]	Ill. No. 6, Jefferson, Ill. (Orient No. 6 Mine, Washed[f], (-1/8 in. to 100 mesh)		26	0.68	0.85	0.08	1.61										0.50
			27	0.72	0.82	0.07	1.61										0.71
			33	0.67	0.78	0.08	1.54										0.54
			34	0.75	0.69	<0.05	1.43										1.86[g]
			Average[h]	0.71	0.79	0.06	1.55										0.58
			Std. Dev.	±0.04	±0.07	±0.03	±0.09										±0.11
219	KY. No. 4, Hopkins, KY. (100-200 mesh)	Bit, HVB	28	0.77	0.72	0.63	2.14										0.11
			29	0.85	0.74	0.57	2.16	35.5	6.42	58.1	12,966	3.74	73.8	5.32	2.16	1.76	0.14
			Average[h]	0.81	0.73	0.60	2.15										0.12
			Std. Dev.	±0.06	±0.01	±0.04	±0.01										±0.02
026	Ill. No. 6, Saline, Ill. (100-200 mesh)	Bit, HVC	30	1.62	1.09	0.69	3.40	35.0	9.87	55.1	12,540	3.36	66.8	5.03	3.40	1.45	0.17
			31	1.74	1.10	0.69	3.53										0.21
			32	1.50	1.31	0.60	3.41									0.	0.19
			Average[h]	1.62	1.17	0.66	3.45										0.19
			Std. Dev.	±0.12	±0.12	±0.05	±0.07										±0.02
Island Creek Coal Co., No. 9, Union, County KY. (100-200 mesh)		Bit	40	1.87	1.77	0.09	3.73	40.0	10.5	49.5	13,135	1.40	72.8	5.25	3.73	1.40	0.20
			43	1.82	1.78	0.10	3.70										0.19
			Average[h]	1.85	1.78	0.10	3.72										0.19
			Std. Dev.	±0.04	±0.01	[illegible]	±0.02										±0.01

a: Dry basis
b: As determined basis
c: H and O have been corrected for moisture
d: Vanadium <50 ppm in all 8 analyses
e: Coal obtained directly from the mine
f: Unwashed coal is 2.2 wt. % total sulfure, 22 wt. ash
g:
h:

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le 3. Selected Raw Coals Analyses
tch Chlorination Process for Coal Desulfurization)

isture[b]	Ultimate Analysis (wt. %)[a,c]							Ash Elemental Analysis (wt. % of ash)											Trace Elements (ppm in coal)[b,d]			
	C	H	S	N	Cl	O (by diff.)	Ash	Si	Fe	AL	Ca	K	S	Ti	Na	Mg	P	Mn	Pb	As	Se	Hg
					0.17																	
1.99	71.4	5.51	3.86	1.06	0.31	6.91	10.9	24.6	30.5	12.1	2.80	1.70	1.64	0.50	0.35	0.45	<0.01	0.02				
					0.31																	
					0.16														96	7	5	0.2
					0.04														<50	5	6	<0.1
2.20	72.0	5.36	3.90	1.40	0.09	6.12	11.2	26.5	29.5	13.6	2.11	1.73	1.23	0.66	0.32	0.45	0.01	0.04				
					0.16																	
					0.13														186	7	5	0.3
					0.11																	
1.48	71.3	6.14	3.96	1.37	0.13	4.57	12.4	27.5	27.6	13.9	2.21	1.80	1.46	0.67	0.32	0.43	<0.01	0.01				
					0.15																	
1.89 ±0.37	71.6 ±0.4	5.67 ±0.41	3.91 ±0.05	1.28 ±0.19	0.16 ±0.08	5.87 ±1.19	11.5 ±0.8	26.2 ±1.5	29.2 ±1.5	13.3 ±0.9	2.37 ±0.37	1.74 ±0.05	1.44 ±0.21	0.64 ±0.04	0.33 ±0.02	0.44 ±0.01	<0.01	0.02 ±0.02	110 ±70	6 ±1	5 ±0.6	0.2 ±0.2
5.37	76.3	5.05	1.65	1.71	0.48	7.58	7.21	25.6	16.4	13.5	1.54	1.97	1.04	0.87	1.51	0.59	0.13	0.02	165	10	5	0.3
					0.47																	
4.06	74.6	5.69	1.57	1.74	0.51	9.47	6.37	27.2	13.9	14.8	1.18	2.09	0.68	0.94	2.37	0.57	0.007	-				
4.76	75.1	5.30	1.62	1.68	0.48	8.94	6.78	24.1	15.4	13.1	1.31	1.81	0.76	0.82	1.52	0.42	<0.01	0.03	241	7	4	1.3
																			183	10	4	<0.1
					0.53																	
					0.50																	
					0.55																	
					0.45																	
					0.53																	
					0.55																	
4.73 ±0.66	75.3 ±0.9	5.35 ±0.32	1.61 ±0.04	1.71 ±0.03	0.50 ±0.04	8.67 ±0.98	6.79 ±0.42	25.6 ±1.6	15.3 ±1.2	13.8 ±0.9	1.34 ±0.18	1.96 ±0.14	0.83 ±0.19	0.88 ±0.06	1.80 ±0.49	0.53 ±0.09	0.05 ±0.07	0.02 ±0.01	197 ±40	9 ±2	4 ±0.6	0.5 ±0.7
					0.50																	
					0.71																	
					0.54																	
					1.86[g]																	
					0.58 ±0.11																	
					0.11																	
3.74	73.8	5.32	2.16	1.76	0.14	10.46	6.42	23.7	25.4	12.6	0.82	[illegible]	0.58	0.61	0.34	0.62	0.11	0.04				
					0.12 ±0.02																	
3.36	66.8	5.03	3.40	1.45	0.17	13.23	9.87	25.9	22.0	12.9	1.01	2.18	0.76	0.71	0.34	0.49	0.03	0.02	<50	3	8	0.2
					0.21																	
				0.	0.19																	
					0.19 ±0.02																	
1.40	72.8	5.25	3.73	1.40	0.20	6.05	10.5	25.4	20.0	11.2	3.04	2.07	1.71	0.65	0.81	0.43	<0.01	0.02	<50	3	3	0.4
					0.19																	
					0.19 ±0.01																	

ly from the mine
wt. % total sulfure, 22 wt. % ash

g: Excluded from the average

h: Standard deviation = $\sqrt{\Sigma (x_i - \bar{x})^2/(N - 1)}$

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samples and/or analytical deviations. For PSOC 276 coal with eleven samples, standard deviations were: organic sulfur ±14%, pyritic sulfur ±8% and total sulfur ±2%. Average values of sulfur forms and standard deviations are listed for each of the coals in Table 3. PSOC 282 coal was analyzed for two mesh sizes, -100 to +200 mesh and -1/8 inch to +100 mesh. Sulfur forms were not significantly different as a result of this particle size difference.

Proximate analysis, ultimate analysis, ash elemental analysis and trace elements were determined for three (3) coal samples each for PSOC 276 and PSOC 282 and single coal samples for PSOC 219, 026 and Island Creek coal. Analyses and standard deviations are listed in Table 3. Trace elements analyses include Pb, As, Se, Hg, V.

Size Distribution

Two tons each of coals PSOC 276 and 282 were ground from run of the mine coal and then sieved in a trommel screen to provide coal samples for testing in the range of -100 to +200 mesh size and also in the range of -1/8-inch to +100 mesh. Analyses of both sizes of coal samples were conducted to obtain the size distribution as shown in Table 4. For -100 to +200 mesh only 0.7 wt. % was larger than +100 mesh and 16.9 wt. % was finer than 200 mesh. For -1/8-inch to +100 mesh, 7 wt. % was greater than 16 mesh, with approximately 47.8 wt. % of the coal between 16 and 60 mesh and 20.2 wt. % finer than 100 mesh.

EXPERIMENTAL DATA

A total of 44 test runs were conducted with 15 runs on coal PSOC 276, 19 runs on coal PSOC 282, 2 runs on PSOC 219, 3 runs on PSOC 026 and 5 runs on Island Creek Coal (Western Kentucky Union County #9 Seam). See Table 5.

Table 4. Size Distributions of Ground and Sieved Raw Coals (PSOC 282 and PSOC 276)

Coal PSOC276 (Ground and Sieved to -100 +200 mesh) Size Screening	
Screen Mesh Size	Coal, Wt. %
retained on 60	0.3
60-80	0.2
80-100	0.2
100-120	10.2
120-170	54.7
170-200	17.7
200-270	10.2
270-325	1.0
passes 325	5.7
Coal PSOC 282 (Ground and Sieved to -1/8 inch to +100 mesh)	
Screen Mesh Size	Coal, Wt. %
retained on 16	7.0
16-35	25.5
35-60	22.3
60-80	17.2
80-100	7.8
100-200	14.8
200-325	3.6
passes 325	1.8

Coal Desulfurization Data

A summary of operating conditions for the Chlorination reaction and attendant coal desulfurization data for organic, pyritic and total sulfur is presented in Table 5. Coal and desulfurization data are presented for reaction times of 15, 30, 45 and 90 minutes with methylchloroform and water as solvents. Operating conditions range from: 63 to 130°C, 0 - 60 psig, chlorine feed rates of 5 to 24 SCFH. Methylchloroform runs were generally confined to 65°C with a few runs up to 100°C and water runs were conducted at 65 to 130°C.

Table 5. Bench-Scale Batch Reactor Data — Coal Desulfurization by Low Temperature Chlorinolysis

(Conditions: coal, 2 kilograms, −100 to +200 mesh; solvent to coal, 2/1; preheat steam condensate added to reactor, 300-500 grams at 65°C, 1200 grams at 95°C, 2500 grams at 130°C, additional water in solvent runs zero except for 160 grams in runs 7, 44, 1075 grams in run 39 and moisture in coal; steam condensate added during chlorination in runs (1, 4, 5, 7, 8, 11, 12, 13, 16, 20, 24, 28); agitator speed runs (1-5) at 275 RPM, runs (6-44) at 565 RPM; chlorine injection runs (1 7) 1/4-inch tubing, runs (8-19), fritted glass diffuser, runs (20-44), 1/4 X 1/2-inch diameter teflon tubing drilled with 1/74 to 1/16-inch holes, nominal size 1/32-inch.)

Run # and Date	Time (Min.)	Temp. (°C)	Pressure (PSIG)	Chlorine Feed (SCFH)	Chlorine Feed (kg)	Organic Sulfur Residual (Wt. %)	Organic Sulfur Removal (%)	Pyritic Sulfur Residual (Wt. %)	Pyritic Sulfur Removal (%)	Sulfate Sulfur Residual (Wt. %)	Total Sulfur Residual (Wt. %)	Total Sulfur Removal (%)	Chlorine Before Dechlorination (Wt. %)	Chlorine After Dechlorination (Wt. %)	Chlorine Injector	Remarks
								COAL: PSOC 276		SOLVENT: METHYLCHLOROFORM						
7–5/24/79	0	62	3.5	20		1.17	–	2.64	–	0.05	3.87	–	0.13		1/4-inch tube	Chlorine vented continuously through reactor.
	15	66	1.0	20		1.35	−15	1.03	61	<0.05	2.38	39	3.88			
	30	63	1.5	20		1.24	− 6	0.62	77	0.05	1.92	50	5.21			
	45	63	1.5	20		1.20	− 3	0.50	81	<0.05	1.71	56	7.35			
	Bulk			20[a]	1.32[a]	1.24	− 6	0.39	85	0.05	1.68	57	6.94			
	Dechlorinated Bulk					1.14	3	0.31	88	<0.05	1.45	63		0.75		
10–6/5/79	0	66	5.5	12												
	15	69	7.0	–		1.29	−10	1.51	43	<0.05	2.80	28	2.52		Two coarse fritted glass cylinders	Erratic chlorine flow
	30	66	7.0	–		1.41	−21	0.99	62	<0.05	2.40	38	3.99			
	45	61	13.0	–		1.31	−12	0.64	76	<0.05	1.95	50	6.10			
	Bulk			10	0.68	1.35	−15	0.54	80	<0.05	1.89	51	5.83			
	Dechlorinated Bulk					1.36	−16	0.33	87	<0.05	1.70	56		0.88		
1–5/4/79	0	64	0	22												
	15	67	2.5	–		1.31	−12	1.19	55	<0.05	2.50	35	2.94		1/4-inch tube	
	30	64	14	–		1.28	− 9	0.65	75	<0.05	1.92	50	6.01			
	45	66	27	10		1.32	−13	0.37	86	<0.05	1.69	56	9.30			
	Bulk			16	1.05	1.31	−12	0.34	87	<0.05	1.65	57	9.91			
	Dechlorinated Bulk					1.15	2	0.37	86	<0.05	1.52	61	–	1.29		
2–5/8/79	0	58	0	15												
	15	101	26.5	15											1/4-inch tube	Cooling coil ruptured
	30		1	–												
	45		1	–												
	Bulk			15	1.00	1.29	−10	0.78	70	<0.05	2.07	47	5.38	–		Coal sample recovered from solvent recovery tank.
3–5/10/79	0	66	0	19												
	15	66	5	22		1.29	−10	1.10	58	<0.05	2.39	38	2.64		1/4-inch tube	
	30	65	27	9		1.27	− 9	0.58	78	<0.05	1.85	52	7.09			
	45	68	50	8		1.22	− 4	0.48	82	<0.05	1.70	56	9.91			
	Bulk			15	1.00	1.24	− 6	0.49	81	<0.05	1.74	55	10.8	–		

Table 5 (2 Cont'd)

Run # and Date	Time (Min.)	Temp. (°C)	Pressure (PSIG)	Chlorine Feed (SCFH)	Chlorine Feed (kg)	Organic Sulfur Residual (Wt. %)	Organic Sulfur Removal (%)	Pyritic Sulfur Residual (Wt. %)	Pyritic Sulfur Removal (%)	Sulfate Sulfur Residual (Wt. %)	Total Sulfur Residual (Wt. %)	Total Sulfur Removal (%)	Chlorine Before Dechlorination (Wt. %)	Chlorine After Dechlorination (Wt. %)	Chlorine Injector	Remarks
COAL: PSOC 276 SOLVENT: WATER																
8–5/30/79	0	67	0.5	12												
	15	66	0.5	12		1.24	– 6	1.53	42	<0.05	2.78	28	3.29		One coarse	Chlorine vented continuously,
	30	60	5.0	12		1.32	–13	0.98	63	<0.05	2.31	40	4.22		fritted glass	chlorine injection tube snapped off
	45	64	0.5	12		1.36	–16	0.66	75	<0.05	2.02	48	5.04		cylinder	at 20 minutes, poor mixing –
	Bulk			12	0.78	1.44	–23	0.74	72	<0.05	2.17	44	4.09			impeller slipping on shaft.
	Dechlorinated Bulk					1.22	– 4	0.66	75	<0.05	1.89	51		0.60		
9–6/1/79	0	66	0.5	13												
	15	70	2	11		1.33	–14	1.80	32	<0.05	3.13	19	2.23		Two coarse	
	30	67	3	13		1.29	–10	1.58	40	<0.05	2.88	26	3.41		fritted glass	
	45	74	5	12		1.35	–15	1.08	59	<0.05	2.43	37	6.66		cylinders	
	Bulk			12	0.78	1.47	–26	0.95	64	<0.05	2.42	37	5.88			
	Dechlorinated Bulk					1.24	– 6	0.77	71	<0.05	2.01	48		1.03		
4–5/15/69	0	66	0	18												
	15	71	37	10		1.16	1	1.79	32	<0.05	2.95	24	3.28		1/4-inch	
	30	65	42	9		1.40	–20	1.21	54	<0.05	2.62	32	4.47		tube	
	45	67	40	9		1.30	–11	1.19	55	<0.05	2.49	36	5.37			
	Bulk			11	0.75	1.35	–15	0.99	62	<0.05	2.34	40	5.16			
	Dechlorinated Bulk					1.22	– 4	1.48	44	<0.05	2.70	30		0.80		
11–6/7/79	0	81	1.0	23												
	15	88	37	4		1.21	– 3	2.04	23	<0.05	3.26	16	0.74		Two coarse	Run aborted with liquid chlorine in
	30	–	–	0		–	–	–	–	–	–	–	–		fritted glass	flowrater.
	45	–	–	0		–	–	–	–	–	–	–	–		cylinders	
	Bulk			16	0.36	–	–	–	–	–	–	–	–	–		
12–6/8/79	0	88	0	12												
	15	88	2	11		1.30	–11	2.01	24	<0.05	3.32	14	1.94		Two coarse	
	30	92	5	15		1.37	–17	1.51	43	<0.05	2.88	26	4.54		fritted glass	
	45	92	9.5	14		1.49	–27	0.98	63	<0.05	2.48	36	7.86		cylinders	
	Bulk			13	0.88	1.40	–20	0.87	67	<0.05	2.36	39	8.01			
	Dechlorinated Bulk					1.20	– 3	0.90	66	0.06	2.16	44		0.98		
5–5/18/79	0	96	4	16												
	15	99	33	4		1.17	0	2.01	24	<0.05	3.17	18	1.65		1/4-inch	Chlorine injection tubing failed
	30	97	38	4		1.34	–15	1.74	34	<0.05	3.08	20	2.17		tube	from corrosion at slurry surface,
	45	101	40	3		1.34	–15	1.50	43	<0.05	2.84	27	2.13			chlorine injection near slurry
	Bulk			6	0.39	1.19	– 2	1.98	25	<0.05	3.17	18	1.53			surface.
	Dechlorinated Bulk					1.07	9	2.07	22	<0.05	3.14	19		0.23		

Table 5 (3 Cont'd)

Run # and Date	Time (Min.)	Temp. (°C)	Pressure (PSIG)	Chlorine Feed (SCFH)	Chlorine Feed (kg)	Organic Sulfur Residual (Wt. %)	Organic Sulfur Removal (%)	Pyritic Sulfur Residual (Wt. %)	Pyritic Sulfur Removal (%)	Sulfate Sulfur Residual (Wt. %)	Total Sulfur Residual (Wt. %)	Total Sulfur Removal (%)	Chlorine Before Dechlorination (Wt. %)	Chlorine After Dechlorination (Wt. %)	Chlorine Injector	Remarks
6–5/21/79	0	98	6	17												
	15	100	28	22		1.21	– 3	1.53	42	<0.05	2.74	29	4.60		1/4-inch	
	30	104	44	24		1.27	– 9	1.10	58	<0.05	2.37	39	8.92		tube	
	45	–	48	–		1.22	– 4	0.92	65	<0.05	2.14	45	10.8			
	Bulk			22	1.47	1.19	– 2	1.18	55	<0.05	2.36	39	9.94			
	Dechlorinated Bulk					1.31	–12	0.81	69	<0.05	2.12	45		1.34		
16–6/18/79	0	128	26	9												
	15	121	32	9		1.37	–17	1.31	50	<0.05	2.68	31	2.26		Two extra-	Chlorine vented – at 25, 28, and
	30	124	32	9		1.38	–18	1.21	54	<0.05	2.59	33	3.50		coarse	38 min.
	45	121	33	8		1.26	– 8	1.07	59	<0.05	2.32	40	5.25		fritted glass	1 of 2 injection tube diffusers
	60	119	34	9		1.40	–20	0.97	63	<0.05	2.37	39	6.26		cylinders	broke during the run.
	Bulk			9	0.79	1.32	–13	1.12	58	<0.05	2.44	37	5.31	0.91		
13–6/12/79	0	129	32	14												
	15	129	38	8		1.21	– 3	1.47	44	<0.05	2.68	31	1.94		Two coarse	Chlorine diffuser plugged during
	30	118	40	2		1.31	–12	1.28	52	<0.05	2.58	[illegible]	2.14		fritted glass	the run.
	45	123	48	2		1.39	–19	1.24	53	<0.05	2.63	32	2.20		cylinders	
	Bulk			6	0.37	1.23	– 5	1.81	28	<0.05	3.15	19	1.82	1.48		
14–6/13/79	0	123	23	20												
	15	130	34	26		1.33	–14	1.48	44	<0.05	2.81	27	3.08		Two extra-	Chlorine vented – at 32 min.
	30	126	37	6		1.29	–10	1.05	60	<0.05	2.33	40	5.29		coarse	Injection tube broke during the run.
	45	123	40	6		1.26	– 8	1.12	58	<0.05	2.38	39	5.93		fritted glass	
	Bulk			15	0.99	1.28	– 9	0.83	69	<0.05	2.11	45	6.08		cylinders	
	Dechlorinated Bulk					1.30	–11	0.89	66	<0.05	2.19	43		0.71		
COAL: PSOC 282 SOLVENT: METHYLCHLOROFORM																
25–7/18/79	0	66	3	11		0.72	–	0.77	–	0.10	1.59	–	0.51			
	15	64	4	6		–	–	–		–	–	–			Teflon tube	Mass balance run – no samples taken
	30	66	4	8		–	–	–		–	–	–			with	
	45	71	5	9		–	–	–		–	–	–			1/32" holes	
	Bulk			8	0.52	0.67	7	0.31	60	0.07	1.06	33	7.22	2.61		
17–6/29/79	0	61	0	7												
	15	73	2	7		0.64	11	0.49	36	0.05	1.16	27	6.36		One coarse	Chlorine diffuser probably plugged
	30	74	7	4		0.44	39	0.49	36	0.10	1.03	35	9.98		and one	during run.
	45	65	9	2		0.46	36	0.50	35	0.10	1.06	33	13.2		extra-coarse	
	Bulk			5	0.36	0.30	58	0.62	19	0.16	1.07	33	14.8	2.94	fritted glass cylinders	

Table 5 (4 Cont'd)

Run # and Date	Time (Min.)	Temp. (°C)	Pressure (PSIG)	Chlorine Feed (SCFH)	Chlorine Feed (kg)	Organic Sulfur Residual (Wt. %)	Organic Sulfur Removal (%)	Pyritic Sulfur Residual (Wt. %)	Pyritic Sulfur Removal (%)	Sulfate Sulfur Residual (Wt. %)	Total Sulfur Residual (Wt. %)	Total Sulfur Removal (%)	Chlorine Before Dechlorination (Wt. %)	Chlorine After Dechlorination (Wt. %)	Chlorine Injector	Remarks
21–7/10/79	0	67	6	21												
	15	79	10	22		0.64	11	0.45	42	0.07	1.17	26	7.54		Teflon tube	Chlorine vented – at 83 min.
	30	77	28	19		0.48	33	0.46	40	0.05	0.99	38	14.5		with	
	45	61	30	6		0.32	56	0.55	29	0.06	0.94	41	16.9		1/16" holes	
	60	65	38	2		–	–	–	–	–	–	–	–			
	75	–	40	1		–	–	–	–	–	–	–	–			
	90	58	34	1		0.13	82	0.69	10	0.17	1.00	37	20.0			
	Bulk			10	1.32	0.62	14	0.25	63	<0.05	0.87	45	16.1			
	Dechlorinated Bulk					0.64	11	0.15	81	<0.05	0.79	50		2.50		
23–7/13/79	0	66	0	15												
	15	78	10	22		0.59	18	0.48	38	0.11	1.17	26	7.92		Teflon tube	Chlorine vented – at 68, 74, and
	30	71	27	16		0.36	50	0.54	30	0.11	1.02	36	13.3		1/32" holes	80 min.
	45	62	42	7		0.17	76	0.71	8	0.12	0.99	38	17.4			
	60	–	43	3		–	–	–	–	–	–	–	–			
	75	60	38	7		–	–	–	–	–	–	–	–			
	90	63	40	7		–	–	–	–	–	–	–	–			90 min. sample could not be taken.
	Bulk			11	1.51	0.65	10	0.22	71	<0.05	0.87	45	18.9	3.84		
19–6/25/79	0	68	2	26												
	15	92	18	22		0.71	1	0.51	34	<0.05	1.22	23	7.51		One coarse	Chlorine diffuser probably plugged
	30	84	14	11		0.54	25	0.45	42	0.05	1.05	34	[illegible]		and one	during run.
	45	73	12	5		0.41	43	0.52	32	0.06	0.99	38	[illegible]		extra-coarse	
	Bulk			16	1.10	0.61	15	0.29	62	0.06	0.97	39	[illegible]	2.18	fritted glass	
															cylinder	
38– 8/9/79	0	64	0	18												
	15	92	28	25		0.50	31	0.55	29	0.09	1.13	29	10.5		Teflon tube	
	30	79	40	7		0.45	37	0.56	27	<0.05	1.01	36	15.5		1/32" holes	
	45	76	46	–		–	–	–	–	–	–	–	–			
	Bulk			15	1.00	0.72	0	0.22	71	<0.05	0.95	40	14.8	–		
39–8/10/79	0	61	0	22												Run 39 used 2 kg coal obtained from
	15	90	26	30		0.55	24	0.30	61	<0.05	0.84	47	22.4		Teflon tube	run 38 treatment. Runs 38 and 39
	30	91	34	33		0.35	51	0.44	43	<0.05	0.78	51	29.6		1/32" holes	represent a 2 stage treatment.
	45	77	46	9		0.08	89	0.67	13	<0.05	0.75	53	34.3			
	Bulk			26	1.77	0.67	7	0.05	94	<0.05	0.72	55	34.4	2.13		

Table 5 (5 Cont'd)

Run # and Date	Time (Min.)	Temp. (°C)	Pressure (PSIG)	Chlorine Feed (SCFH)	Chlorine Feed (kg)	Organic Sulfur Residual (Wt. %)	Organic Sulfur Removal (%)	Pyritic Sulfur Residual (Wt. %)	Pyritic Sulfur Removal (%)	Sulfate Sulfur Residual (Wt. %)	Total Sulfur Residual (Wt. %)	Total Sulfur Removal (%)	Chlorine Before Dechlorination (Wt. %)	Chlorine After Dechlorination (Wt. %)	Chlorine Injector	Remarks
COAL: PSOC 282, +100 MESH SOLVENT: METHYLCHLOROFORM																
27–7/20/79	0	64	6	17		0.71	–	0.79	–	0.06	1.55	–	0.58			
	15	64	5	12		0.66	7	0.58	27	0.06	1.30	16	5.28		Teflon tube	Chlorine vented – at 50 and 70 min.
	30	63	8	10		0.57	20	0.52	34	0.06	1.15	26	8.88		1/32" holes	
	45	67	15	11		0.49	31	0.54	32	0.08	1.11	28	13.1			
	60	68	15	5		–	–	–	–	–	–	–	–			
	75	64	19	0		–	–	–	–	–	–	–	–			
	90	56	11	4		0.45	37	0.54	32	<0.05	0.99	36	17.9			
	Bulk			8	1.05	0.69	3	0.35	56	<0.05	1.04	33	14.8	2.19		
34–8/2/79	0	62		12												
	15	84	23	27		0.76	– 7	0.56	29	<0.05	1.31	15	6.46		Teflon tube	Chlorine vented – at 36, 52, 56, 65,
	30	81	31	11		0.69	3	0.52	34	<0.05	1.21	22	11.4		1/32" holes	and 76 min.
	45	62	32	9		0.51	28	0.60	24	<0.05	1.10	29	14.3			
	60	–	36	3		–	–	–	–	–	–	–	–			
	75	62	36	3		–	–	–	–	–	–	–	–			
	90	62	36	3		0.43	39	0.64	19	<0.05	1.06	32	18.7			
	Bulk			10	1.37	0.63	11	0.39	51	<0.05	1.01	35	17.5	1.25		
COAL: PSOC 282 SOLVENT: WATER																
15–6/15/79	0	64	0	12												
	15	69	0.5	13		0.71	1	0.61	21	<0.05	1.32	17	3.80		Two	
	30	71	1	13		0.74	– 3	0.41	47	<0.05	1.15	28	7.14		extra-coarse	
	45	73	4	13		0.73	– 1	0.35	55	<0.05	1.07	33	10.5		fritted glass	
	Bulk			13	0.86	0.59	18	0.36	53	<0.05	0.95	40	10.4		cylinders	
	Dechlorinated Bulk					0.68	6	0.18	77	<0.05	0.86	46		0.94		
18–6/22/79	0	87	2	16												
	15	91	7	17		0.76	– 6	0.54	30	<0.05	1.29	19	4.86		One coarse	Chlorine diffuser probably plugged
	30	84	7	8		0.71	1	0.42	45	<0.05	1.14	28	7.66		and one	during the run.
	45	86	6	5		0.71	1	0.40	48	<0.05	1.11	30	9.59		extra-coarse	
	Bulk			12	0.80	0.72	0	0.42	45	<0.05	1.14	28	9.25	0.65	fritted glass	
															cylinder	
20–6/27/79	0	88	0	~14		–	–	–	–	–	–	–	–		Teflon tube	Injection tube plugged, chlorine leak.
	15	–	–	–		–	–	–	–	–	–	–	–		with many	Run aborted, no samples.
	30			0		–	–	–	–	–	–	–	–		1/74" holes	
	45			0		–	–	–	–	–	–	–	–			
	Bulk			16	0.34	–	–	–	–	–	–	–	–			

Table 5 (6 Cont'd)

Run # and Date	Time (Min.)	Temp. (°C)	Pressure (PSIG)	Chlorine Feed (SCFH)	Chlorine Feed (kg)	Organic Sulfur Residual (Wt. %)	Organic Sulfur Removal (%)	Pyritic Sulfur Residual (Wt. %)	Pyritic Sulfur Removal (%)	Sulfate Sulfur Residual (Wt. %)	Total Sulfur Residual (Wt. %)	Total Sulfur Removal (%)	Chlorine Before Dechlorination (Wt. %)	Chlorine After Dechlorination (Wt. %)	Chlorine Injector	Remarks
22–7/12/79	0	89	0	10												
	15	86	30	13		0.75	– 4	0.50	35	<0.05	1.26	21	4.45		Teflon tube	Chlorine vented – at 66, 77, and
	30	85	30	11		0.73	– 1	0.42	45	<0.05	1.16	27	6.72		1/32" holes	85 min.
	45	91	34	11		0.71	1	0.40	48	<0.05	1.11	30	10.1			
	60	81	36	11		–	–	–	–	–	–	–	–			
	75	93	39	14		–	–	–	–	–	–	–	–			
	90	96	36	14		0.55	24	0.37	52	<0.05	0.91	43	16.5			
	Bulk			12	1.66	0.56	22	0.31	60	<0.05	0.88	45	16.8			
	Dechlorinated Bulk					0.62	14	0.16	79	<0.05	0.78	51		2.78		
36–8/6/79	0	97	1	16												
	15	97	34	20		0.75	– 4	0.49	36	<0.05	1.23	23	5.41		Teflon tube	
	30	96	45	12		0.76	– 6	0.38	51	<0.05	1.15	29	9.56		1/32" holes	
	45	94	46	9		–	–	–	–	–	–	–	–			
	Bulk			15	1.03	0.75	– 4	0.39	61	<0.05	1.05	34	10.9	–		
37–8/7/79	0	–	0	14												Run 37 used 2 kg coal obtained from
	15	93	32	11		0.71	1	0.23	70	<0.05	0.95	40	14.4		Teflon tube	run 36 treated coal. Runs 36 and 37
	30	84	32	5		0.71	1	0.22	71	<0.05	0.93	42	15.4		1/32" holes	represent a 2 stage treatment.
	45	89	44	15		0.69	4	0.19	75	<0.05	0.89	44	17.9			
	Bulk			10	0.69	0.70	3	0.17	78	<0.05	0.87	45	17.2	0.80		
35–8/3/79	0	88	0	17												
	15	98	28	33		0.76	– 6	0.48	38	<0.05	1.24	22	6.28		Teflon tube	Chlorine vented – at 72 min.
	30	96	50	16		0.70	3	0.37	52	<0.05	1.07	33	11.9		1/32" holes	
	45	96	55	6		0.67	7	0.30	61	<0.05	0.97	39	13.8			
	60	–	56	3		–	–	–	–	–	–	–	–			
	75	–	57	4		–	–	–	–	–	–	–	–			
	90	90	54	4		0.61	15	0.31	60	<0.05	0.92	42	16.2			
	Bulk			12	1.65	0.68	6	0.26	66	<0.05	0.95	40	16.2	1.10		
24–7/17/79	0	128	25	6												
	15	114	29	11		0.77	– 7	0.53	31	<0.05	1.30	18	2.42		Teflon tube	Chlorine vented – at 33, 38, 47, 51,
	30	126	44	8		0.71	1	0.43	44	<0.05	1.14	28	3.74		1/32" holes	58, 62, 68, 75, and 82 min.
	45	129	48	3		0.77	– 7	0.42	45	<0.05	1.19	25	3.89			Injection tube partly plugged during
	60	128	46	2		–	–	–	–	–	–	–	–			the run.
	75	128	51	2		–	–	–	–	–	–	–	–			
	90	129	50	2		0.59	18	0.35	55	<0.05	0.94	41	11.4			
	Bulk			5	0.65	0.74	– 3	0.38	51	<0.05	1.12	30	3.24	0.44		

Table 5 (7 Cont'd)

Run # and Date	Time (Min.)	Temp. (°C)	Pressure (PSIG)	Chlorine Feed (SCFH)	Chlorine Feed (kg)	Organic Sulfur Residual (Wt. %)	Organic Sulfur Removal (%)	Pyritic Sulfur Residual (Wt. %)	Pyritic Sulfur Removal (%)	Sulfate Sulfur Residual (Wt. %)	Total Sulfur Residual (Wt. %)	Total Sulfur Removal (%)	Chlorine Before Dechlorination (Wt. %)	Chlorine After Dechlorination (Wt. %)	Chlorine Injector	Remarks
								COAL: PSOC 282, +100 MESH			SOLVENT: WATER					
26–7/19/79	0	63	3	10												
	15	66	8	11		0.61	14	0.65	18	0.05	1.31	15	3.38		Teflon tube	Chlorine vented – every 2 to 4 min.
	30	68	11	12		0.61	14	0.60	24	0.05	1.26	19	5.97		1/32" holes	
	45	64	10	12		0.68	4	0.49	38	<0.05	1.17	25	8.61			
	60	66	11	12		–	–	–	–	–	–	–	–			
	75	66	10	12		–	–	–	–	–	–	–	–			
	90	65	8	12		0.56	21	0.36	54	<0.05	0.92	41	14.2			
	Bulk			12	1.56	0.61	14	0.37	53	<0.05	0.98	37	13.2	2.23		
33–7/31/79	0	64	1	13												
	15	68	31	17		0.76	– 7	0.66	16	<0.05	1.42	8	5.49		Teflon tube	Chlorine vented – at 76 and 86 min.
	30	–	37	9		0.81	–14	0.53	33	<0.05	1.33	14	8.40		1/32" holes	
	45	64	37	8		0.78	–10	0.46	42	<0.05	1.23	21	10.1			
	60	–	34	8		–	–	–	–	–	–	–	–			
	75	67	37	7		–	–	–	–	–	–	–	–			
	90	71	37	8		0.73	– 3	0.39	51	<0.05	1.12	28	15.0			
	Bulk			10	1.33	0.73	– 3	0.39	51	<0.05	1.12	28	15.4	0.86		
								COAL: PSOC 219			SOLVENT: METHYLCHLOROFORM					
28–7/23/79	0	60	3	25		0.81	–	0.73	–	0.60	2.15	–	0.12			Coal charge 1.70 kg. Chlorine vented
	15	88	36	21		0.56	31	0.47	36	0.14	1.16	46	12.3		Teflon tube	– at 20, 32, 39, 49, 53, 61, and
	30	67	38	9		0.51	37	0.44	40	0.16	1.10	49	16.4		1/32" holes	84 min.
	45	–	36	4		0.31	62	0.59	19	0.07	0.97	55	17.5			
	60	59	38	4		–	–	–	–	–	–	–	–			
	75	71	29	4		–	–	–	–	–	–	–	–			
	90	–	35	10		0.00	100	0.79	–8	0.17	0.96	55	21.9			
	Bulk			10	1.40	0.66	19	0.18	75	<0.05	0.83	61	19.6	1.44		
									COAL: PSOC 219		SOLVENT: WATER					
29–7/25/79	0	62	6	19												Coal charge 1.90 kg. Chlorine vented
	15	67	29	8		0.83	– 2	0.39	47	0.13	1.34	38	4.53		Teflon tube	– at 69 min.
	30	69	29	10		0.86	– 6	0.32	56	0.11	1.28	40	5.40		1/32" holes	
	45	66	32	10		0.80	1	0.20	73	0.09	1.09	49	7.97			
	60	–	34	11		–	–	–	–	–	–	–	–			
	75	66	32	11		–	–	–	–	–	–	–	–			
	90	70	33	14		0.86	– 6	0.14	81	<0.05	1.00	53	15.8			
	Bulk			11	1.43	0.81	0	0.10	86	<0.05	0.91	58	17.5			
	Dechlorinated Bulk					0.69	15	0.05	93	<0.05	0.74	66	–	1.7		

Table 5 (8 Cont'd)

Run # and Date	Time (Min.)	Temp. (°C)	Pressure (PSIG)	Chlorine Feed (SCFH)	Chlorine Feed (kg)	Organic Sulfur Residual (Wt. %)	Organic Sulfur Removal (%)	Pyritic Sulfur Residual (Wt. %)	Pyritic Sulfur Removal (%)	Sulfate Sulfur Residual (Wt. %)	Total Sulfur Residual (Wt. %)	Total Sulfur Removal (%)	Chlorine Before Dechlorination (Wt. %)	Chlorine After Dechlorination (Wt. %)	Chlorine Injector	Remarks
						COAL: PSOC 026				SOLVENT: METHYLCHLOROFORM						
31–7/27/79	0	65	6	18		1.62	–	1.17	–	0.66	3.45	–	0.19			Coal charge 1.71 kg. Chlorine vented
	15	82	20	34		1.46	10	0.48	59	0.17	2.11	39	8.04		Teflon tube	– at 33, 56, 62, 69, 76, and 78 min.
	30	72	43	7		1.34	17	0.37	68	0.14	1.85	46	13.7		1/32" holes	No chlorine flow between 36 and
	45	64	40	0		1.29	20	0.49	58	<0.05	1.78	48	19.2			55 min., during reactor repair.
	60	61	44	7		–	–	–	–	–	–	–	–			
	75	63	50	3		–	–	–	–	–	–	–	–			
	90	59	37	0		0.88	46	0.69	41	0.17	1.74	50	23.7			
	Bulk			10	1.38	1.57	3	0.11	91	<0.05	1.67	52	21.2	1.40		
								COAL: PSOC 026		SOLVENT: WATER						
30–7/26/79	0	65	–	11												Coal charge 1.70 kg.
	15	67	15	22		1.59	2	0.65	44	0.10	2.34	32	3.92		Teflon tube	
	30	71	31	5		1.69	– 4	0.37	68	<0.05	2.06	40	7.30		1/32" holes	
	45	62	34	6		1.69	– 4	0.20	83	<0.05	1.89	45	10.6			
	60	–	29	6		–	–	–	–	–	–	–	–			
	75	70	29	7		–	–	–	–	–	–	–	–			
	90	71	31	7		1.54	5	0.13	89	0.13	1.81	48	16.4			
	Bulk			9	1.26	1.66	– 2	0.08	93	<0.05	1.75	49	15.8			
	Dechlorinated Bulk					1.37	15	0.06	95	<0.05	1.43	59	–	2.1		
32–7/30/79	0	87	4	16												Coal charge 1.70 kg. Chlorine vented
	15	92	26	18		1.81	–12	0.62	47	<0.05	2.42	30	5.15		Teflon tube	– at 49 and 66 min.
	30	86	32	10		1.72	– 6	0.32	73	<0.05	2.04	41	9.10		1/32" holes	
	45	83	34	14		1.69	– 4	0.23	80	<0.05	1.92	44	12.0			
	60	–	37	9		–	–	–	–	–	–	–	–			
	75	–	37	8		–	–	–	–	–	–	–	–			
	90	91	34	8		1.48	9	0.13	89	0.06	1.67	52	17.4			
	Bulk			12	1.62	1.50	7	0.11	91	0.09	1.69	51	17.9	1.23		
								COAL: ISLAND CREEK		SOLVENT: METHYLCHLOROFORM						
43–8/22/79	0	61	0	11		1.84	–	1.78	–	0.10	3.72	–	0.20		Teflon tube	
	15	82	13	30		1.80	2	1.14	36	0.06	3.00	19	4.92		1/32" holes	
	30	88	35	21		1.65	10	0.66	63	<0.05	2.32	38	11.5			
	45	77	47	13		–	–	–	–	–	–	–	–			
	Bulk			21	1.38	1.67	9	0.31	83	<0.05	1.98	47	15.2	–		

TABLE 5 (9 Cont'd)

Run # and Date	Time (Min.)	Temp. (°C)	Pressure (PSIG)	Chlorine Feed (SCFH)	(kg)	Organic Sulfur Residual (Wt. %)	Organic Sulfur Removal (%)	Pyritic Sulfur Residual (Wt. %)	Pyritic Sulfur Removal (%)	Sulfate Sulfur Residual (Wt. %)	Total Sulfur Residual (Wt. %)	Total Sulfur Removal (%)	Chlorine Before Dechlorination (Wt. %)	Chlorine After Dechlorination (Wt. %)	Chlorine Injector	Remarks
44–8/24/79	0	66	3	5												Coal charge, 1.57 kg, was run 43 bulk
	15	88	25	39		1.38	25	0.33	81	0.08	1.79	52	21.8		Teflon tube	
	30	84	43	16		0.79	57	0.82	54	<0.05	1.59	57	28.9		1/32" holes	
	45	68	45	10		0.61	67	0.95	47	<0.05	1.56	58	31.5			
	Bulk			21	1.38	1.50	18	0.09	95	<0.05	1.59	57	33.2	5.12		
								COAL: ISLAND CREEK			SOLVENT: WATER					
40–8/15/79	0	88	0	19												
	15	92	38	10		1.98	− 8	1.19	33	<0.05	3.17	15	4.20		Teflon tube	
	30	93	41	11		1.84	0	1.10	38	<0.05	2.94	21	[illegible].12		1/32" holes	
	45	97	46	–		–	–	–	–	–	–	–	–			
	Bulk			12	0.78	1.74	5	0.82	54	0.07	2.63	29	8.73	–		
41–8/17/79	0	93	0	13												Coal charge, 1.89 kg, was run 40 bulk.
	15	86	50	13		1.86	− 1	0.58	67	<0.05	2.44	34	8.34		Teflon tube	Chlorine vented – at 5 and 10 min.
	30	84	47	7		1.85	− 1	0.25	86	<0.05	2.10	44	10.9		1/32" holes	and every 1 to 3 min. thereafter. No
	45	79	40	7		1.75	5	0.20	89	0.07	2.03	45	14.3			stirring – impeller broke off before
	Bulk			10	0.68	1.77	4	0.24	87	<0.05	2.01	46	16.4	–		run.
42–8/21/79	0	94	10	15												Coal charge, 1.69 kg, was run 41 bulk.
	15	95	40	11		1.82	1	0.42	76	<0.05	2.24	40	13.3		Teflon tube	Chlorine vented – at 20, 24, 29, 33,
	30	97	40	11		1.69	8	0.32	82	0.07	2.07	44	15.3		1/32" holes	35, and 41 min.
	45	98	47	12		1.76	4	0.24	87	<0.05	2.01	46	17.6			
	Bulk			12	0.79	1.79	3	0.25	86	<0.05	2.04	45	16.7			
	Dechlorinated Bulk					1.57	15	0.17	90	<0.05	1.74	53	–	2.39		

FOOTNOTES

a: Chlorine flow rates are point values except for that listed under the bulk value which represents the chlorine flow rate obtained for the weight of chlorine fed averaged over the time of the run.

b: All sulfur values a e corrected to chlorine free basis.

Inspection of the data in Table 5 indicates no apparent correlation of coal desulfurization with respect to temperature, pressure and chlorine flow rates. A substantial reduction of chlorine flow into the coal slurry did reduce coal desulfurization in run 5 when the chlorine injection tube failed from corrosion and chlorine was injected only into the top surface layer of the coal slurry and into the ullage space of the reactor. Changes in gaseous chlorine injection from a 1/4-inch tube opening located to the side and beneath the agitator impeller to a standard fritted glass diffuser element and finally to a Teflon tube drilled with 1/74- to 1/16-inch diameter holes with a final size of 1/32-inch holes did materially affect the introduction of chlorine into the coal slurry solution but did not translate into a corresponding effect on coal desulfurization. A substantial variation in temperature, pressure and chlorine flow rates existed between runs so that any substantial effect of these variables on the coal desulfurization reaction would have been evident if a large effect existed. Reaction times of 15 and 30 minutes were sufficiently short to allow observation of kinetic reaction effects in this operating range. A reaction time of 45 minutes provided a leveling off and/or peaking of coal desulfurization. Sulfur forms and percentage reductions are indicated in Table 5 for individual runs. The runs are grouped according to coal and solvent with an attempt to list the runs in terms of increasing temperature and/or pressure.

PSOC 276 with Methylchloroform

Five runs were made. Operating conditions were generally at 60-70°C, 1-50 psig, and 10-20 SCFH of Cl_2 for times of 15, 30 and 45 minutes. Organic sulfur removal was negative with an apparent slight increase in organic sulfur which could be attributed to analytical chemistry bias. Pyritic sulfur removal was between 43 and 61% in 15 minutes and increased to a maximum of 88% removal in

45 minutes. Sulfate sulfur values after the filter cake spray wash were less than 0.05 weight per cent. Total sulfur removals were 28 to 38 percent in 15 minutes and reached a maximum of 63% removal in 45 minutes. Chlorine addition to the coal was approximately 3 wt. % in 15 minutes and increased to 7-10 wt. % in 45 minutes. Dechlorination reduced chlorine levels to 0.7-1.3 wt.%.

PSOC 276 With Water

Ten runs were made. Operating conditions were: 60-130°C, 0-48 psig, 6-22 SCFH of Cl_2 and 15, 30, 45 minutes reaction time. Organic sulfur removal was negative with an apparent slight increase in organic sulfur that could be attributed to analytical chemistry bias. Pyritic sulfur removal was 23 to 50% in 15 minutes and up to 75% in 45 minutes. Sulfate sulfur after spray washing of the coal on the vacuum filter was always less than 0.05 wt. %. Total sulfur removal was 14-31% in 15 minutes and up to 51% in 45 minutes. Coal desulfurization results for both pyritic and total sulfur were somewhat less with water than with methylchloroform as a solvent. Chlorine addition to the coal was 2-3 wt. % in 15 minutes and 4-11 wt. % in 45 minutes. This chlorine addition to the coal was slightly less with water than with methylchloroform as a solvent. Dechlorination reduced chlorine levels to 0.2-1.5 wt. %.

PSOC 282 With Methylchloroform

Nine runs were made of which two were with coarse coal particles of -1/8-inch to +100 mesh. Operating conditions were: 61-91°C, 0-46 psig, 5-26 SCFH of Cl_2, reaction times of 15, 30, 45, 90 minutes.

Organic sulfur removal was 0 to 31% in 15 minutes, 7 to 89% (2-step process, run 38) in 45 minutes. However, the high organic sulfur removal indicated in the 45 minute sample was not sustained in the analysis of the coal sample obtained after solvent distillation, vacuum filtration and washing. The 89% organic sulfur removal was reduced to 7% removal. This experience was indicated in six of the nine runs. Pyritic sulfur removal was 27-61% in 15 minutes and 13-35% in 45 minutes, an apparent reduction in pyritic sulfur removal at the longer reaction time. Analysis of the bulk coal after solvent distillation, filtration and washing indicated a reversal of pyritic sulfur removal from that indicated by the 45 minute sample. Pyritic sulfur removals were as high as 94% with a corresponding drop in organic sulfur removal (also in 2-step reaction). Sulfate sulfur removals were generally high with residual sulfur less than 0.05 wt. %. Total sulfur removals were 23-47% in 15 minutes with -100 to +200 mesh coal and only 14-16% in 15 minutes with +100 mesh coal. Total sulfur removals were 33-55% in 45 minutes with -100 to +200 mesh coal and only 28-29% with +200 mesh coal. Extension of the reaction time to 90 minutes with -100 to +200 mesh coal did not substantially increase total sulfur removal. With +100 mesh coal, the added reaction time to 90 minutes increased desulfurization by 10 to 20%.

Chlorine addition to the coal was 5-22 wt. % in 15 minutes and 7 to 35 wt. % in 45 minutes, a general increase with extended chlorination times. Chlorine addition for PSOC 282 coal was appreciably higher than for PSOC 276 coal under comparable chlorination conditions. Residual chlorine values after dechlorination were between 1.2 and 3.8 wt. %, considerably higher values for PSOC 282 coal relative to PSOC 276 coal.

Changes in diffusers for chlorine injection as well as chlorine venting though the system did not appreciably affect desulfurization results.

PSOC 282 With Water

Ten runs were made of which two were with coarse coal of -1/8-inch to +100 mesh. Operating conditions were: 64-129°C, 0-57 psig, 5-16 SCFH of chlorine, reaction times of 15, 30, 45 and 90 minutes.

Organic sulfur removals were from -7 to +24%. Analytical bias probably accounted for the apparent increase in organic sulfur. Pyritic sulfur removals were 21 to 70% in 15 minutes and 45-79% in 45 minutes. Sulfate sulfur values were less than 0.05 wt. % in the processed coal. Total sulfur removal was 17-40% in 15 minutes and 30-45% in 45 minutes. Dechlorination of the coal produced an added 6% in total sulfur removal over the washed but undechlorinated coal.

The coarse coal, +100 mesh, provided somewhat reduced desulfurization than the -100 to +200 mesh coal. Peak total sulfur removal was 21-25% in 45 minutes. Extending reaction time to 90 minutes increased total desulfurization to 28-41%.

Chlorine addition to the coal with water as a solvent was less than with methylchloroform under comparable conditions. Chlorine added was between 4 and 18 wt. % in 45 minutes. Extended reaction times to 90 minutes added chlorine to 11-16 wt. %. Dechlorinated coal had chlorine values of 0.4 to 2.8 wt. %.

PSOC 219 With Methylchloroform

Operating conditions were: 59-88°C, 3-38 psig, 10 SCFH chlorine, reaction times of 15, 30, 45, 90 minutes.

Organic sulfur removal was 31% in 15 minutes and 62% in 45 minutes with an apparent reversal of organic sulfur removal in processing the bulk coal to 19%. This anamoly between the organic sulfur determination before and after distillation, filtration and washing appears prevalent with runs using methylchloroform as solvent. The corresponding pyritic sulfur removal was 36% in 15 minutes and 19% in 45 minutes (corresponding organic sulfur removal of 62%) with the bulk coal sample showing 75% pyritic sulfur removal.

Sulfate sulfur in the original raw coal sample was 0.6 wt. % and was reduced after washing to <0.05-0.17 wt. %. Total sulfur removal was 46% in 15 minutes, 55% in 45 minutes and 55-61% in 90 minutes. Chlorine addition to the coal was 12 wt. % in 15 minutes, 17 wt. % in 45 minutes and 20-22 wt. % in 90 minutes. Dechlorination reduced chlorine addition to 1.4 wt. %.

PSOC 219 With Water

Operating conditions were: 62-70°C, 6-34 psig, 11 SCFH chlorine, reaction times of 15, 30, 45 and 90 minutes. Organic sulfur removal was approximately zero during the chlorination. Dechlorination provided a 15% organic sulfur removal. Pyritic sulfur removal was 47% in 15 minutes, 73% in 45 minutes and 81-86% in 90 minutes with dechlorination increasing pyritic sulfur removal to 93%. Sulfate sulfur levels were <0.05 to 0.13 wt. %. Total sulfur removal was 38% in 15 minutes, 49% in 45 minutes, 53-58% in 90 minutes and 66% after dechlorination. Chlorine addition to the coal was 4.5 wt. % in 15 minutes, 8 wt. % in 45 minutes and 17 wt. % in 90 minutes, appreciably less than with methylchloroform as a solvent at comparable chlorine feed rates to the reactor. Dechlorinated coal contained 1.7 wt. % chlorine.

PSOC 026 With Methylchloroform

Operating conditions were: 59-82°C, 6-50 psig, 10 SCFH Cl_2, reaction times of 15, 30, 45, and 90 minutes. Organic sulfur removal was 10% in 15 minutes, 20% in 45 minutes, 46% in 90 minutes with a reversal in organic sulfur removal after full processing of the bulk coal to 3% removal. Comparable occurrences were noted with PSOC 282 and 219 coals. Pyritic sulfur removal was 59% in 15 minutes, 68% in 30 minutes and declined to 58% in 45 minutes and 41% in 90 minutes with a change of the 90 minute bulk coal sample after full processing to 91% pyritic sulfur removal. This reflected the decrease in pyritic sulfur removal with a corresponding increase in organic sulfur removal and a final reversal of sulfur forms in the bulk sample with total sulfur removal remaining approximately constant after 30 minutes, i.e., 46 to 52% total sulfur removal.

PSOC 026 With Water

Operating conditions were 62-91°C, 4-37 psig, 9-12 SCFH chlorine, reaction times of 15, 30, 45, 90 minutes. Organic sulfur removal was -12 to +9% during chlorination and 15% with dechlorination. Pyritic sulfur removal was 44-47% in 15 minutes, 80-83% in 45 minutes and 89-93% in 90 minutes. Sulfate sulfur was generally reduced to less than 0.05 wt. %. Total sulfur removals went from 30-32% in 15 minutes, 44-45% in 45 minutes, 49-52% in 90 minutes and 59% after dechlorination of the 90-minute sample. Chlorine additions to the coal were 10-12 wt. % in 45 minutes and increased to 16-18 wt. % in 90 minutes. Dechlorination reduced these values to 1.2 to 2.1 wt. %.

Island Creek Coal With Methylchloroform — Two Stage Desulfurization

Two runs were made with the treated coal from the first run representing the coal charge for the second run. The objective was to investigate the possibilities afforded by a two-stage desulfurization reaction. First stage coal was first washed and filtered before being added to the second stage.

Operating conditions were: 61-88°C, 0-47 psig, 21 SCFH chlorine, reaction times of 15, 30 and 45 minutes. Organic sulfur removal in the first stage was a maximum of 10% in 30-45 minutes and increased in the second stage to a maximum of

67% in 45 minutes, with reversal of organic sulfur removal after processing of the bulk coal to only 18%. Pyritic sulfur removal in the first stage was 83% in 15 minutes and fluctuated in the second stage from 81% removal in 15 minutes to 54% in 30 minutes, 47% in 45 minutes and 95% after processing of the bulk coal sample. Total sulfur removals were up to 47% after first stage treatment of 45 minutes and 57% after second stage treatment, a 10% total sulfur removal improvement. First stage chlorination provided chlorine coal addition up to 15 wt. % and the second stage chlorination increased chlorine addition to 33 wt. %. Dechlorination of the two-stage treated coal gave a high residual chlorine of 5.1 wt. %.

Island Creek Coal With Water — Three-Stage Desulfurization

Three runs were made with the treated coal from the first stage treatment representing the coal charge for the next stage, i.e., a three stage coal treatment. Three stage treatment was chosen since the impeller was apparently off the shaft in the second stage. Operating conditions were 79-98°C, 0-47 psig, 10-12 SCFH chlorine, reaction times of 15, 30 and 45 minutes for each stage. Organic sulfur removal in the three stages fluctuated between -8 to +8% with dechlorination increasing organic sulfur removal to 15%. Pyritic sulfur removal was 54% in the first stage, 87-89% in the second stage and 86-87% in the third stage with dechlorination raising removal to 90%. Total sulfur removal was 29% in the first stage, 46% in the second stage and 45-46% in the third stage with dechlorination increasing total sulfur removal to 53%. Chlorine addition to the coal was 8.7 wt. % in the first stage, 16.4 wt. % in the second stage and 17.6 wt. % in the third stage. Dechlorination reduced chlorine content to

2.4 wt. %. The apparent loss of the impeller during the second stage reaction did not impose any noticeable deterioration on coal desulfurization.

Sulfur Forms

Data Summary

Sulfur forms are listed in Table 5 for individual runs. Since temperature, pressure and chlorine flow had no apparent correlation with desulfurization, all of the runs with a given coal and given solvent (methylchloroform or water) were averaged (Table 5), which included runs not representing the best data and average residual sulfur forms plotted with respect to reaction time, Figures 5, 6 and 7. Average sulfur reductions in addition to average sulfur residuals were also calculated for organic, pyritic and total sulfur for each of the coals and solvents and plotted, Figures 8, 9 and 10.

A summary table of average sulfur removals for organic, pyritic and total sulfur is included, Table 6, for a reaction time of 45 minutes. Sulfur removals are indicated both as weight percent sulfur removal and as a percent removal of original sulfur. The data indicates:

(1) No organic sulfur removal for coal PSOC 276 with an apparent (but not significant) increase in organic sulfur.

(2) Remaining coals PSOC 282, 219, 026 and Island Creek showed apparent organic sulfur removal of 46 to 89 percent with methychloroform and 0-24% decrease in organic sulfur with water as a solvent. (Apparent contradictory laboratory scale data exists showing better organic sulfur removal with water as a solvent with coals PSOC 190 and PSOC 219 than with methylchloroform.)

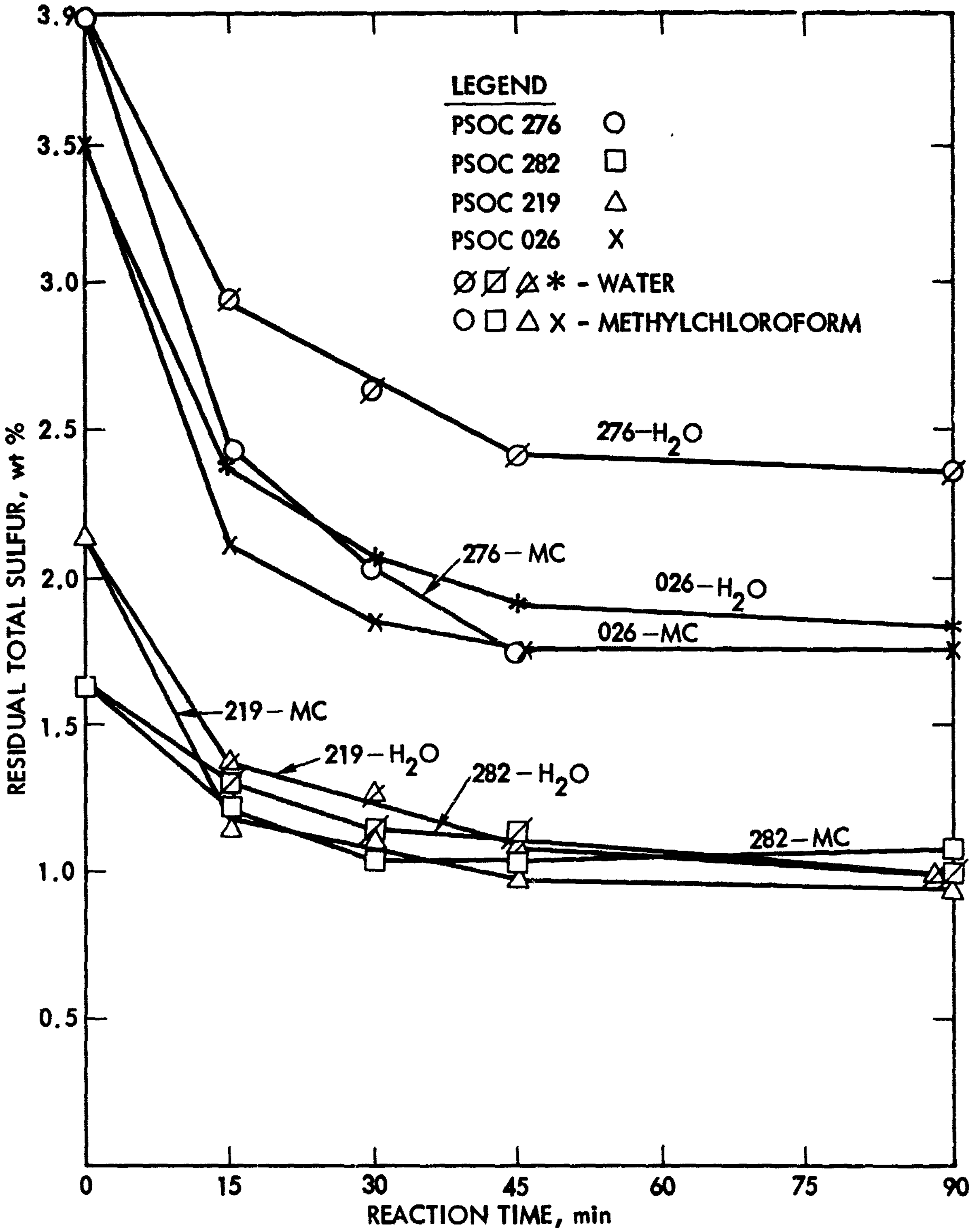

Figure 5. Residual Total Sulfur vs. Reaction Time.
(Coal Desulfurization by Chlorinolysis)
Reference: Table 5.

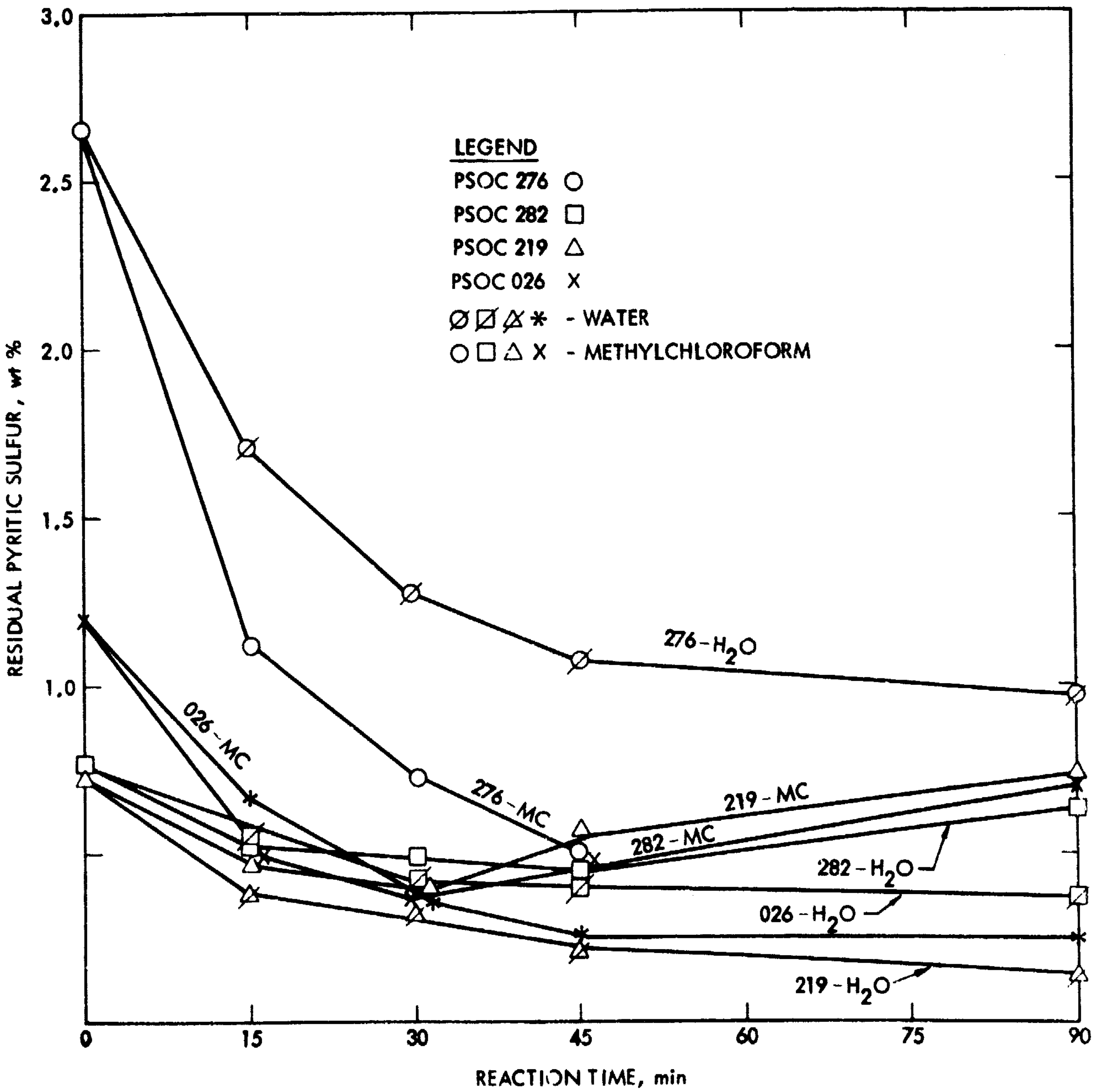

Figure 6. Residual Pyritic Sulfur vs. Reaction Time.
(Coal Desulfurization by Chlorinolysis)
Reference: Table 5.

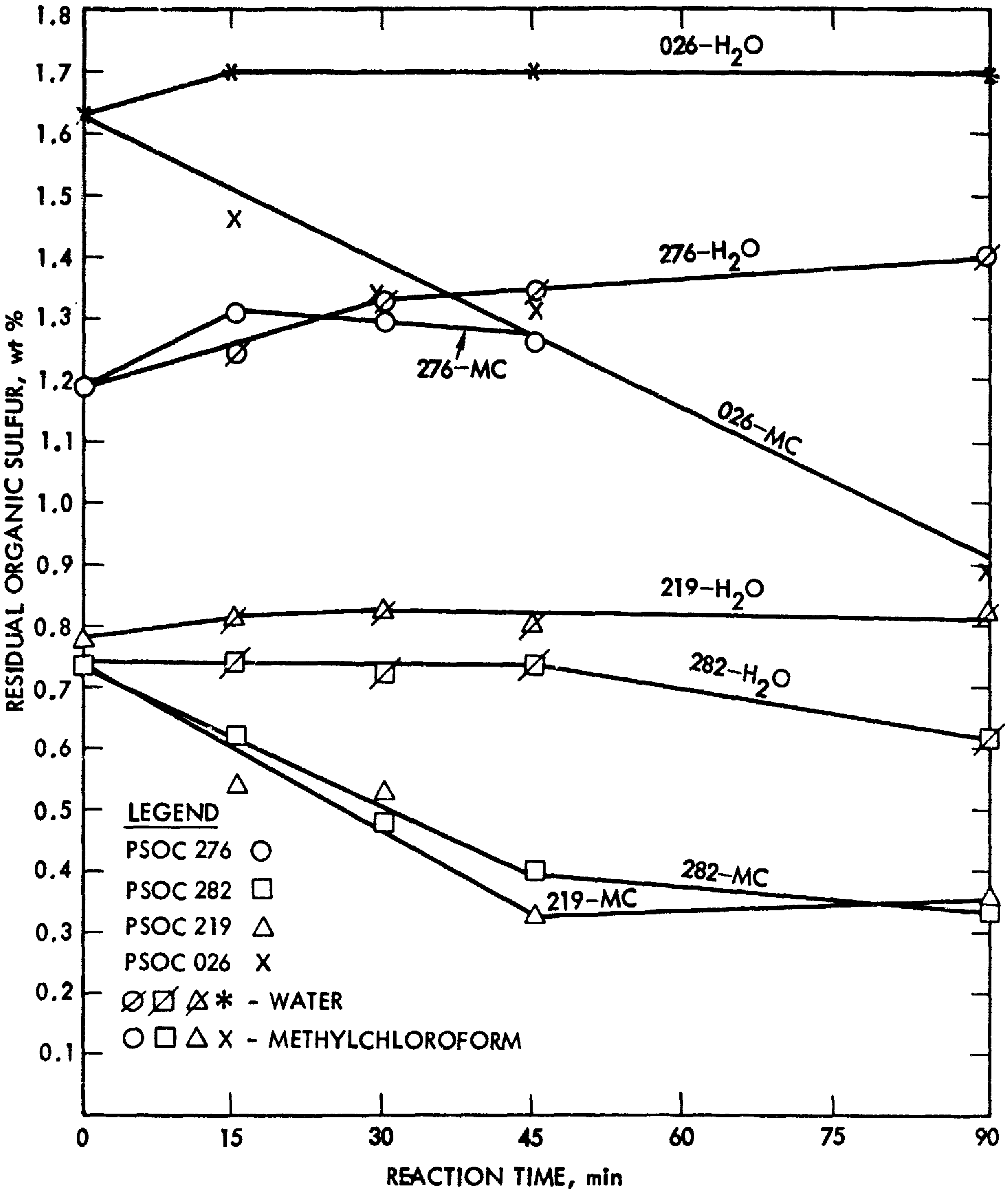

Figure 7. Residual Organic Sulfur vs. Reaction Time.
(Coal Desulfurization by Chlorinolysis)
Reference: Table 5

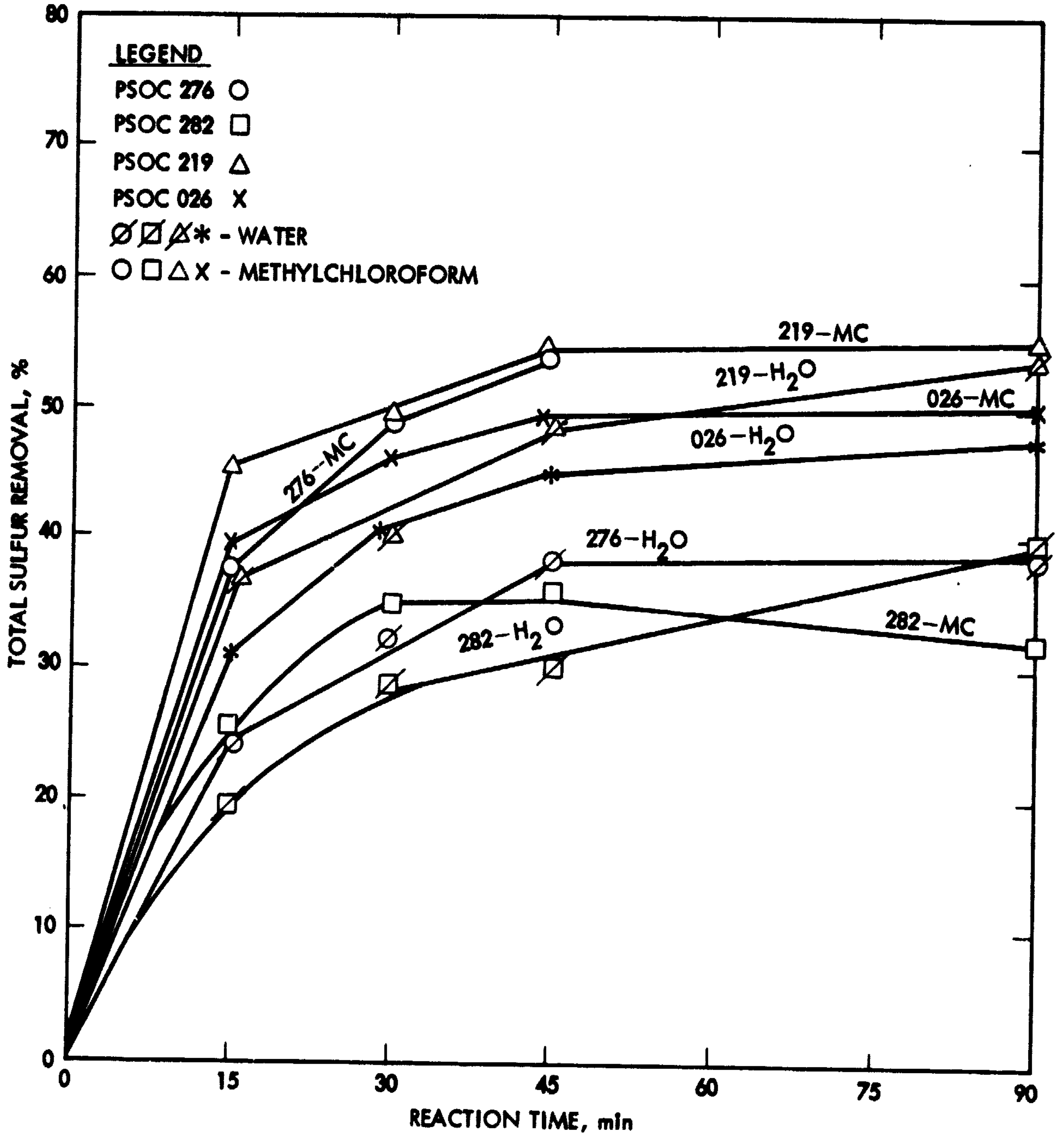

Figure 8. Total Sulfur Removal vs. Reaction Time. (Coal Desulfurization by Chlorinolysis) Reference: Table 5.

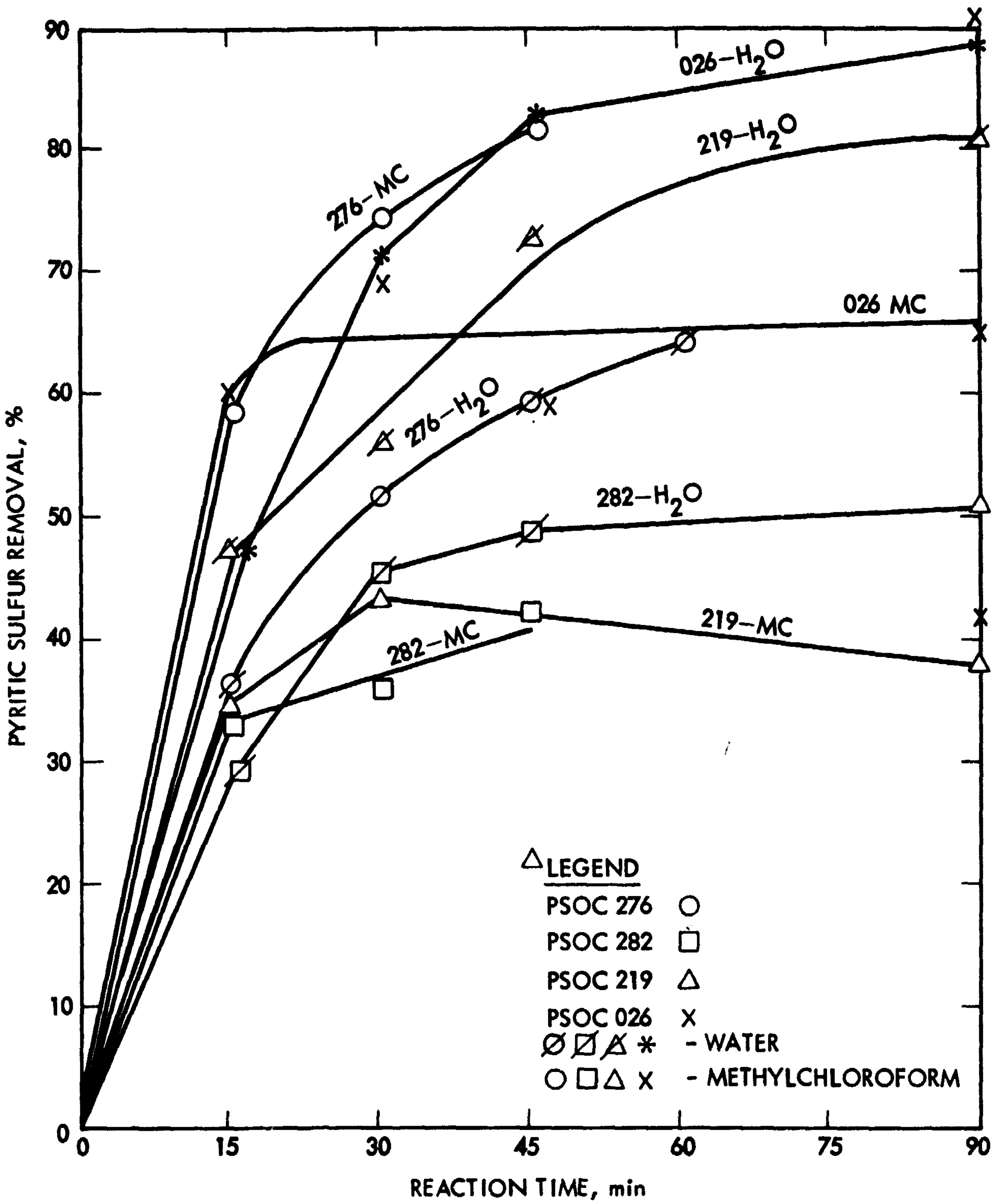

Figure 9. Pyritic Sulfur Removal vs. Reaction Time.
(Coal Desulfurization by Chlorinolysis)
Reference: Table 5.

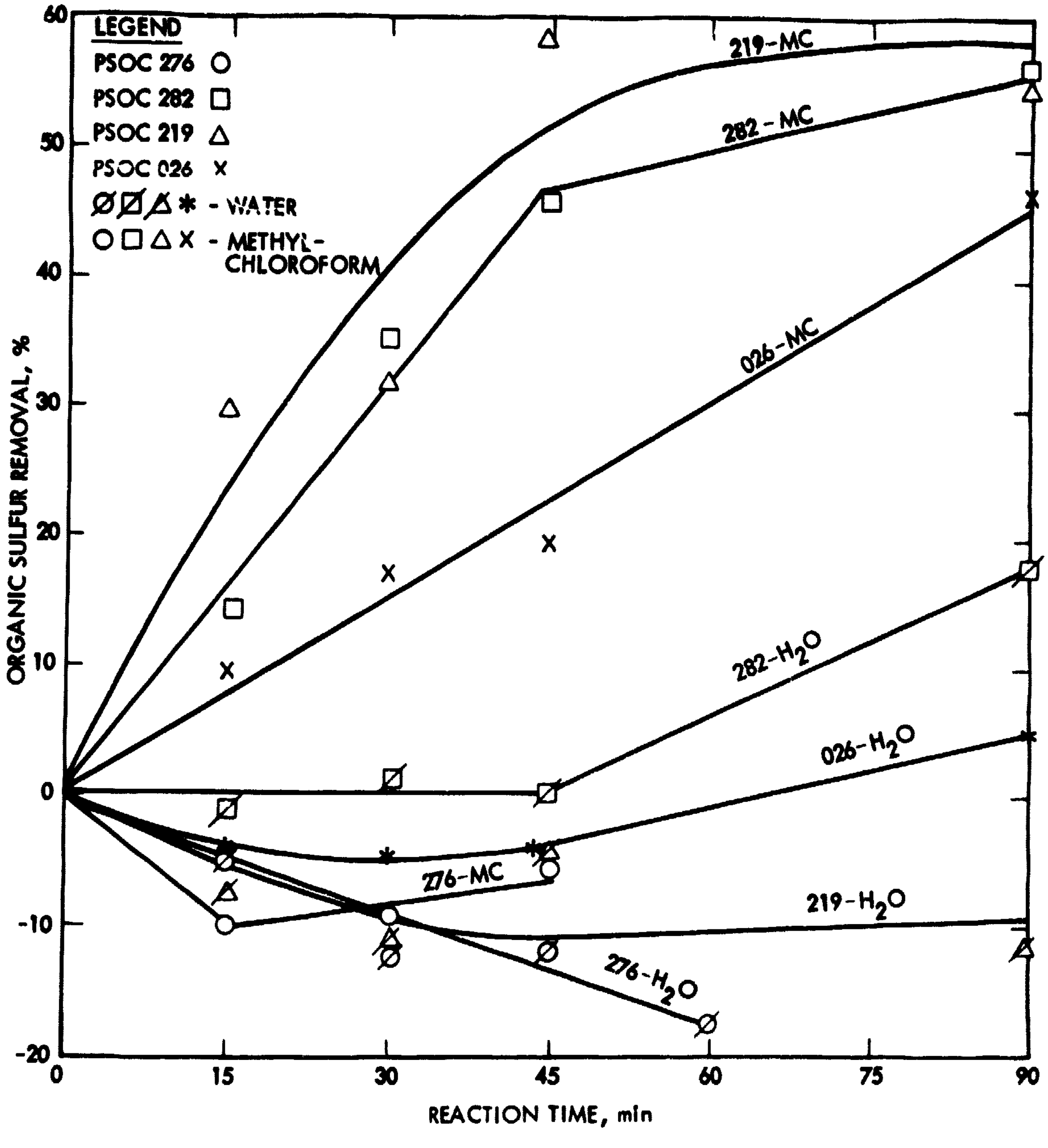

Figure 10. Organic Sulfur Removal vs. Reaction Time. (Coal Desulfurization by Chlorinolysis) Reference: Table 5.

Table 6. Coal Desulfurization Data, Bench-Scale Batch Reactor — 45 Minutes Reaction Time (Condition: 2 kg Coal—100 to +200 mesh. methylchloroform runs at 65°C, water runs at 65-130°C; pressure at 0 - 60 psig; chlorine feedrate at 5 to 24 SCFH; agitator speed 275 - 565 rpm, live steam preheat condensate to coal, 10-20 percent at 65°C, 125 percent at 130°C.) (Reference Table 5.)

Coal	Solvent	Organic Sulfur** Removal (Wt. %)	Organic Sulfur** Removal (%)	Pyritic Sulfur** Removal (Wt. %)	Pyritic Sulfur** Removal (%)	Total Sulfur** Removal (Wt. %)	Total Sulfur** Removal (%)
PSOC-276	MC*	-0.07	-6	2.17	81	2.13	55
PSOC-276	H_2O	-0.14	-12	1.59	60	1.48	38
PSOC-282	MC	0.37	50	0.26	33	0.67	41
PSOC-282	H_2O	0.02	3	0.44	56	0.56	35
PSOC-219	MC	0.45	58	0.16	22	1.17	55
PSOC-219	H_2O	-0.03	-4	0.54	73	1.05	49
PSOC-026	MC	0.43	19	0.61	59	1.69	49
PSOC-026	H_2O	0.19	-4	0.99	82	1.58	45
Island Creek	MC	0.17	9	1.47	82	1.74	47
Island Creek	H_2O	0.10	5	0.96	54	1.09	29

*Methylchloroform.

**Average data represented that include runs not representing the best data.

(3) Apparent increases in organic sulfur are not considered significant since analytical accuracy is probably less than measured organic sulfur increases.

(4) Maximum total sulfur removal is greater with methylchloroform as a solvent for coals PSOC 276, 282 and Island Creek Coal relative to water (58-63% vs. 45-53%). Remaining coals show slight decreases of total sulfur removal with methylchloroform versus water. Coals PSOC 219 and 026 show approximately 60% total sulfur removal and PSOC 282 shows approximately 45 to 55% total sulfur reduction.

(5) Pyritic sulfur removals for coals PSOC 282, 026 and 219 were greater with water, 56 to 82% versus 33 to 59% for methylchloroform. This data is a reversal of that noted for PSOC 276 and Island Creek coal in which methylchloroform aided pyritic sulfur removal relative to water.

(6) Although some apparent reductions in organic and pyritic sulfur values are indicated by extending the reaction time from 45 to 90 minutes, Figures 5 to 10, the apparent increased reductions in one sulfur form are apparently nullified by an apparent increase in the alternate sulfur form (organic vs. pyritic) such that the total sulfur reduction appears to be a maximum at 45 minutes.

(7) Dechlorination of chlorinated coals showed a total sulfur reduction increase of 4-11% with some of the reduction exhibited in organic sulfur but the largest reduction in pyritic sulfur.

(8) A two-stage chlorination reaction using fresh solvent and coal washing between stages results in an improved desulfurization in the second stage over the first stage for organic, pyritic and total sulfur. Total sulfur removal was increased 10 to 17%.

Reproducibility of Sulfur Forms Data Among Laboratories

A comparison is presented of the analytical results obtained from four different analytical laboratories when analyzing a portion of the same treated coal sample, Table 7. Samples of PSOC 276 coal that were chlorinated, washed and dried, test runs 7 and 9, and PSOC 282 coal, test run 17, were submitted to: Colorado School of Mines Research Institute; Department of Energy - Pittsburgh Mining Technology Center; Galbraith Laboratories, Inc.; and Standard Laboratories, Inc. Care was exercised to provide a representative treated coal sample to each of the laboratories from the same bulk sample of treated coal. The analytical data are tabulated for sulfur forms, chlorine and ash for each of the test runs by laboratory. The data were averaged and a standard deviation obtained for each set of analyses. The allowable ASTM deviation for analyses between laboratories is also included.

The average of the results from all four laboratories generally met the ASTM guidelines for allowable deviations. However, the results generally indicated that in each set of results there was one laboratory value with a significant discrepancy from the other three values. Also, if one compares the minimum and maximum values from each set of data the discrepancy between laboratories is outside the allowable ASTM range. Also, when one considers values of organic and pyritic sulfur less than 1 wt. %, the standard deviation may amount to 50% or more of the average sulfur value, providing substantial uncertainty in the determination.

Chlorine determinations were generally within 10% between laboratories although in one case the standard deviation was 34%.

Ash determination were within 10 to 20% on the average but given individual values differed much more substantially.

Table 7. Reproducibility of Sulfur Forms Analyses Among Laboratories

Coal Type	Sample	LAB	Sulfur Analyses (wt %) Organic	Pyritic	Sulfate	Total	Chlorine (wt %)	Ash (wt %)
PSOC 276	RUN 7 Bulk Chlorinated, Washed and Dried Coal	CSMRI[c]	1.24	0.39	0.05	1.68	6.94	7.75
		DOE[d]	1.32	0.35	0.00	1.68	6.99	7.69
		Galbraith[e]	1.17	0.26	0.08	1.51	7.18	5.69
		Standard[f]	1.06	0.45	0.04	1.55	5.63	7.34
		Average	1.20	0.35	0.04	1.61	6.69	7.12
		Standard Deviation[g]	0.11	±0.08	±0.03	±0.09	±0.71	±0.97
		ASTM[a] Allowed Range	--	0.30	0.04	0.10	--	--
PSOC 276	RUN 9 Bulk Chlorinated, Washed and Dried Coal	CSMRI	1.47	0.95	<0.05	2.42	5.88	8.63
		DOE	1.39	0.93	0.00	2.33	5.08	8.28
		Galbraith	1.29	0.71	0.05	2.05	5.27	5.29
		Standard	1.19	0.88	0.03	2.10	4.50	8.39
		Average	1.34	0.87	0.02	2.23	5.18	7.65
		Standard Deviation	±0.12	±0.11	±0.02	±0.18	±0.57	±1.58
		ASTM[a] Allowed Range	--	0.30	0.04	0.20	--	--
PSOC 282	RUN 17 Bulk Chlorinated, Washed, and Dried Coal	CSMRI	0.35	0.57	0.14	1.06	14.0	8.69
		DOE	0.97	0.04	0.01	1.02	14.84	8.94
		Galbraith	0.54	0.39	0.12	1.04	14.32	7.25
		Standard	<0.29	0.55	unknown[b]	0.84	5.99	8.31
		Average	0.54	0.39	0.09	0.99	12.29	8.30
		Standard Deviation	±0.31	±0.25	±0.07	±0.10	±4.21	±0.74
		ASTM[a] Allowed Range	--	0.30	0.04	0.10	--	--

Ash and Sulfur forms are Dry-Chlorine Free basis, Chlorine is dry basis.

a: ASTM D2492-77 and D3177-75 (Eschka Method) - MAXIMUM ABSOLUTE DIFFERENCE
b: Brown precipitate, not the sulfate.
c: Colorado School of Mines Research Institute, Golden, Colorado
d: Dept. of Energy, Pittsburgh Mining Technology Center
e: Galbraith Laboratories, Inc., Knoxville, Tenn.
f: Standard Laboratories, Inc., Charleston, W. Virginia.
g: unbiased; $\sigma = \sqrt{\sum_i (x_i - \bar{x})/(n - 1)}$

Leco Acid-Base Total Sulfur Analyses

A comparative evaluation is presented in Table 8 for the Leco Acid-Base Analyses of Total sulfur in raw and treated coal samples. Comparison was made of Leco total sulfur values with total sulfur values obtained by the Colorado School of Mines Research Institute using the Eschka method. Leco analyses were conducted on treated coal samples that were first dechlorinated to eliminate chlorine interference. Agreement between the Leco and Eschka methods for total sulfur was generally good with a deviation between methods of less than 0.15 wt. % in general and only 2 out of 19 values substantially different, i.e., 20% discrepancy.

Coal Product Analyses

Proximate

Proximate analyses of raw and treated coals are included in Table 9. Raw and treated coal comparisons are made for three runs for PSOC 276, for six runs for PSOC 282 coal including treated coal samples at 15, 30, 45 minutes in run 21. Single run comparisons of raw and treated coal analyses were made for PSOC 219, 026 and Island Creek Coal. Comparisons are between raw and dechlorinated coal samples with the exception of PSOC 276 and PSOC 282 in which proximate analyses are included for chlorinated samples.

Volatile matter suffers no apparent reduction on chlorination of the coal. However, some of the carbonaceous volatile matter may be replaced by volatile HCl from chlorine addition to the coal. Dechlorination reduces volatile matter by 8 to 15 wt. %.

Table 8. Leco Acid-Base Analyses vs. Eschka Method* for Total Sulfur

Run No.	Total Sulfur by Leco Method[e] (Wt. %)[a]	Total Sulfur by Eschka (Wt. %)[b]	Total Sulfur Difference (Leco-Eschka) (Wt. %)
		Raw Coal	
1	3.92	3.87[d]	.05
3	4.00	3.87	.13
5	4.02	3.87	.15
6	4.02	3.87	.15
15	1.58	1.59[d]	-.01
17	1.57	1.59	-.02
		Dechlorinated Coal	
1	1.34	1.52	-.18
3	1.47	1.58	-.11
4	2.23	2.70	-.47
5	3.14	3.14	0.00
6	2.05	2.12	-.07
7	1.45	1.44	.01
8	1.95	1.88	.07
9	2.13	2.01	.12
10	1.58	1.68	-.10
12	2.17	2.14	.03
13	3.25	-	-
14	1.86	2.19	-.33
15	0.93	0.86	.07
16	2.29	-	
17	0.93	-	
18	0.95	-	
19	0.77	-	
28	0.75[c]	-	
29	0.66[c]	0.74	-.08

*Colorado School of Mines Research Institute Analyses

[a]Dry basis raw coal or assumed dry basis, bulk sample specially dechlorinated in quartz tube under steam, 45-50 min., 400°C.

[b]Dry basis raw coal or dry basis, dechlorinated bulk sample.

[c]Assumed dry basis, dechlorinated bulk sample.

[d]Average overall raw coal analyses within that coal type.

[e]Sulfur combusted and peroxidized to $SO_4^{=}$, Cl^- interference correction with Hg(CN)OH reagent, resistance furnance method.

Table 9. Proximate Analyses of Raw and Treated Coals

Component	Basis	PSOC 276							PSOC 282										
		RUN [illegible] - 5/[illegible]/79			RUN 9-6/[illegible]/79		RUN 14 - 6/13/79		RUN 15 - 6/15/79		RUN 18 - 6/22/79	RUN 19 - 6/25/79	RUN 20 - 6/27/79	RUN 21 - 7/10/79					RUN 22 - 7/12/79
		RAW	Chlorinated*	Dechlorinated*	RAW	Dechlorinated	RAW	Dechlorinated	RAW	Dechlorinated	Chlorinated	Chlorinated	RAW	RAW	15 MIN	30 MIN	45 MIN	Dechlorinated	Dechlorinated
Volatile Matter (wt. %)	Dry	37.2	37.4	25.3	37.6	24.9	35.7	25.[illegible]	34.7	23.9	36.8	38.7	36.8	35.5	35.0	38.6	38.9	27.3	27.0
Ash (wt. %)	Dry	10.9	7.[illegible]	8.45	11.2	8.95	12.4	9.88	7.21	7.13	5.39	4.88	6.37	6.78	5.57	5.17	5.20	0.36	5.92
Fixed Carbon (wt. %)	Dry	51.8	55.4	66.4	51.2	66.2	50.9	65.5	55.1	70.0	57.9	56.4	56.8	57.7	59.4	56.2	55.6	66.3	67.1
Heating Value Btu/lb.	Dry	12,822	12,042	12,712	12,966	12,727	12,457	12,559	13,280	12,787	11,985	11,236	13,341	13,346	12,422	11,617	10,837	11,983	12,234
Moisture (wt. %)	As Received	1.99	2.44	0.79	2.20	0.49	1.43	0.95	5.37	1.58	1.66	5.85	4.06	4.76	2.78	2.73	1.94	1.35	0.44

Component	Basis	PSOC 219		PSOC 027		Island Creek	
		RUN 29 - 7/25/79		RUN 30 - 7/26/79		RUN 40 - 8/15/79	RUN 42 - 8/21/79
		RAW	Dechlorinated	RAW	Dechlorinated	RAW	Dechlorinated
Volatile Matter (wt. %)	Dry	35.1	27.7	35.0	26.2	40.0	24.8
Ash (wt. %)	Dry	6.42	4.70	9.87	7.58	10.5	5.81
Fixed Carbon (wt. %)	Dry	58.1	67.6	55.1	66.2	49.5	69.4
Heating Value Btu/lb.	Dry	12,966	12,309	12,540	11,907	13,135	12,072
Moisture (wt. %)	As Received	3.74	3.57	3.36	2.03	1.40	0.23

*Samples are bulk coal, except as indicated

Ash values are reduced by chlorination and then increased by the dechlorination procedure. The net reduction in ash values is of the order of 1 to 4 wt. %. The initial reduction of ash is largely pyritic sulfur reduction and attendant iron and other trace metals. A loss in volatile material during dechlorination will result in a proportionate increase in relative ash weight.

Fixed carbon values remain relatively constant through chlorination but increase by about 9 to 20% after dechlorination, a value proportionate to the loss of volatile matter.

Moisture values of the raw coal samples were in the range of 1.4 to 5.4 wt. %. Dechlorinated coal samples had a moisture content of 0.23 to 3.6 wt. %.

Heating values are included in the proximate analysis. Heating values varied from a slight increase (PSOC 276) on desulfurization to a significant (1100 to 1300 B.T.U./lb.) decrease for PSOC 282 and Island Creek coal.

Heating values of chlorinated coal before dechlorination suffer a substantial change in heating value because of the substantial chlorine addition to the coal.

Ultimate

A comparison of ultimate analyses between raw and treated coals was made for three (3) runs each for PSOC 276 and 282 coals and for single runs for PSOC 219, 026 and Island Creek Coal, Table 10. In all cases treated coal samples included dechlorination with the exception of run 3 (PSOC 276) coal in which an additional analyses was conducted on an undechlorinated coal sample.

Table 10. Ultimate Analyses of Raw and Treated Coals

Component (wt %)	PSOC 276							PSOC 282						PSOC 219		PSOC 026		Island Creek	
	RUN 3 - 5/10/79			RUN 9 - 6/1/79		RUN 14 - 6/13/79		RUN 15 - 6/15/79		RUN 20 - 6/27/79	RUN 21 - 7/10/79		Run 22 - 7/25/79	RUN 29 - 7/26/79		RUN 30 - 7/26/79		RUN 40 - 8/15/79	RUN 42 - 8/21/79
	RAW	Chlori-nated	Dechlori-nated	RAW	Dechlori-nated	RAW	Dechlori-nated	RAW	Dechlori-nated	RAW	RAW	Dechlori-nated	Dechlori-nated	RAW	Dechlori-nated	RAW	Dechlori-nated	RAW	Dechlori-nated
C	71.4	66.1	74.6	72.0	75.0	71.3	73.2	76.3	76.8	74.6	75.1	73.1	75.1	73.8	75.7	66.8	73.3	72.8	74.8
H	5.51	4.70	4.31	5.36	4.27	6.14	3.99	5.05	3.98	5.69	5.30	3.47	3.74	5.32	3.56	5.03	3.72	5.25	4.11
S	3.86	1.55	1.58	3.90	2.01	3.96	2.19	1.65	0.86	1.57	1.62	0.79	0.78	2.16	0.74	3.40	1.43	3.73	1.74
N	1.06	1.09	1.45	1.40	1.50	1.37	1.32	1.71	1.64	1.74	1.68	1.48	1.47	1.76	1.56	1.45	1.33	1.40	1.38
Cl	0.31	10.8		0.09	1.03	0.13	0.74	0.48	0.97	0.51	0.48	2.66	2.89	0.14	2.36	0.17	3.34	0.20	2.13
O (by difference)	6.91	8.5	9.57	6.12	7.29	4.57	8.68	7.58	9.64	9.49	8.94	12.1	10.0	10.46	11.4	13.33	9.29	6.05	9.92
ASH	10.9	7.17	8.45	11.2	8.95	12.4	9.88	7.21	6.13	6.37	6.78	6.36	5.92	6.42	4.70	9.87	7.58	10.5	5.81
Heating Value (Btu/lb)	12,822	12,042	12,712	12,986	12,727	12,457	12,509	13,[illegible]80	12,787	13,341	13,346	11,983	12,234	12,966	12,309	12,540	1[illegible],907	13,135	12,072

Dry Basis; H & O have been corrected for moisture.

Generally, after treatment, carbon increased by as much as 3 to 6 wt. %, hydrogen decreased by 1 to 2 wt. %; nitrogen values did not change significantly; oxygen values increased by 1-3 wt. % with PSOC 026 having a 4 wt. % decrease in oxygen (probably analytical error in raw coal oxygen value) and ash values decreased by 1 to 4 wt. %.

Trace Element

Analyses were performed on raw and chlorinated coal samples for coals PSOC 276, 282, 026 and Island Creek coal, Table 11. Elements analyzed were lead, arsenic, selenium, mercury and vanadium.

Variations in trace element content between raw coal samples as well as a lack of precision in the analyses gave trace element removal results that were questionable. Only arsenic and mercury showed substantial removals that were significant, respectively 50-60% and 80%. Vanadium was not detected, i.e., detection limit was 50 ppm. Lead and selenium had questionnable removals.

Ash Elements

Analysis of ash composition for a comparison of raw and treated coal samples is indicated in Table 12. Treated coal analyzed was chlorinated and not dechlorinated coal samples.

Elements included in the ash composition approximately in order of decreasing concentration are: Silicon, iron, aluminum, calcium, potassium, sulfur, titanium, sodium, magnesium, phosphorus and manganese. Chlorination and water wash of the coal samples provides removal in PSOC 276, 282, 219, 026 and Island Creek coal of: Iron, 43-75%; calcium 35-86%, sulfur 25-72%. Aside from sodium and phosphorus reduction in PSOC 282 coal of ~55%, there were no other significant ash element reductions.

Table 11. Trace Element Analyses of Raw and Treated Coals

Element (ppm)	PSOC 276							PSOC 282							PSOC 026			Island Creek Coal		
	RUN 6 - 5/21/79		RUN 7 - 5/24/79		RUN 12 - 6/8/79			RUN 15 - 6/15/79		RUN 21 - 7/10/79		RUN 22 - 7/12/79			RUN 30 - 7/26/79			RUN 40 - 8/15/79	RUN 42 - 8/21/79	
	RAW	Chlorinated[a]	RAW	Chlorinated	RAW	Chlorinated	Removal (%)[c]	RAW	Chlorinated	RAW	Chlorinated	RAW	Chlorinated	Removal (%)	RAW	Chlorinated	Removal (%)	RAW	Chlorinated	Removal (%)
Pb	96	104	<50[b]	218	186	144	-107 ±200	165	187	241	98	184	97	31 ±39	<50	<50	--	<50	<50	--
As	7	4	5	2	7	4	50 ±10	10	3	7	4	10	3	60 ±15	3	1	67	3	4	-33
Se	5	7	6	5	5	5	-8 ±30	5	5	4	6	4	5	-25 ±25	8	6	25	3	4	-33
Hg	0.2	0.3	<0.1[b]	0.2	0.3	0.1	-30 ±85	0.3	0.1	1.3	0.1	0.1	0.1	80 ±18	0.2	<0.1	50	0.4	0.02	95
V	ND	ND	ND	ND	ND	ND	--	ND	ND	ND	ND	ND	ND	--	ND	ND	--	ND	ND	--

All values are ppm in coal (not ash), as determined basis

ND = Not detected

Detection limits: As:2 ppm, Hg:0.1 ppm, Pb:50 ppm, Se:2 ppm, V:50 ppm

a. Bulk sample in all cases.
b. The detection limit is assumed for the calculation of removal %.
c. With a standard deviation expressed in %.

Table 12. Ash Elemental Analysis of Raw and Treated Coals

Element (Amt Ash wt. %)	PSOC 275							PSOC 282							PSOC 219			PSOC 026			Island Creek Coal		
	RUN 3-5/10/79		RUN 9-6/1/79		RUN 14-6/13/79			RUN 15-6/15/79		RUN/20-6/27/79	RUN 21-7/10/79		RUN/22-7/12/79		RUN 29-7/25/79			RUN 30-7/26/79			RUN 42-8/15/79	RUN 42-8/21/79	
	RAW	Chlorinated	RAW	Chlorinated	RAW	Chlorinated	Removal (%)	RAW	Chlorinated	RAW[a]	RAW	Chlorinated	Chlorinated[a]	Removal (%)	RAW	Chlorinated	Removal (%)	RAW	Chlorinated	Removal (%)	RAW	Chlorinated	Removal (%)
Si	24.8	29.7	26.5	28.8	27.5	29.4	-12 ±8	25.6	26.4	27.18	24.1	26.2	25.8	-6 ±4	23.7	30.5	-29	25.9	29.9	-15	25.4	32.2	-27
Fe	30.5	8.74	29.5	13.0	27.6	13.7	59 ±11	16.4	8.54	13.95	15.4	8.98	10.0	45 ±4	25.4	5.25	79	22.0	12.64	43	20.0	5.09	75
Al	12.3	13.3	13.6	13.7	13.9	13.1	-1 ±7	13.5	13.3	14.77	13.1	13.1	13.0	0.5 ±0.7	12.6	11.6	8	12.9	12.8	1	11.2	12.3	-10
Ca	2.80	0.42	2.11	0.42	2.21	0.47	81 ±3	1.54	0.52	1.18	1.31	0.50	0.52	64 ±3	0.82	0.53	35	1.01	0.66	35	3.04	0.44	86
K	1.70	1.95	1.73	1.89	1.80	1.81	-8 ±7	1.97	2.04	2.09	1.81	1.92	1.85	-5 ±1.4	2.14	1.99	7	2.18	2.02	7	2.07	2.45	-18
S	1.64	0.38	1.23	0.34	1.46	0.46	72 ±5	1.04	0.46	0.68	0.76	0.55	0.59	42 ±20	0.58	0.63	-9	0.76	0.57	25	1.71	0.51	70
Ti	0.60	0.68	0.66	0.75	0.67	0.78	-14 ±1.5	0.97	0.92	0.94	0.82	0.85	0.86	-5 ±1.4	0.61	0.58	5	0.71	0.77	-8	0.65	0.83	-28
Na	0.35	0.39	0.32	0.43	0.32	0.32	-15 ±17	1.51	0.70	2.37	1.52	0.65	0.59	56 ±2	0.34	0.36	-6	0.34	0.39	-15	0.81	0.80	1
Mg	0.45	0.05	0.45	0.38	0.43	0.34	42 ±41	0.59	0.53	0.57	0.42	0.48	0.45	-2 ±17	0.62	0.49	21	0.49	0.52	-6	0.43	0.50	-16
P	<0.01	<0.01	0.01	0.01	<0.01	<0.01	0	0.13	0.06	0.007	<0.01	<0.01	0.07	55	0.11	0.11	0	0.03	0.08	-170	<0.01	0.07	-600
Mn	0.02	0.04	0.04	0.01	0.01	0.02	-650 ±1100	0.02	0.04	-	0.03	0.02	0.03	-35 ±95	0.04	0.03	25	0.02	0.01	50	0.02	0.03	-50
Ash Fraction[b] of Coal	10.9	8.04	11.2	8.63	12.4	8.25	28 ±5	7.24	5.83	6.36	6.81	5.47	5.72	20 ±0.1	6.43	4.88	24	9.89	7.54	24	10.5	9.03	14

a. No removal calculated from these columns.
b: wt. , dry, chlorine-free basis.

Coal Filtrate and Wash Water Analyses

Water filtrate and wash water solutions obtained from the chlorinated coal processing were combined and analyzed for the following components: Cl^-, $SO_4^=$, Fe, Ca, Na, Al, Mg, K. The volume of water solution and amount of dried, filtered coal for each run are listed in Table 13, along with the analyses. Additionally, the components are related to their concentration in the coal, as wt. %. Chlorides, sulfates and iron are present in the largest concentration as expected with calcium, sodium, aluminum, magnesium and potassium present in slight concentrations. The pH values were always less than 1 because of the high HCl and H_2SO_4 content.

Chlorinator Gas Analyses

Gas samples were taken at the end of a 90-minute chlorination of PSOC 282 coal in the 1-1/2 inch off gas line from the batch reactor. Run 34 was with methyl chloroform solvent at temperatures of 62-84°C and 7-36 psig. Run 35 was with water as a solvent at somewhat higher temperatures of 88-96°C and 28-57 psig. Analyses are reported in Table 14 for the two runs. HCl, Cl_2, methylchloroform and nitrogen comprised over 96.5% of the gases in run 34 with small amounts of CO_2, $CoCl_2$, CCl_4 and $CHCl:CCl_2$. In comparison, run 35 (water as solvent) had a high CO_2 concentration (51.4%) with N_2, HCl, Cl_2 comprising an additional 47%; only small amounts of methyl chloroform, $COCl_2$, CCl_4 and $CHCl:CCl_2$ were present. No definite conclusions can be drawn from the analyses except to indicate that the formation of chlorinated compounds from the coal and/or solvent occurs in relatively small quantities. The relatively high CO_2 value may indicate somewhat greater coal oxidation at the higher reaction temperature.

Table 13. Coal Filtrate and Wash Water Analyses

Coal Type	Run #	Filtrate and Wash Water Components (grams/liter) Cl⁻	$SO_4^=$	Fe	Ca	Na	Al	Mg	K	pH	Filtrate and Washwater Volume (liter)	Product Coal[b] (g)	Removal (wt % of dried filtered coal) in Solution Cl⁻	$SO_4^=$	Fe	Ca	Na	Al	Mg	K
PSOC 276	1	41.3	7.40	6.40	0.17	0.12	0.04	0.03	0.01	<1	11.5	1413	33.6	6.02	5.21	0.14	0.10	0.033	0.024	0.008
	3[a]	39.8	8.68	6.76	0.32	0.11	0.04	0.05	0.01	<1	9.72	1706	22.7	4.95	3.85	0.18	0.063	0.023	0.029	0.006
	4	54.1	6.65	9.52	0.44	0.10	0.06	0.04	0.01	<1	9.0	1813	26.9	3.30	4.73	0.022	0.050	0.030	0.020	0.005
	5	29.2	4.74	5.34	0.44	0.11	0.06	0.04	0.01	<1	9.8	1740	16.4	2.67	3.01	0.25	0.0[illegible]	0.034	0.023	0.006
	6	126.3	11.9	20.0	0.53	0.12	0.11	0.23	0.02	<1	8.3	1895	56.2	5.21	8.76	0.23	0.055	0.048	0.101	0.009
	7	59.7	12.4	12.9	0.33	0.14	0.06	0.05	0.01	<1	8.8	1322	39.7	8.25	8.59	0.22	0.093	0.040	0.033	0.007
	8	40.2	6.52	4.18	0.38	0.15	0.04	0.07	0.01	<1	6.9	1473	19.0	3.08	1.97	0.18	0.071	0.019	0.033	0.005
	9	65.0	10.0	7.56	0.35	0.16	0.09	0.07	0.02	<1	9.1	1383	42.8	6.58	4.97	0.23	0.105	0.059	0.046	0.013
	10	18.0	4.17	2.00	0.18	0.18	0.04	0.04	0.01	<1	23.0	1514	27.3	6.33	3.04	0.27	0.27	0.061	0.061	0.015
	12[a]	95.4	15.5	8.10	0.57	0.15	0.08	0.06	0.02	<1	6.2	1725	35.4	5.57	2.91	0.205	0.054	0.029	0.022	0.007
	13	38.3	7.64	4.44	0.43	0.18	0.17	0.06	0.04	<1	9.1	1597	21.9	4.38	2.54	0.246	0.103	0.097	0.034	0.023
	14	79.2	9.47	9.38	0.39	0.17	0.20	0.06	0.06	<1	9.7	1758	43.7	5.23	4.62	0.22	0.094	0.110	0.033	0.033
	16	66.3	6.74	5.60	0.32	0.12	0.13	0.04	0.04	<1	9.8	1666	39.0	3.96	3.29	0.19	0.071	0.076	0.024	0.024
PSOC 282, 100-200 Mesh	15	84.4	5.09	3.12	0.22	0.28	0.06	0.04	0.02	<1	6.0	1870	27.1	1.63	1.00	0.071	0.090	0.019	0.013	0.006
	17	34.3	2.47	2.18	0.10	0.24	0.04	0.07	0.01	<1	9.5	1280	25.5	1.83	1.62	0.074	0.18	0.030	0.015	0.007
	18	73.2	3.90	3.12	0.21	0.32	0.08	0.06	0.02	<1	7.2	1868	28.2	1.50	1.20	0.081	0.123	0.031	0.023	0.008
	19	51.7	2.91	2.44	0.12	0.25	0.06	0.02	0.01	<1	9.5	1932	25.4	1.43	1.20	0.059	0.123	0.030	0.010	0.005
	21[a]	45.6	2.42	2.62	0.09	0.14	0.06	0.02	0.02	<1	11.5	1148	45.7	2.42	2.62	0.090	0.140	0.060	0.020	0.020
	22	225.0	5.11	8.12	0.17	0.24	0.08	0.04	0.02	<1	6.0	1745	77.4	1.76	2.79	0.058	0.083	0.028	0.014	0.007
	23	42.6	2.81	2.96	0.07	0.16	0.06	0.02	0.02	<1	8.7	1167	31.9	2.11	2.22	0.052	0.120	0.045	0.015	0.015
	24	39.4	2.31	4.68	0.10	0.18	0.13	0.04	0.04	<1	7.2	1450	19.7	1.16	2.34	0.050	0.090	0.065	0.020	0.020
	25	27.4	2.34	2.08	0.09	0.16	0.03	0.03	0.01	<1	10.0	1301	21.1	1.80	1.60	0.069	0.123	0.023	0.023	0.008
	35	94.1	3.30	6.14	0.15	0.28	0.08	0.02	0.02	<1	6.6	1603	38.7	1.36	2.53	0.062	0.115	0.033	0.008	0.008
	36	5.45	0.19	0.31	0.05	0.04	0.02	0.02	<0.01	<1	21.0	2190	5.23	0.18	0.30	0.048	0.038	0.019	0.019	<0.010
	37	28.5	0.46	1.55	0.04	0.04	0.03	0.02	<0.01	<1	22.0	2045	30.7	0.495	1.67	0.043	0.043	0.032	0.022	<0.011
	38	17.2	1.14	1.06	0.10	0.07	0.04	0.03	<0.01	<1	21.1	2053	17.7	1.17	1.09	0.103	0.072	0.042	0.031	<0.010
	39	20.2	0.23	1.15	0.04	0.04	0.02	0.02	<0.01	<1	24.2	1436	34.0	0.39	1.94	0.067	0.067	0.034	0.034	<0.017
	26	58.5	2.45	3.08	0.12	0.17	0.03	0.02	0.01	<1	10.0	1609	36.4	1.52	1.91	0.075	0.106	0.019	0.012	0.006
PSOC 282, +100 Mesh	27	39.3	2.05	3.32	0.09	0.13	0.04	0.03	0.01	<1	9.2	1197	30.4	1.58	2.57	0.070	0.100	0.031	0.023	0.008
	33	25.4	0.97	1.65	0.11	0.08	0.04	0.04	0.01	<1	14.5	1398	26.3	1.01	1.71	0.114	0.083	0.041	0.041	0.010
	34	30.6	1.61	3.46	0.13	0.10	0.07	0.05	0.01	<1	10.7	1591	20.7	1.09	2.34	0.088	0.068	0.047	0.034	0.007
PSOC 219	28	49.2	4.55	4.56	0.05	0.03	0.09	0.04	0.02	<1	9.8	1344	35.9	3.32	3.33	0.036	0.022	0.066	0.029	0.015
	29	124.1	8.75	10.9	0.09	0.06	0.93	0.07	0.03	<1	4.8	1409	42.3	2.98	3.71	0.031	0.020	0.317	0.024	0.010
PSOC 025	30	117.6	12.1	11.4	0.10	0.05	0.68	0.06	0.34	<1	6.2	1557	47.2	4.86	4.58	0.040	0.020	0.273	0.024	0.016
	31	42.4	5.99	4.94	0.07	0.04	0.11	0.03	0.03	<1	9.1	1020	37.8	5.34	4.41	0.062	0.036	0.098	0.027	0.027
	32	114.9	10.2	13.2	0.09	0.03	0.14	0.04	0.04	<1	6.5	1469	50.8	4.51	5.84	0.040	0.013	0.062	0.018	0.018
Island Creek	40	35.8	3.32	2.84	0.40	0.07	0.06	0.04	0.02	<1	16.4	1979	29.7	2.75	2.35	0.33	0.058	0.050	0.033	0.017
	41	9.98	0.17	0.68	0.07	0.05	0.02	0.03	<0.01	<1	21.1	1800	11.7	0.199	0.80	0.082	0.059	0.023	0.035	<0.012
	42	23.4	1.17	2.00	0.05	0.05	0.02	0.02	0.01	<1	21.7	1606	31.6	1.58	2.70	0.068	0.068	0.027	0.027	0.014
	43	31.8	3.55	3.26	0.23	0.05	0.05	0.02	0.02	<1	21.6	1646	41.7	4.66	4.28	0.30	0.066	0.066	0.026	0.026
	44	24.6	0.46	3.58	0.05	0.04	0.02	0.02	0.01	<1	21.8	1190	45.1	0.34	6.56	0.092	0.073	0.037	0.037	0.018

a: No analyses for runs 2, 11, and 20
Distilled water was used in all cases
b: Dry basis, processed coal (not including coal in equipment water rinse)

Table 14. Chlorinator Gas Analyses

(Gas samples obtained from 1-1/2 inch off gasline in batch reactor at end of 90 minute chlorination.)

Gas Component	Run 34* (Vol. %)	Run 35** (Vol.%)
N_2	1.7	21
O_2	0.09	0.15
Ar	0.01	0.01
CO_2	1.4	51.4
HCl and Cl_2 (by diff.)	87.3	26.0
CH_3CCl_3	7.5	0.26
$CoCl_2$	0.45	1.1
CCl_4	0.5-1.5	0.14
$CHCl:CCl_2$	0.05	0.03

Note: Analyses by mass spectrometer, Analytical Research Laboratory, Monrovia, California.

*Solvent methylchloroform
**Solvent water

Material Balance — Chlorination, Solvent Recovery and Coal Filtration Wash

An overall material balance was obtained for the chlorination, solvent recovery and coal filtration wash for the 44 test runs, Table 15. Material balances were obtained on the coal including ash and organic matter, methylchloroform solvent, sulfur and chlorine.

Batch Reactor Feed

Raw coal charged to the reactor was analyzed for moisture and the dried weight reported to the nearest gram. The coal charge was approximately 2000 grams with a few runs at significantly smaller charge weights because of a limited supply of the given coals. Weights of the raw coal fractions are reported as organic, ash, sulfur and chlorine fractions. Ash and sulfur weights were obtained from the ash and sulfur analyses obtained by the Colorado School of Mines Research Institute on the raw coal samples submitted for each run. Chlorine feed rates

Table 15. Material Balance - Chlorination, Solvent R
(Coal, Solvent, Chlorine, Sulfur

	Batch Reactor Feed (grams)							Samples Removed from Reactor (grams)						Chlorinated, Washed & Dried Coal (gr			
		Raw Coal															
Run #	Raw Coal[b]	Organic Fraction[c]	Ash	Cl*	Sulfur	Chlorine	Methyl-chloroform	Treated Coal	Organic Fraction	Ash[e]	Sulfur[e]	Chlorine[e]	Methyl-chloroform	Treated Coal[f]	Organic Fraction[f]	Ash	Sulfur
1	2000	1694	226	3.2	77.2	1050	4000	571	479	~65	22.0	~137	~672	1438	1171	103	21.6
2	1998	1692	226	3.2	77.1	1000	4000	--	--	--	--	--	--	--	--	--	--
3	1999	1693	226	3.2	77.2	1000	4000	474	402	~54	18.3	139	453	1741	1401	125	27.0
4	1999	1693	226	3.2	77.2	750	0	182	155	21	7.0	70	0	1847	1584	126	41.0
5	1999	1693	226	3.2	77.2	390	0	142	122	16	5.5	31	0	1822	1577	161	56.9
6	1998	1692	226	3.2	77.1	1470	0	168	138	19	6.5	111	0	1987	1585	163	42.3
7	1998	1692	226	3.2	77.1	1320	4000	195	166	22	7.5	101	225	1826	1539	132	28.5
8	2000	1694	226	3.2	77.2	780	0	145	124	16	5.6	54	0	1848	1609	125	38.4
9	1999	1693	226	3.2	77.2	780	0	162	136	18	6.3	67	0	1835	1536	149	41.9
10	1999	1693	226	3.2	77.2	680	4000	264	224	30	10.2	83	352	1689	1430	131	30.1
11	1998	1692	226	3.2	77.1	360	0	71	62	8	2.8	6.1	0	--	--	--	--
12	·1997	1691	226	3.2	77.1	880	0	206	171	23	7.9	83	0	1822	~1492	145	39.5
13	1999	1693	226	3.2	77.2	370	0	132	113	15	5.1	25	0	1811	1532	190	56.0
14	1999	1693	226	3.2	77.2	590	0	124	104	14	4.8	57	0	1936	1630	150	38.3
15	1992	1816	134	10.1	31.7	860	0	233	200	16	3.7	90	0	1946	1625	102	16.5
16	1999	1693	226	3.2	77.2	790	0	157	134	18	6.1	64	0	1874	1580	151	43.3
17	1996	1819	135	10.1	31.7	880	4000	455	372	31	6.4	225	450	1641	1274	123	14.9
18	1993	1816	135	10.1	31.7	800	0	185	159	13	2.9	67	0	1978	1668	107	20.4
19	1993	1816	135	10.1	31.7	1100	4000	264	~218	18	4.2	138	244	·1954	·1555	·95	>16.2
20	1993	1816	135	10.1	31.7	340	0	--	--	--	--	--	--	--	--	--	--
21	1990	1814	134	10.1	31.6	1320	4000	252	200	17	4.0	~150	179	2111	1659	97	15.4
22	1993	1816	135	10.1	31.7	1660	0	251	210	17	4.0	~153	0	2120	1647	101	15.5
23	1997	1820	135	10.1	31.8	1510	4000	240	195	16	3.8	146	205	~2188	1667	92	15.5
24	1994	1817	135	10.1	31.7	650	0	135	117	9	2.2	49	0	1879	1707	90	21.0
25	1994	1817	135	10.1	31.7	520	4000	0	0	0	0	0	0	>1683	·1462	83	>16.5
26	1997	1792	157	11.6	31.0	1560	0	511	424	40	7.9	~316	0	1807	1448	103	17.7
27	1997	1792	157	11.6	31.0	1050	4000	489	389	38	7.6	286	537	1891	1465	126	19.7
28	1656	1511	107	2.4	35.6	1400	4000	343	263	22	7.4	282	343	1598	1214	61	10.7
29	1900	1734	123	2.4	40.9	1430	0	283	241	18	6.1	160	0	1930	1500	78	14.5
30	1698	1467	169	2.4	58.6	1260	0	265	215	26	9.1	154	0	1652	1262	105	24.3
31	1706	1474	170	2.4	58.9	1380	4000	354	260	35	12.2	294	346	1567	1121	93	20.7
32	1698	1467	169	2.4	58.6	1620	0	204	162	20	7.0	166	0	1739	1300	103	24.2
33	1995	1790	156	11.6	30.9	1330	0	339	279	27	5.3	171	0	1698	1317	103	16.1
34	1998	1792	157	11.6	31.0	1370	4000	308	245	24	4.8	202	280	1961	1493	109	16.3
35	1995	1818	135	10.1	31.7	1650	0	216	178	15	3.5	~167	0	2257	1770	103	18.1
36	1996	1819	135	10.1	31.7	1030	0	71	61	5	1.1	28	0	~2191	~1833	~99	~20.6
37	~2100	~1756	95	229	19.7	690	0	129	101	6	1.2	58	0	2051	1599	85	14.8
38	1997	1820	135	10.1	31.8	1000	4000	146	118	10	2.3	52	114	~2141	~1711	~96	~17.3
39	~1997	~1596	90	296	16.2	1660	4000	175	116	8	1.4	166	134	2189	1353	73	10.3
40	1999	1716	206	4.0	74.4	780	0	138	114	14	5.1	32	0	~1980	~1619	~141	~47.5
41	~1893	~1548	135	165	45.4	680	0	156	128	11	3.7	62	0	~1800	~1380	~95	~30.2
42	~1692	~1297	89	278	28.4	790	0	112	86	6	2.0	61	0	1648	1221	124	28.0
43	1999	1716	206	4.0	74.4	1380	4000	124	102	13	4.6	53	99	~2273	~1745	144	~38.2
44	~1566	~1202	99	238	26.3	1380	4000	176	114	11	3.0	158	121	1726	1050	85	18.3
Ave.																	

NOTES: a - Excludes samples
b - Dry basis
c - Dry weight less sulfur, chlorine & ash
d - Chlorine content of raw coal, runs 37, 39, 41, 42, 44 includes chlorine from previous chlorination
e - Total of solid + liquid sample

f - Includes all coal recovered except for samples
g - Includes all methylchloroform recovery in syst
h - Ash in solution, i.e., Fe, CA, NA, Al, Mg, K
i - Sum of recovered organic fraction, ash, sulfur

FOLDOUT FRAME

lorination, Solvent Recovery and Coal Filtration Wash
nt, Chlorine, Sulfur Accounting)

Chlorinated, Washed & Dried Coal (grams)					Solvent Recovery Tank (grams)	Filtrate & Wash Water (grams) (a,g)			Scrubber (grams)	Total Accounting (Mass & %)											
										Raw Coal		Organic Fraction		Ash		Sulfur		Chlorine		Methyl-chloroform	
ated al[f]	Organic Fraction[f]	Ash	Sulfur	Chlorine	Methyl-chloroform	Ash[h]	Sulfur	Chlorine	Chlorine	(g)	%	(g)	%	(g)	%	(g)	%	(g)	%	(g)	%
1438	1171	103	21.6	142	~2740	77.8	28.4	475	65	1971	98.6	1650	97	246	109	72.0	93	~819	~78	~3412	~85
--	--	--	--	--	0	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
1741	1401	125	27.0	188	2631	70.8	28.1	387	133	2130	106	1803	106	250	110	73.4	95	~847	~85	3084	77
1847	1584	126	41.0	95	0	91.6	20.1	487	38	2049	102	1739	103	239	105	68.0	88	~690	~92	0	--
1822	1577	161	56.9	28	0	58.9	15.5	286	57	2016	101	1699	100	236	104	77.8	101	402	103	0	--
1987	1585	163	42.3	197	0	174.4	37.9	1065	17	2164	108	1723	102	356	156	81.7	106	1390	95	0	--
1826	1539	132	28.5	127	3141	118.7	36.4	525	--	2054	103	1705	101	273	121	72.4	94	753	57	3366	84
1848	1609	125	38.4	76	0	33.5	15.1	279	292	1970	98.5	1733	102	175	77	59.1	77	701	90	0	--
1835	1536	149	41.9	108	0	75.0	30.3	592	2	1995	99.8	1672	99	242	107	78.4	102	769	99	0	--
1689	1430	131	30.1	98	2981	56.3	32.0	414	18	1946	97.3	1654	98	217	96	72.3	94	613	90	3333	83
--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
1822	~1492	145	39.5	~146	0	55.7	32.0	610	<2	1970	98.5	~1663	98	224	99	79.5	103	~841	96	0	--
1811	1532	190	56.0	33	0	48.6	23.3	350	<2	1986	99.3	1645	97	254	112	84.3	109	410	111	0	--
1936	1630	150	38.3	118	0	89.8	30.6	768	<2	2065	103	1734	102	254	112	73.7	95	945	95	0	--
1946	1625	102	16.5	202	0	22.4	10.2	506	<2	2005	101	1825	100	140	105	30.4	96	800	93	0	--
1874	1580	151	43.3	100	0	61.2	22.0	650	<2	2019	101	1714	101	230	102	71.4	92	816	103	0	--
1641	1274	123	14.9	230	2773	24.6	7.8	326	30	1864	93.2	1646	90	179	132	29.2	97	811	92	3223	81
1978	1668	107	20.4	183	0	27.4	9.4	527	<2	2017	101	1827	101	147	109	32.7	103	779	97	0	--
1954	1555	95	16.2	>287	2994	27.6	9.2	491	11	1954	98.0	1773	98	141	1:4	29.6	93	927	84	3238	81
--	--	--	--	--	--	--	--	--	<2	--	--	--	--	--	--	--	--	--	--	--	--
2111	1659	97	15.4	340	3564	33.9	9.3	574	78	2046	103	1859	102	148	110	28.7	91	~1092	83	3743	94
2120	1647	101	15.5	356	0	52.0	10.2	150	98	2067	104	1857	102	170	126	29.7	94	~757	46	0	--
2188	1667	92	15.5	~413	3347	28.8	8.2	373	366	2037	102	1862	102	137	101	27.6	87	1298	86	3552	89
1879	1707	90	21.0	61	0	37.5	5.6	286	7	1999	100	1824	100	136	101	28.8	91	403	62	0	--
1683	1462	83	16.5	122	2154	24.2	7.8	274	2	1603	80.2	1462	80	107	79	24.3	77	398	77	2154	54
1807	1448	103	17.7	238	0	34.2	8.2	585	390	2095	105	1872	104	177	'33	33.8	109	~1529	~98	0	--
1891	1465	126	19.7	280	2595	33.5	6.3	364	153	2096	105	1854	103	197	25	33.6	108	1083	103	3132	78
1598	1214	61	10.7	313	2848	46.5	14.9	482	173	1641	99.1	1477	98	129	21	33.0	93	1250	89	3191	80
1930	1500	78	14.5	338	0	57.9	14.0	596	36	1931	102	1741	100	154	.25	34.5	85	1130	79	0	--
1652	1262	105	24.3	261	0	77.1	25.2	735	12	1746	103	1477	101	208	123	58.6	100	1162	92	0	--
1567	1121	93	20.7	332	2695	47.5	18.2	386	220	1609	94.3	1381	94	175	103	51.1	87	1232	89	3041	76
1739	1300	103	24.2	311	0	88.0	22.1	942	6	1728	102	1462	100	211	125	53.3	91	1425	88	0	--
1698	1317	103	16.1	262	0	27.9	4.7	368	4	1792	89.6	1596	89	158	101	26.1	84	805	61	0	--
1961	1493	109	16.3	343	2998	41.1	5.8	329	234	1951	97.5	1738	97	174	111	26.8	87	1108	81	3278	82
2257	1770	103	18.1	366	0	44.2	7.3	621	7	2149	107	1948	107	162	120	28.8	91	~1161	~70	0	--
2191	~1833	~99	~20.6	~239	0	9.5	1.3	115	15	2040	102	~1894	~104	113	84	23.1	73	397	39	0	--
2051	1599	85	14.8	353	0	37.2	3.4	677	12	2076	98.9	1700	~97	128	135	19.4	98	1050	114	0	--
2141	~1711	~96	~17.3	~317	3454	27.6	8.0	363	93	2000	100	~1829	~100	134	99	27.7	87	825	83	3568	89
2189	1353	73	10.3	753	3600	31.0	1.9	490	43	1891	94.5	1469	~92	112	124	13.6	84	1452	74	3734	93
1980	~1619	~141	~47.5	~173	0	56.2	18.2	588	7	2019	101	~1733	~101	211	102	70.9	95	800	103	0	--
1800	~1380	~95	~30.2	~295	0	18.2	1.2	210	384	1832	96.8	~1508	~97	124	92	35.2	77	951	~113	0	--
1648	1221	124	28.0	275	0	46.6	8.4	507	16	1800	106	1307	~101	177	199	38.4	135	859	~80	0	--
2273	~1745	144	~38.2	~346	3802	78.4	25.5	686	21	2154	108	1847	~108	235	114	68.3	92	1106	80	3901	98
1726	1050	85	18.3	573	3575	81.1	3.3	535	112	1604	102	1164	~97	177	179	24.6	93	1378	85	3696	92
										100.3±3.5		99.3±3.5			114		94		86		83±6.8

coal recovered except for samples
methylchloroform recovery in system
on, i.e., Fe, CA, WA, Al, rig, K
red organic fraction, ash, sulfur and chlorine in raw coal

were obtained by weighing of the liquid chlorine cylinder before and after each run to an accuracy of better than 1 gram. Methychloroform was weighed at 4000 grams to an accuracy of 1 gram.

Reactor Samples

Coal slurry samples of the reactor, including methylchloroform solvent were obtained for each chlorination run at 15, 30, 45 and sometimes 90 minutes. Each sample was weighed. The assumption was made that the coal slurry samples were representative of the reactor contents and that the total organic sulfur, ash and solvent removal were proportionate to the sample size. Chlorine in the samples was assumed to be proportional to the size of sample and related to the amount of chlorine feed over the reaction time of the sample. The total weight of samples removed represented as much as 20 weight percent of the batch reactor feed.

Chlorinated, Washed and Dried Coals

The weights of dry treated coal after washing for sulfate and chloride removal and drying are tabulated by organic, ash, sulfur and chlorine fractions and total weight, i.e., treated coal. The ash, sulfur and chlorine weights were obtained by analyses (Colorado School of Mines Research Institute). The treated coal weight represents the combined weight of organic, ash, sulfur and chlorine fractions. Because of the substantial chlorine content, the weight of treated coal sometimes exceeds the weight of raw coal feed.

Solvent Recovery

Methylchloroform recovered by distillation from the coal slurry to the solvent recovery tank is reported after correction for the coal and water phase that came over during the solvent distillation. In several runs, solvent was recovered from the gas holding tank and is included with that obtained from the solvent recovery tank. Analyses of the coal-water slurry after distillation (runs 31, 43) indicated less than 0.05 weight percent solvent.

Filtrate and Wash Water

Ash, sulfur and chlorine weights were obtained from the combined filtrate and wash water weight and analyses. The weight of ash included the weight of iron, calcium, sodium, aluminum, magnesium and potassium ions. The combined weights represent up to 10% of the total reactor feed.

Total Accounting (Chlorination and Wash)

<u>Raw Coal</u>. An accounting of the raw coal feed was made from a summation of the weight of recovered organic fraction, ash and sulfur from the samples, processed coal and wash water and filtrate. Average coal recovery over 41 runs was 100 ±3.5%.

<u>Coal Organic Fraction</u>. The organic fraction was defined as that portion of the coal exclusive of ash, sulfur and chlorine. The recovered organic fraction was based on the coal samples and processed coal and averaged 99.3 ±3.5% over 41 runs.

<u>Ash Fraction</u>. The substantial corrosion of exposed metal surfaces and test coupons contributes to the ash fraction recovered from the reactor in the filtrate and water solution. For this reason the ash accounting appears high at 114%. This may obscure some coal handling losses by increasing the weight of the recovered coal fraction.

Sulfur. Accounting consists of sulfur contained in samples, processed coal, filtrate and wash water analyses. Average recovery over 41 runs was 94%.

Chlorine. Accounting includes chlorine in the reactor samples, both liquid and solid phases, processed coal, filtrate and wash water and scrubber solution. Average accounting over 41 runs was 86%. Losses through leaks and sampling were evident from the pungent odor.

Methylchloroform. Accounting of methylchloroform was made from the samples and distillation recovery tank. Losses of hot solvent by flashing and evaporation were noted in taking reactor samples and in recovering the solvent during distillation. Although solvent recoveries up to 98% were noted, the average solvent recovery in 17 runs was 83 ±7%.

Coal Dechlorination

Thirty-six dechlorination runs were made with coals PSOC 276, 282, 219, 026 and Island Creek. Dechlorination conditions are listed in Table 16. The Lindberg furnace is normally preheated to 400°C, the furnace tube is purged with nitrogen and charged with up to 2 kilograms of chlorinated, washed and dried coal through one end of the tube. Dechlorination times for runs 1 to 13 are 60 minutes including a coal preheat time to reach 400°C of 20 to 30 minutes followed by a 30 minute time for dechlorination at 400°C. Runs 14 to 44 had a total dechlorination time of 90 minutes with dechlorination at 400°C of 60 minutes, except as noted. A nitrogen purge of 30 SCFH was maintained during the dechlorination and cooling period. Coal was cooled to 300 to 350°C before being removed to a water

Table 16. Coal Dechlorination Data

(Conditions: Dechlorination temperature 400°C, tube rotation 4 RPM, preheat time 20 minutes to reach 400°C, nitrogen purge before and during dechlorination, coal cooled to 300 to 350°C before removal, 30 SCFH N_2 flow during dechlorination, coal mesh size -100 to +200, except as noted)

Run No.	Dechlorination Time[h] (min)	Cooling Time (400° to 300°C) (min)	Input Coal Mass[a] (g)	Input Coal Chlorine Content (wt. %)	Recovered Coal Mass[b] (g)	Recovered Coal Chlorine Content[c] (wt. %)	Mass of[d] Chlorine Removed (g)	Total Mass Recovery[e] (%)	Product Coal Recovery (%)	Coal Type
1	60	25	484	9.91	394	1.29	41.7	90	89	PSOC 276
2[f]	-	-	-	-	-	-	-	-	-	
3	60	25	1584	10.8	1298	-	-	-	-	
4	60	60	1703	5.16	1475	0.80	74.3	91	91	
5	60	38	-	1.53	1372	0.23	22.3	-	-	
6	43	45	1572	9.94	1285	1.34	135.2	90	89	
7	60	45	924	6.94	780	0.75	57.2	91	90	
8	Total of 150		1365	4.09	1190	0.60	47.6	91	90	
9	60	55	1253	5.88	1080	1.03	60.8	91	91	
10	60	35	1395	5.83	1177	0.88	69.1	89	89	
11[f]	-	-	-	-	-	-	-	-	-	
12	60	95	1461	8.01	1240	0.98	102.7	92	91	
13	60	75	1481	1.82	1251	1.48	5.0	85	85	
14	90	40	1397	6.09	1182	0.70	75.3	90	89	
16	90	45	1526	5.31	1259	0.91	67.2	87	86	
15	100	15	1560	10.4	820	0.94	147.7	62	58	PSOC 282 (-100 to +200 mesh)
17	90	37	939	14.0	859	2.94	103.9	103	103	
18	90	45 - 60	1740	9.25	1438	0.65	149.6	91	90	
19	90	30 - 45	1737	14.7	1356	2.18	217.5	91	89	
20[f]	-	-	-	-	-	-	-	-	-	
21	90	30 - 35	823	16.1	561	2.49	112.0	82	79	
22	90	35	1427	16.8	1059	2.77	200.2	88	87	
23	90	63	1056	18.9	797	3.84	159.0	91	89	
24	90	45	1338	3.24	1136	0.44	37.5	88	87	
25	90	30	1224	7.22	1015	2.61	56.4	88	87	
35	Total of 140		1427	16.2	1118	1.10	215.5	93	93	
37[g]	90	45	1887	17.2	1430	0.80	309.5	92	91	
39[g]	90	[illegible]	1306	34.4	793	2.13	421.4	93	91	
26	90	35	1512	13.2	1233	2.23	165.9	93	92	PSOC 282 (-1/8-inch to +100 mesh)
27	90	30	[illegible]	14.8	952	2.19	146.7	94	94	
33	90	30	1234	15.4	904	0.86	179.4	88	86	
34	90	47	[illegible]	17.5	1145	1.25	240.5	94	93	
28	60	-	1213	19.6	863	1.44	220.3	89	87	PSOC 219
29	65	70	1006	17.5	983	1.68	159.1	114	116	
30	60	50	1275	15.8	872	2.13	172	83	81	PSOC 026
31	105	30	910	21.2	-	1.40	180	-	-	
32	90	30	[illegible]	17.9	933	1.23	239	86	83	
42[g]	95	55	1097	16.7	878	2.37	157.2	94	94	Island Creek
44[g]	90	45	1060	33.2	634	5.12	297.6	88	85	
Average									88	

a: dry basis
b: assumed dry basis, center zone + end zone coals
c: chlorine analyses of furnace center zone coal product, runs 13 to 27 and 31-44, other analyses are of the total coal product
d: calculated: chlorine = input coal mass x (Cl before dechlorination - Cl after), by analysis
e: recovery = 100 x (total recovered coal + chlorine removed) ÷ input coal
f: run aborted - no sample to dechlorinate
g: no samples from the first runs of staged runs
h: total coal retention time during dechlorination not including cooling time.

cooled coal receiver blanketed with nitrogen. The furnace tube was rotated at 4 RPM during the entire period. Average coal sample processed was 1200 gram with an average 12% coal loss amounting to ~140 grams/test.

PSOC 276

Thirteen dechlorination runs were made. Initial chlorine values were between 1.5 to 10.4 weight percent and residual chlorine values after dechlorination were 0.23 to 1.48 weight percent. Product coal recovery was 85 to 91%. Coal handling losses were considered the largest loss rather than losses of oil and tar matter from the coal. Carefully controlled dechlorination experiments in the Phase I laboratory program indicated a measured loss of only 0.7% coal as oil and tar at 400°C for 30 minutes. Substantial amounts of coal fines were observed to be carried along with the nitrogen purge to the scrubber unit.

PSOC 282

Thirteen runs were made with PSOC 282 with mesh size at -100 to +200 mesh and 4 runs at mesh size of -1/8 inch to +100 mesh. The coarse coal showed a greater average recovery, 91% as opposed to the finer coal which averaged a recovery of 87%. This probably represented a reduction in coal fines carried along with the nitrogen purge. Initial chlorine values with PSOC 282 were higher 3.24 to 34.4 wt. % than with PSOC 276 because of more intense and extended chlorination of the coal. Residual chlorine values after dechlorination were also somewhat higher, 0.65 to 3.84 wt. % despite the extended dechlorination time from 60 to 90 minutes. However, chlorine in the raw coal was 0.5 wt. % to start. The added chlorine in the case of 0.65 wt. % chlorine in the dechlorination sample was therefore only 0.15 wt. %.

PSOC 219

Coal dechlorination for 2 runs was from 17-20 wt. % to 1.4-1.7 wt. % chlorine. Coal recovery was 87-116%.

PSOC 026

Three runs with coal at 16-21 wt. % initial chlorine reduced chlorine to 1.2-2.1 wt. %. Coal recovery was 78 to 81%.

Island Creek

Chlorine values in 2 dechlorination runs were reduced from 17-33 wt. % to 2.4-5.1 wt. %. Coal recovery was 85 to 94%.

Coal Dechlorinator Scrubber

A sodium carbonate scrubber unit provided treatment of the nitrogen purge gas during dechlorination to contain the evolved HCl. Data for test runs 10 and 12 are listed in Table 17. A water scrubber solution of 46 liters of water and 1880 grams of sodium carbonate was used to provide 91-95% HCl recovery at a final chloride concentration of 1.5-2.0 gram/liter. For HCl recovery in commercial practice a concentration buildup of HCl will be required by limiting the water and providing countercurrent flow of HCl gases and scrubber solution.

RESULTS AND CONCLUSIONS

The bench scale batch reactor experiments with 2 kilograms of coal/batch provided a broader range of pressure, temperature and chlorine flow rate conditions than that originally explored in the laboratory scale experiments. Unfortunately, the expectations of improved coal desulfurization with increases in operating temperature and/or pressure did not materialize. The introduction of water in lieu of methylch. roform as a solvent showed considerable promise for total sulfur

Table 17. Coal Dechlorinator Scrubber Analyses

Run #	Coal Input to Dechlorinator			Coal Output from Dechlorinator			Dechlorinator Scrubber[c]			Total Chlorine Recovered (g)	Chlorine Recovery (%)
	Mass[a] (g)	Chlorine (Wt. %)	Chlorine Content (g)	Mass[b] (g)	Chlorine (Wt. %)	Chlorine Content (g)	Cl^- (g/l)	Volume (liters)	Total Chloride (g)		
Scrubber Blank	-	-	-	-	-	-	0.03	46	1.38	-	-
10	1395	5.83	81.3	1177	0.88	10.36	1.45	46	66.70	77.1	95
12	1461	8.01	117.0	1240	0.98	12.15	2.04	46	93.84	106.0	91

[a]Dry basis

[b]Assumed dry

[c]1880g sodium bicarbonate in 46 liters tap water

removal although organic sulfur removal with water as a solvent was substantially less than with methychloroform. Substantial process improvements are required in order to achieve EPA sulfur compliance levels for coal treated by the chlorinolysis process.

Process Operating Conditions

No significant correlations were found among pressure, temperature and chlorine flow rates with coal desulfurization. Reaction times of 45 minutes appeared adequate to achieve maximum coal desulfurization with no substantial benefits in extending reaction time to 90 minutes. Particle size is an important parameter with particles of +100 mesh showing a falloff in desulfurization relative to that obtained with -100 to +200 mesh. The amount of operating data are still sparse and much more data on the bench-scale batch chlorination are required for a comprehensive evaluation of the process.

Sulfur Forms

Maximum sulfur removal for the five coals tested were: total sulfur removals of 52-63% with methylchloroform and 45-66% with water; organic sulfur removals of 46-89% with methylchloroform and 0 to 24% with water for four of the 5 coals, PSOC 276 showed no organic sulfur removal with either methylchloroform or water; Pyritic sulfur removal was up to 71-95% with methylchloroform and 72-95% with water, with methylchloroform favoring pyritic sulfur removal in PSOC 276 and Island Creek coals and water favoring pyritic sulfur removal in the other three coals; sulfate sulfur was generally reduced to less than 0.05 wt. % by a spray water wash of the coal vacuum filter cake.

Thermal dechlorination at 400°C improved coal desulfurization by 4-11% over the chlorination process.

A second stage chlorination of washed, chlorinated coal and fresh solvent provided a 5-17% improvement in desulfurization over the first stage treatment but achieved only a maximum total desulfurization of 58%, comparable to the best of single stage desulfurizations.

Apparent anomalies between organic and pyritic sulfur values exist which need to be resolved. This includes the apparent transformation between organic and pyritic sulfur values that occur at the time of solvent distillation from the coal slurry. Recall, however, that organic sulfur is determined by difference and changes in pyritic sulfur values provide a reverse change in organic sulfur values.

Comparative sulfur form analyses from independent coal laboratories showed relatively good agreement, within ASTM standards, with minor exceptions. Leco acid-base analyzer showed relatively good agreement with Eschka analysis for total sulfur.

Coal Analyses

Proximate analyses of the 5 processed coals showed a volatile matter decrease of 8-15 wt %, ash reduction of 1-4 wt. %, fixed carbon increase of 9-20 wt.% and heating value losses in the range of 0-1300 B.T.U./lb.

Trace element analyses for processed coal indicated a 50-80% reduction for arsenic and mercury, with questionnable reduction for lead and selenium and vanadium being undetected (<50 ppm).

Ash elemental analyses for the 5 processed coals showed a reduction for iron of 43-75% and calcium of 35-86%.

Coal Filtrate and Wash Water

The wash and filtrate water analyses were:

Cl^- – 5.5-12.4 g/l (5.2-42 wt. % coal)

$SO_4^=$ – 0.19-15.5 g/l (0.18-5.6 wt. % coal)

Fe^{+++} – 0.3-20 g/l (0.3-81 wt. % coal)

Ca, Na, Al, Mg, K <0.57 g/l (<0.25 wt. % coal).

Material Balances

An overall material balance on the combined chlorination, solvent distillation, coal filtration and water wash for 41 test runs provided the following material recovery/accounting:

Raw Coal – 100 ±3.5%

Organic Coal Fraction – 99.3 ±3.5%

Ash – 114%

Sulfur – 94%

Chlorine – 86%

Methylchloroform (17 runs) – 83 ±7%

Exposed metal and test coupon corrosion contributed to the high ash accounting. Solvent vapor losses from the samples and recovery tank contributed to losses. Added solvent cooling reduced losses in later runs with solvent recoveries up to 98%.

Dechlorination

Thirty-six dechlorination runs (400°C) reduced chlorine values by 90+% with chlorine in feed coal of 1.5-33 wt. % and in dechlorinated coal of 0.23 to 5.1 wt. %. Product coal recovery averaged 88 ±5% and chlorine recoveries of

91-95%. Coal handling losses rather than volatile matter was considered the major loss factor with significant losses of coal fines in the nitrogen purge gas to the scrubber. Provisions for recovery of coal fines in the purge gas and improvements in containing coal during handling, charging and removal from the dechlorinator should eliminate the majority of the loss. Provision for oil and tar recovery in the purge gas line is necessary to identify the loss of volatile matter. Dechlorination of the coal needs to reach chlorine levels comparable with that present in raw coals in order to reduce potential corrosion problems of high chlorine content. Raw coals have chlorides in the range of 0.1 to 0.5 wt. %.

FUTURE WORK

Additional batch reactor testing on bituminous, sub-bituminous and lignite coals is planned under a range of operating conditions to provide both improvements in coal desulfurization and an improved understanding of the process.

Laboratory research will be conducted to resolve the anomalies that exist between organic and pyritic sulfur value determinations. The anomaly may in part reside in the ASTM procedure for pyritic sulfur determinations that relies on the iron determination to estimate the pyritic sulfur value, especially when Fe could be introduced by corrosion. The best approach is a direct measure of sulfur.

Physical and chemical coal pretreatment will be considered prior to chlorination as a means of increasing chlorine accessibility to the coal sulfur.

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PART II

CONTINUOUS FLOW — MINI-PILOT PLANT FOR COAL DESULFURIZATION BY CHLORINATION

EQUIPMENT

The mini-pilot plant for coal desulfurization by low temperature chlorination is designed to feed pulverized coal (14-200 mesh) at a nominal rate of 2 kg/hr. Nominal solvent and water flow rates are 4 kg and 1.4 kg per hour respectively. 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 11a, 11b. Nominal design variation in flow rates with corresponding changes of retention time are in the range of -50 to +100% variation. Stainless steel surfaces in the chlorinator will be 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 18, Figures 12-17). The instrumentation and parts lists for the mini-pilot plant are included respectively as Tables 19 and 20. 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 12a, 12b.
4. Flash distillation unit, Figure 13
5. Condenser, Figure 14
6. Solvent recovery tank, Figure 15
7. Horizontal belt vacuum filter and wash
8. Dechlorinator, Figure 16
9. Product coal storage hopper, Figure 17

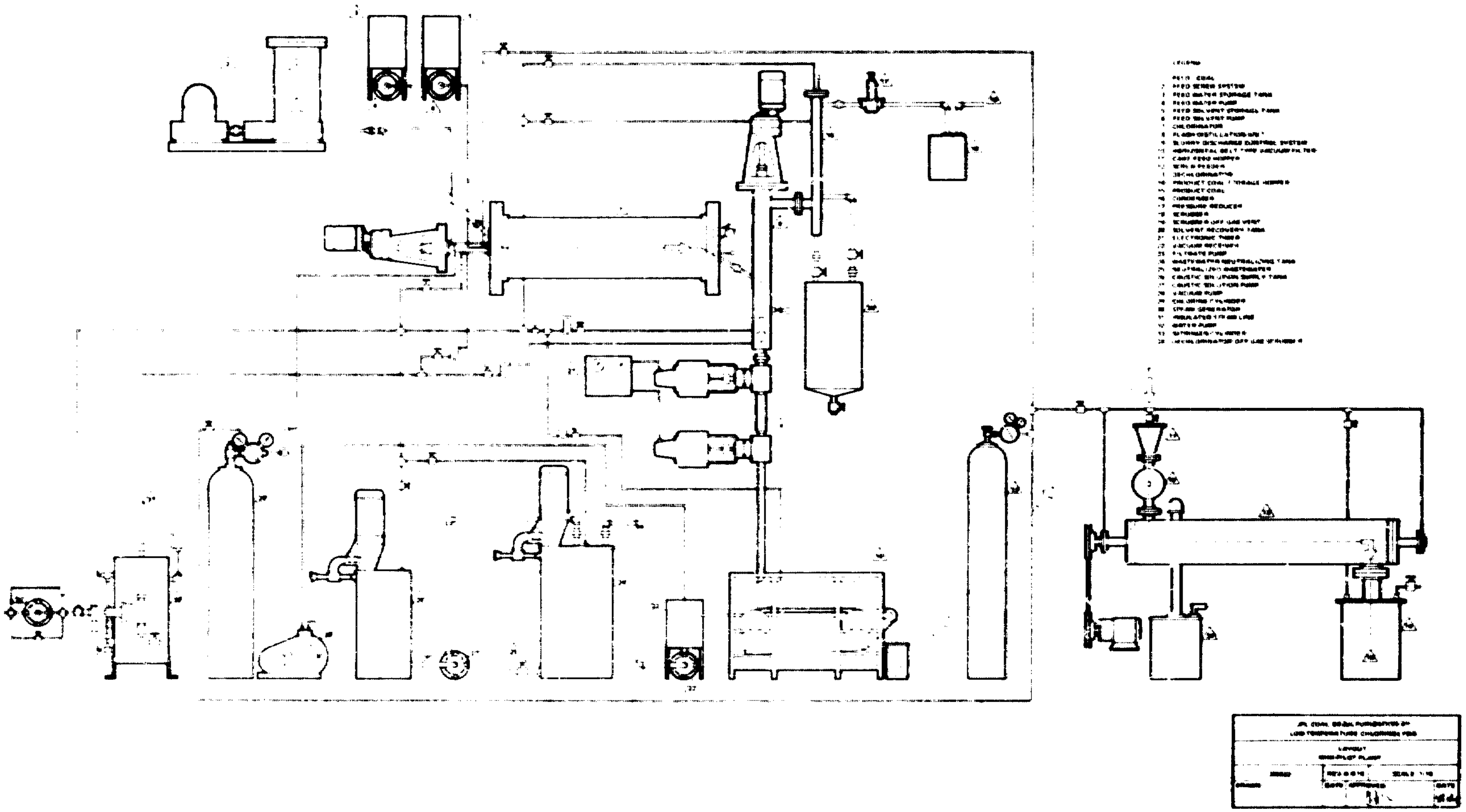


Figure 11a. Equipment Flow Schematic — Mini-Pilot Plant

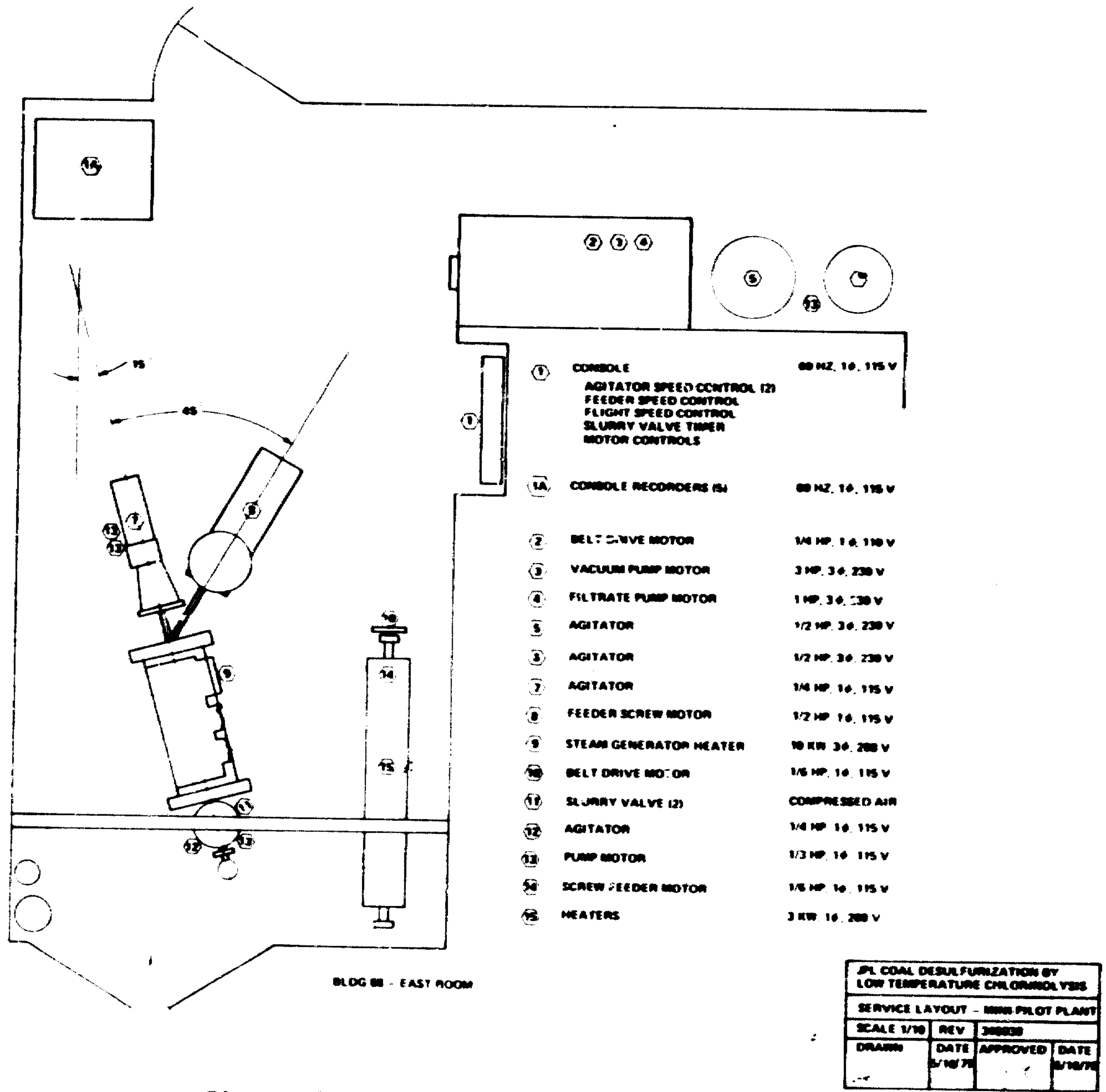


Figure 11b. Equipment Layout - Mini-Pilot Plant

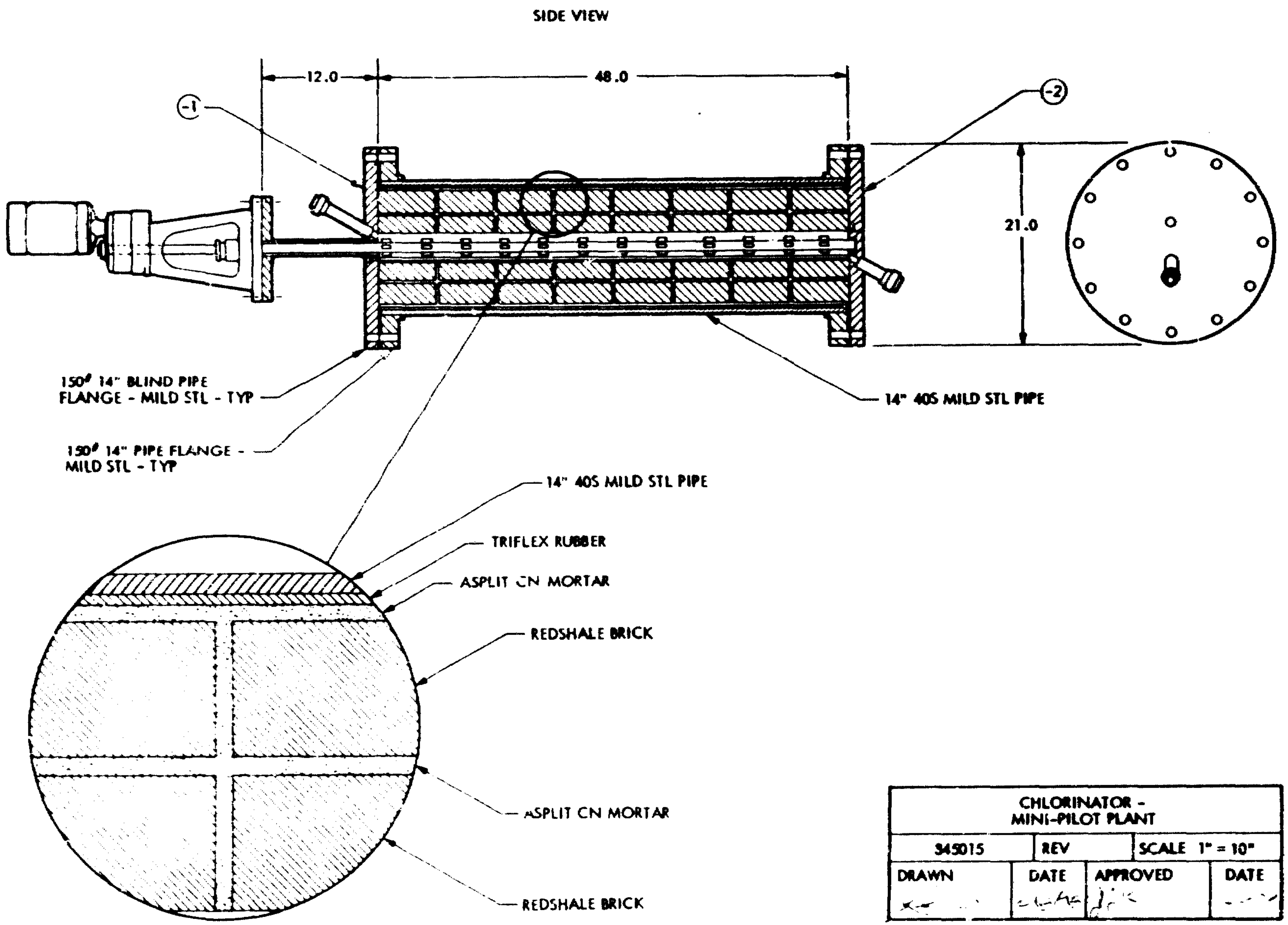


Figure 12a. Chlorinator - Mini-Pilot Plant

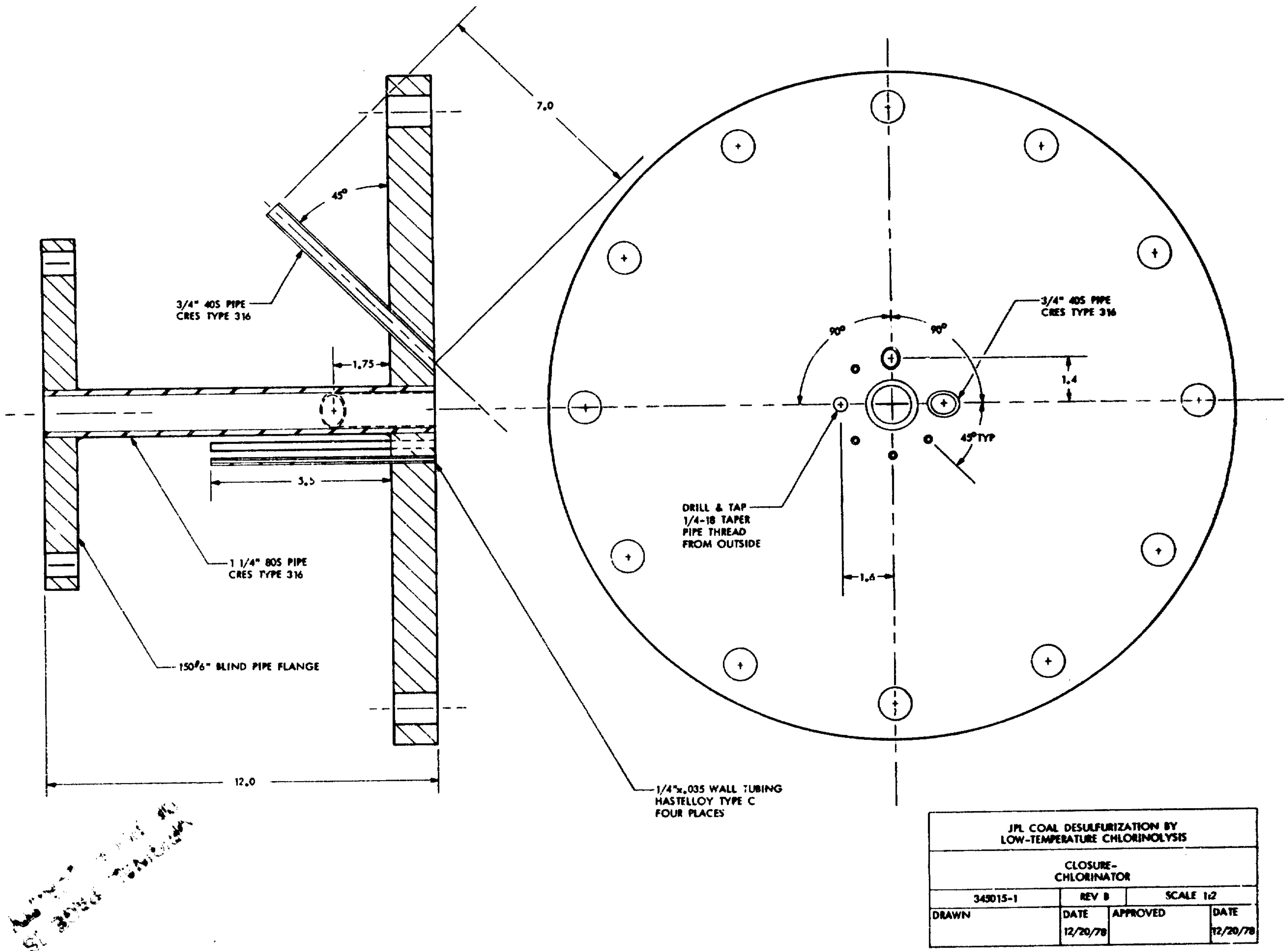


Figure 12b. Closure-Chlorinator — Mini-Pilot Plant

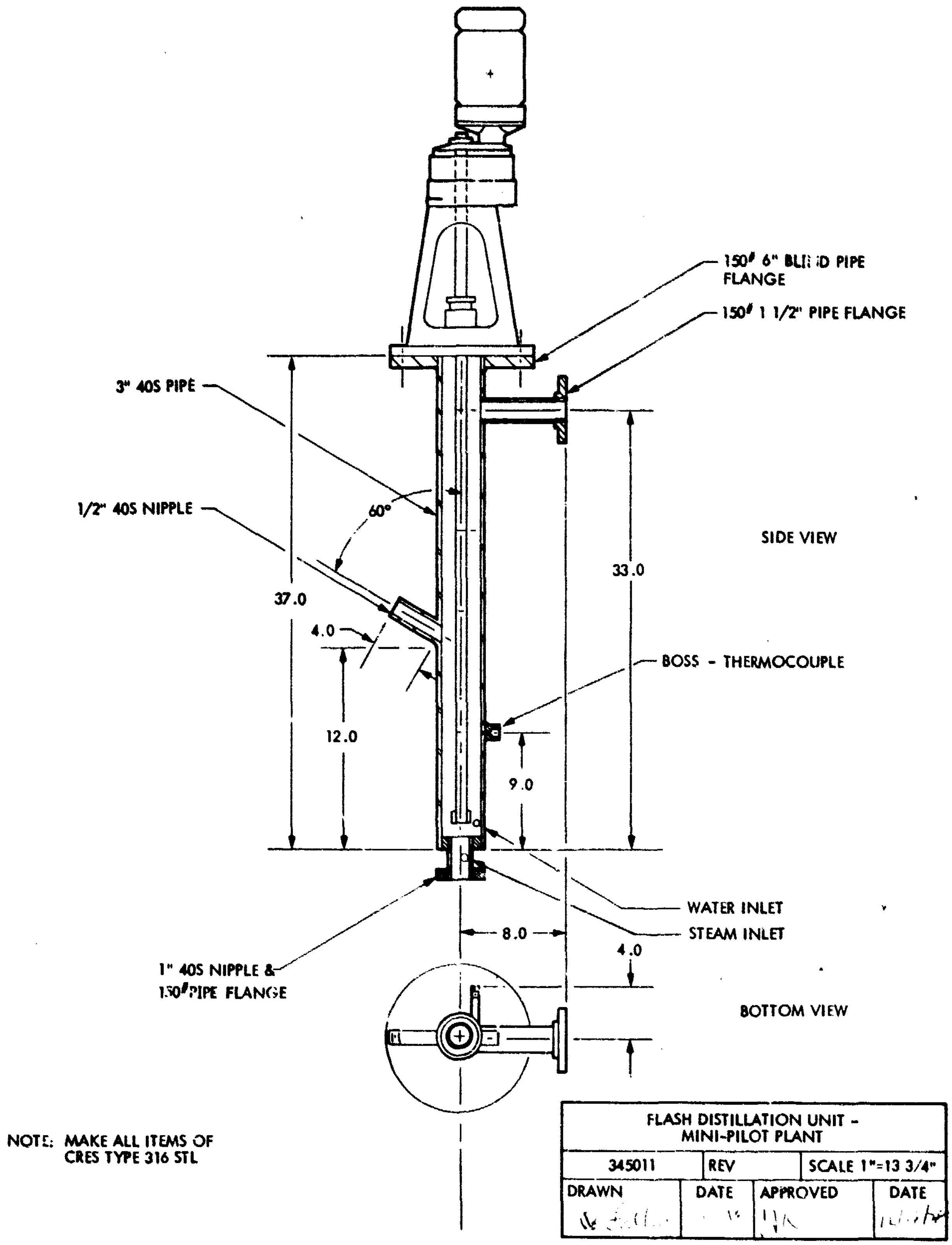


Figure 13. Flash Distillation Unit – Mini-Pilot Plant

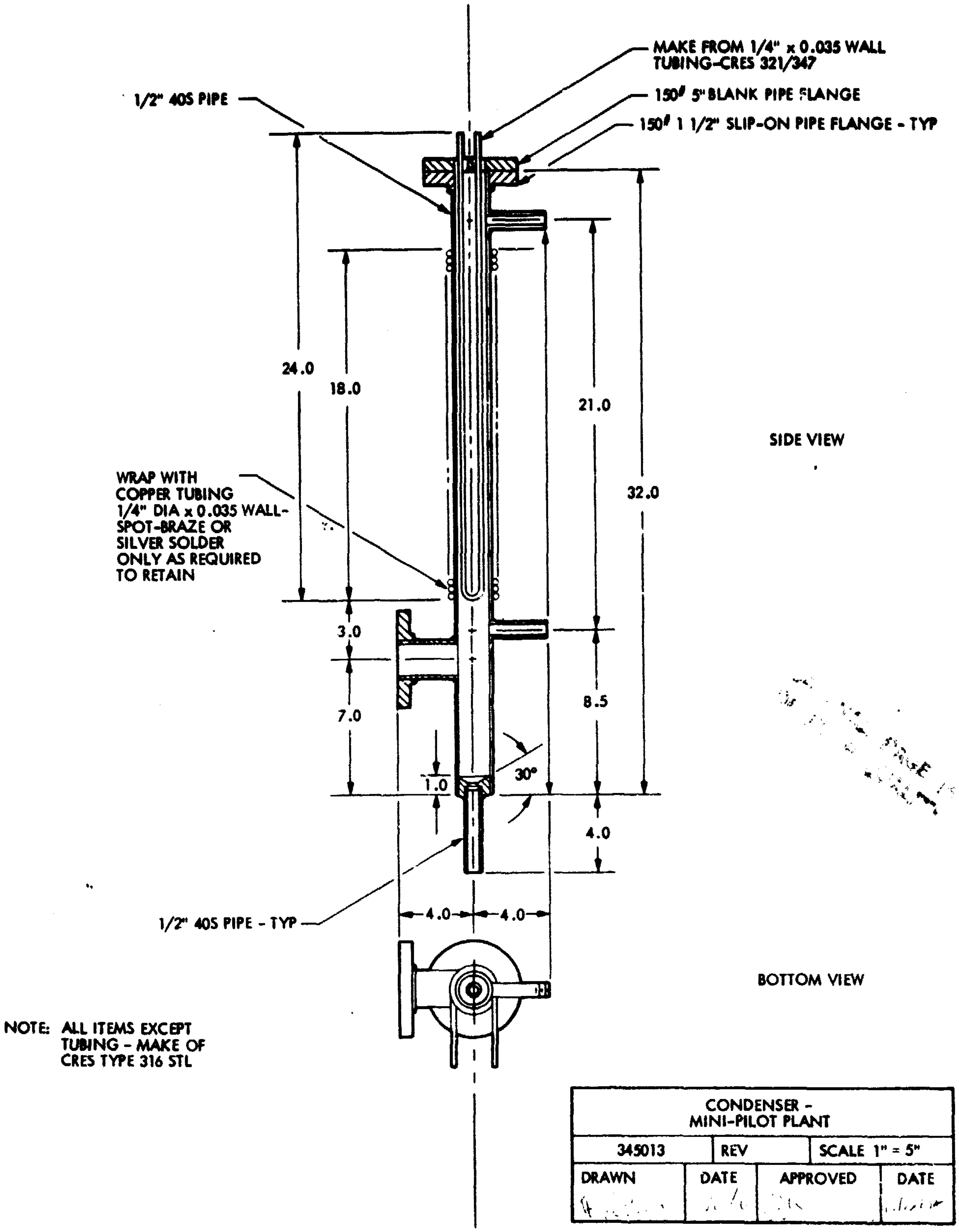


Figure 14. Condenser – Mini-Pilot Plant

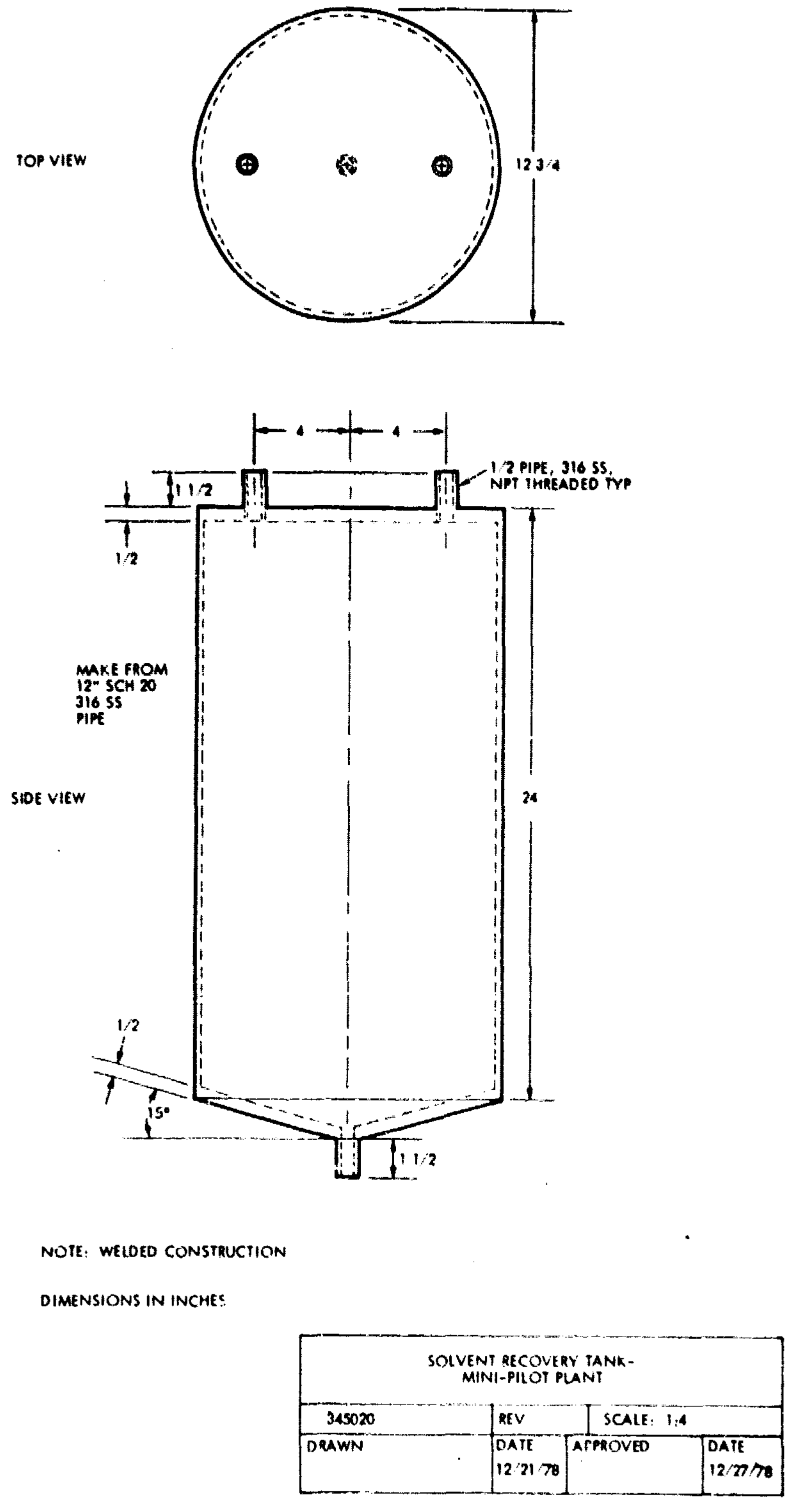


Figure 15. Solvent Recovery Tank — Mini-Pilot Plant

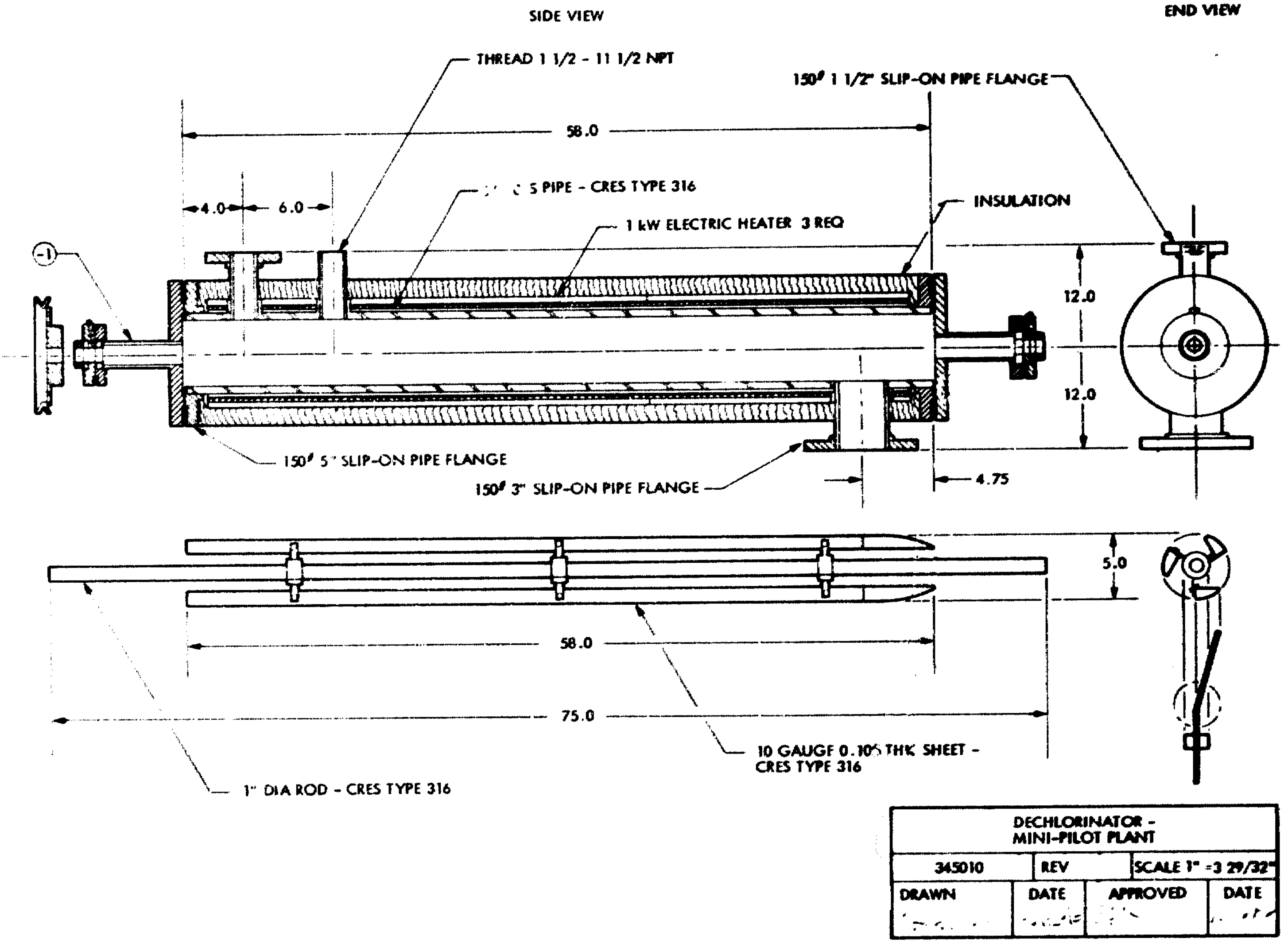


Figure 16. Dechlorinator — Mini-Pilot Plant

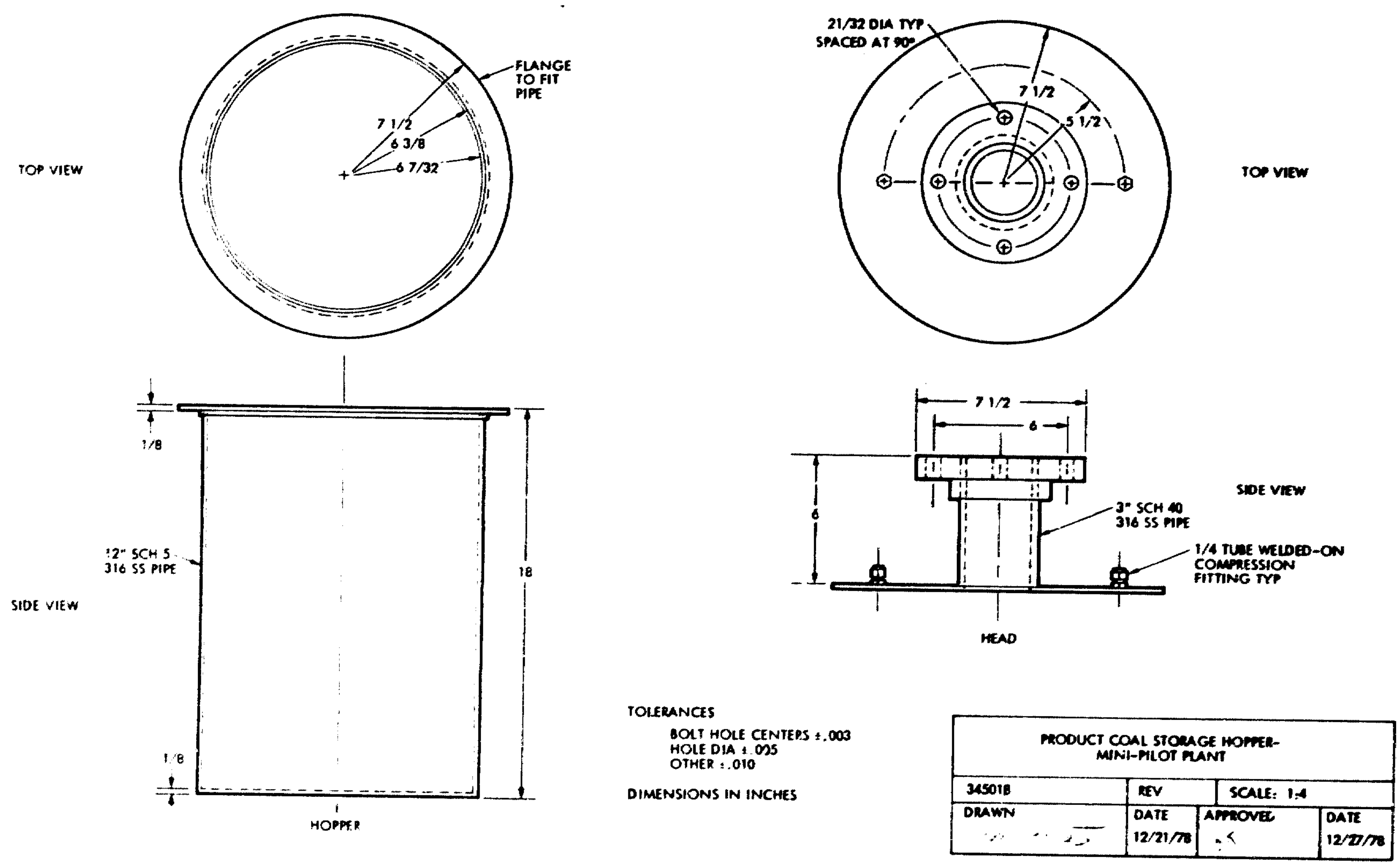


Figure 17. Product Coal Storage Hopper — Mini-Pilot Plant

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 which has a capacity to hold enough 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 square wire type feed screw installed at a feed angle of 45° with respect to the horizontal plane.

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.

Chlorinator

The chlorinator (Figures 12a, 12b) is a carbon steel pipe lined with Kynar glass laminate and acid-proof brick. The chlorinator is closed from both ends with Hastelloy C-276 covered carbon steel flanges that allow entry through various flanges and bosses of coal slurry, steam, chlorine gas, stirring shaft, thermocouple, pressure transducer, pressure gauge, and pressure rupture disc.

Flash Distillation Unit

This unit, Figure 13, is a 316 stainless steel cylinder vessel equipped with a side port feed and coal slurry discharge line at the bottom. The unit is equipped with a Chemineer agitator model No. VLA-2 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 is ported for installation of a thermocouple. Two RED Slurry Valves equipped with automatic timers are installed

Table 18. Major Units — Coal Desulfurization by Low Temperature Chlorination 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 is adjustable from 1 to 5 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, minimum capacity 1 GPH for water and 2.3 GPH for solvent, discharge pressure 100 psig.
Chlorinator-Provide chlorination of agitated ground coal-solven slurry. Drawing No. 345015	Stebbins Engineering and Manufacturing Co., Watertown, N.Y.	Carbon steel pipeline reactor lined with 60 mil Kynar glass laminate and one layer each of 2-1/2 in. thick Semacid and Visil acid proof-brick laid solidly with Pennwalt K-14 mortar.
		Separable reactor head ported for feed and chlorinated coal slurry, agitator shaft, teflon bushing, steam, chlorine, thermocouple, pressure transmitter, pressure gauge, pressure inlet, pressure relief, rupture disc, and cooling water. Maximum operating pressure: 100 psig. Residence time for coal slurry containing 2 kg/hr of coal, 1.0 kg/hr of water, and 4 kg/hr of solvent 60 min.
Agitator for Chlorinator	Chemineer Agitator, Dayton, Ohio	Chemineer Model No. VLA-2. Top entering agitator, 1/4 HP at 430 rpm maximum, SCR variable speed, 1 inch shaft diameter, 60 inches long supported at far end by teflon bushing, ten 2 in. x 3/8 inc. radial impellers, 6 ring teflor stuffing box, 6 inch 150 pound ASA flange, all parts in contact with the slurry are Hastelloy C-276.

Table 18 (Cont'd)

System/Treatment	Manufacturer/ Fabricator	Specification
Flash Distillation Unit		
Vaporize solvent from coal slurry, Drawing No. 345015	JPL, Pasadena, California	Stainless steel 316 vessel equipped with Chemineer agitator model No. VLA-2. Volume, liquid space: 0.086 ft^3, gas space 0.065 ft^3. Maximum operating pressure, 100 psig. Maximum operating temperature, 100°C. Slurry residence time: 25 min.
Agitator for Flash Distillation Unit	Chemineer Agitator, Dayton, Ohio	Chemineer Model No. VLA-2. Top entering agitator, 1/4 HP at 430 rpm maximum, SCR variable speed drive, 3/4 inch shaft diameter, 35 inches long, 2 inch propeller, 6 ring teflon stuffing box, 6 inch a50 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. Drawing No. 345013	JPL, Pasadena, California	Stainless steel 316 condenser cooling surface area: 0.59 ft^2. Maximum operating pressure: 100 psig.
Solvent Recovery Tank		Stainless steel 316 pressure vessel. Capacity 1.8 cubic feet.
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 18 (Cont'd)

System/Treatment	Manufacturer/ Fabricator	Specification
Dechlorinator		
Remove chlorine and moisture from coal. Drawing No. 345010	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	JPL, Pasadena, California	1.26 ft^3 (50 kg) cylindrical hopper equipped with nitrogen purge.
Volumetric Twin Screw Feeder for Dechlorinator	Priority Systems, Inc. Covina, California	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, Obio	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.

Table 19. Instrumentation -- Coal Desulfurization by Low Temperature Chlorination Mini-Pilot Plant

System	Manufacturer/Supplier	Specifications
<u>Chlorinator</u>		
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 diaphragm.
Rupture Disc	Fike Metal Products North Hollywood, CA	Model No. 1/2 30 SB. The inlet is 303 stainless steel, and the holddown ring and outlet are carbon steel. The disc is aluminum coated with Teflon. The rupture pressure is 150 psig, +10%, -5% at 72°F.
Thermocouple	California Alloy Co. El Monte, CA	Temperatures are monitored by means of iron-constantan (Type J) thermocouples calibrated from 0 to 1200°F.
Chlorine Flowmeter	Union Carbide Corp. Long Beach, CA	Linde Model FM4311-6. The chlorine flowmeter has a special cabrication for gaseous chlorine under standard conditions. The calibrated range is from 0.2 to 29 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 lbs/hr, at 100 psig.
<u>Flash Distillation Unit</u>		
Thermocouple	California Alloy Co. El Monte, CA	Temperatures are monitored by means of iron-constantan (Type J) thermocouples calibrated from 0 to 1200°F.

Table 19 (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 20 lbs/hr, at 100 psig.
Differential Pressure Level Sensor	Fisher Control Co. Marshalltown, Iowa	Fisher type 1151 DP differential pressure transmitter to control 21" H_2O level. Transmitter output 4-20 MA. Connected in series to Armclec I/P transducer, Model 58, Fisher type 4152 pressure controller, and rotary valve at the flash distillation coal slurry discharge line.
Condenser		
Thermocouple	California Alloy Co. El Monte, CA	Temperatures are monitored by means of iron-constantan (Type J) thermocouples calibrated from 0 to 1200°F.
Differential Pressure Reducing Regulator	Fisher Controls Co. Marshaltown, Iowa	Fisher type 95HD. Differential pressure range 15 to 150 psi. Maximum inlet pressure, 300 psig.
Dechlorinator		
Thermocouple	California Alloy Co. El Monte, CA	Temperatures are monitored by means of iron-constantan (Type J). Thermocouples calibrated from 0 to 1200°F.

Table 20. Complete Parts List – Coal Desulfurization by Low Temperature Chlorination Mini-Pilot Plant

Item	Capacity, Size, or Operating Condition
<u>Pressure Screw Feeder</u>	
Pressure Vessel	1.09 cubic feet
Pressure Gauge	0-150 Psig
Variable Speed Motor	1/2 HP capacitor start motor
Screw Feeder	1 to 10 Kg/hr. of pulverized coal
<u>Water and Solvent Pumps</u>	
Metering Pumps	Maximum feed rate: 1 GPM for water and 2-3 GPH for solvent. Pressure, 1-100 Psig.
<u>Chlorinator</u>	
Closure (2)	See drawing 345015
Connecting Pipe	1/2" schedule 40 pipe
Chem. Agitator, Model No. VLA-2	See Table 18
Steam Control Valve	0-100 Psig.
Steam Flowmeter	0-20 lbs/hr, 100 Psig
Steam Injection	1/4" tubing
Thermocouple	See Table 19
Pressure Transmitter with Hastelloy C-276 Flange and Diaphragm	See Table 19
Screw Type Rupture Unit Assembly	1/2" NPT inlet and outlet
Rupture Disc, Teflon Coated	Rupture Pressure, 150 Psig, See Table 19
Pressure Gauge	0-150 Psig.
Bleed Valve	To release trapped gas
Chlorine Cylinder	Standard
Chlorine Regulator	0-150 Psig.
Chlorine Flowmeter	0-140 SCFH
Chlorine Feed Line	1/4" tubing
Slurry Outlet Line	1/2" schedule 40 pipe
Kynar-lined Ball Valve	1/2" NPT
<u>Flash Distillation Unit</u>	
Head Flange	See drawing 345011
Connecting Pipe	1/2" schedule 40 pipe
Chem. Agitator, Model No. VLA-2	See Table 18
Steam Control Valve	0-100 Psig.
Steam Flowmeter	0-120 lbs/hr, 100 Psig.
Thermocouple	See Table 19
Water Control Valve	0-100 Psig, 0-5 Liter/hr

Table 20. Complete Parts List — Coal Desulfurization by Low Temperature Chlorination Mini-Pilot Plant (Cont'd)

Item	Capacity, Size, or Operating Condition
<u>Flash Distillation Unit</u> (Continued)	
Water Flowmeter	0-5 liter/hr
Water Lines	1/4" tubing
Gas Outlet + Condenser	1 1/2" schedule 40 pipe
Slurry Outlet Lie to Vacuum Filter	1" schedule 40 pipe
Slurry Valve	1", 150 lb/O" flange
<u>Condenser</u>	
Connecting Pipe	1 1/2" schedule 40 pipe
Copper Cooling Coil	1/2" Tubing
Stainless Steel 316 Cooling Coil	1/4" Tubing
Thermocouple	See Table 19
Solvent Outlet Line	1/2" schedule 40 pipe
Ball Valve	1/2" NPT
Solvent Recovery Tank	See drawing 345020
Back Pressure Regulator	See Table 19
Scrubber	5 gallon Polypropylene tank
<u>Vacuum Filtration of Coal Slurry and Spray Wash System</u>	
Horizontal Belt Vacuum Drum Filter (1 unit)	See Table 18
Filtrate Pump	Centrifugal, 0-7 liter/hr
Water Spray Nozzle	1/4" tubing
Wastewater Neutralizing Tank	See drawing 345021
Caustic Solution Supply Tank	See drawing 345017
Cake Storage Hopper	20 lbs.
Filter Cloth	Filter 100-200 mesh particle
<u>Dechlorinator</u>	
Coal Feed Hopper	10 lbs
Feed Screw	5 lbs/hr
Feed Screw Motor	5 lbs/hr
Dechlorinator Unit (1)	See drawing No. 345010
Electric Heaters (3)	1 KW each
Off-Gas Exhaust	1 1/2" pipe
Dechlorinator Off-Gas Scrubbers	2 gallon Polypropylene Tank
Insulation	Glas fiber, 3" thick
Nitrogen Line	1/4" tubing
Thermocouple	See Table 19
Product Coal Storage Hopper	See drawing 345018

Table 20. Complete Parts List — Coal Desulfurization by Low Temperature Chlorination Mini-Pilot Plant (Cont'd)

Item	Capacity, Size, or Operating Condition
Steam Generator	
Steam Generator (1 unit)	See Table 18
Insulated Steam Line	1/4" tubing
Bleed Valve	To release trapped steam
Miscellaneous	
Electrical Panel & Wiring	
Instrument and Control Panel	
Recorder for Thermocouple	15 Channel
Recorder for Pressure Measurements	2 Channel
Flanges	
Pipe Fittings	
Tube Fittings	

in series at the bottom of the flash distillation unit to provide controlled discharge of the coal slurry.

Condenser

This unit (Figure 14) is a 316 stainless steel vessel with copper cooling coil wrapped around it. The solvent vapors are condensed in this unit and collected in a solvent recovery tank for reuse.

Solvent Recovery Tank

This unit (Figure 15) is a 316 stainless steel pressure vessel designed to collect solvent from condenser.

Horizontal Belt Vacuum Filter and Wash

The coal slurry from the flash distillation unit is discharged into a coal slurry receiver and manually transported to the vacuum filter. The filter consists of a horizontal belt covered with porous filter cloth. The center of the belt is under vacuum, thus filtering the coal slurry 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 filter cake of coal breaks loose from the belt into a receiver as the belt turns under across a pulley and the coal is manually transported to the dechlorinator feed hopper.

Dechlorinator

The dechlorinator (Figure 16) consists of a stationary cylinder fabricated from 316 stainless steel schedule 80 pipe. Heating is accomplished by three electric heaters (1 KW each) wrapped around the dechlorinator cylinder. The rotary flights are provided inside the dechlorinator cylinder to provide continuous mixing as well as forward feed of coal particles. Filter cake 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 17) provided with a nitrogen purge to prevent oxidation of the coal heated in the dechlorinator.

Wastewater and caustic solution tanks are included, Figures 18 and 19.

Equipment support structures and dollies are included, Figures 20-27.

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 the equipment inventories of material preliminary

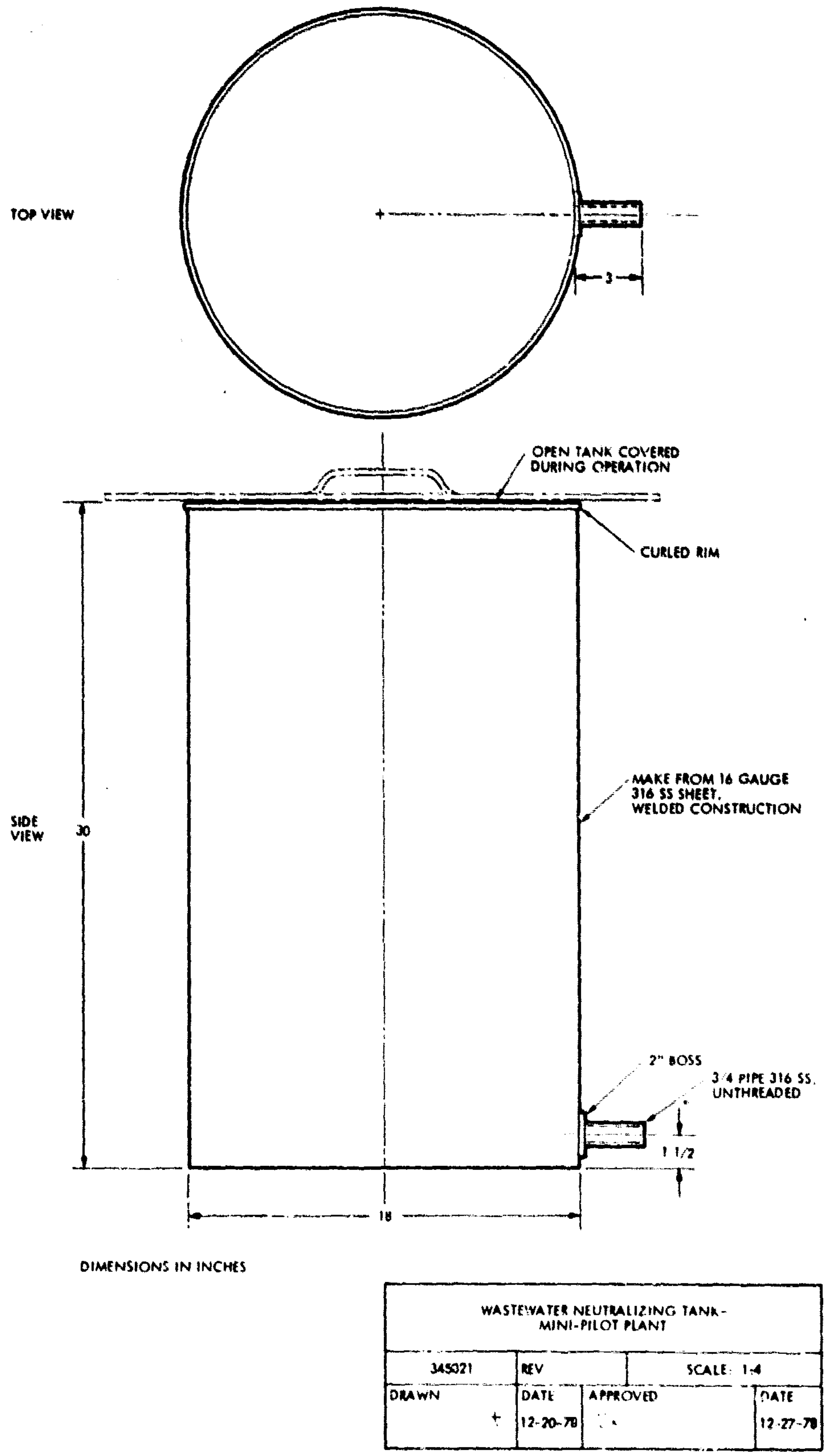
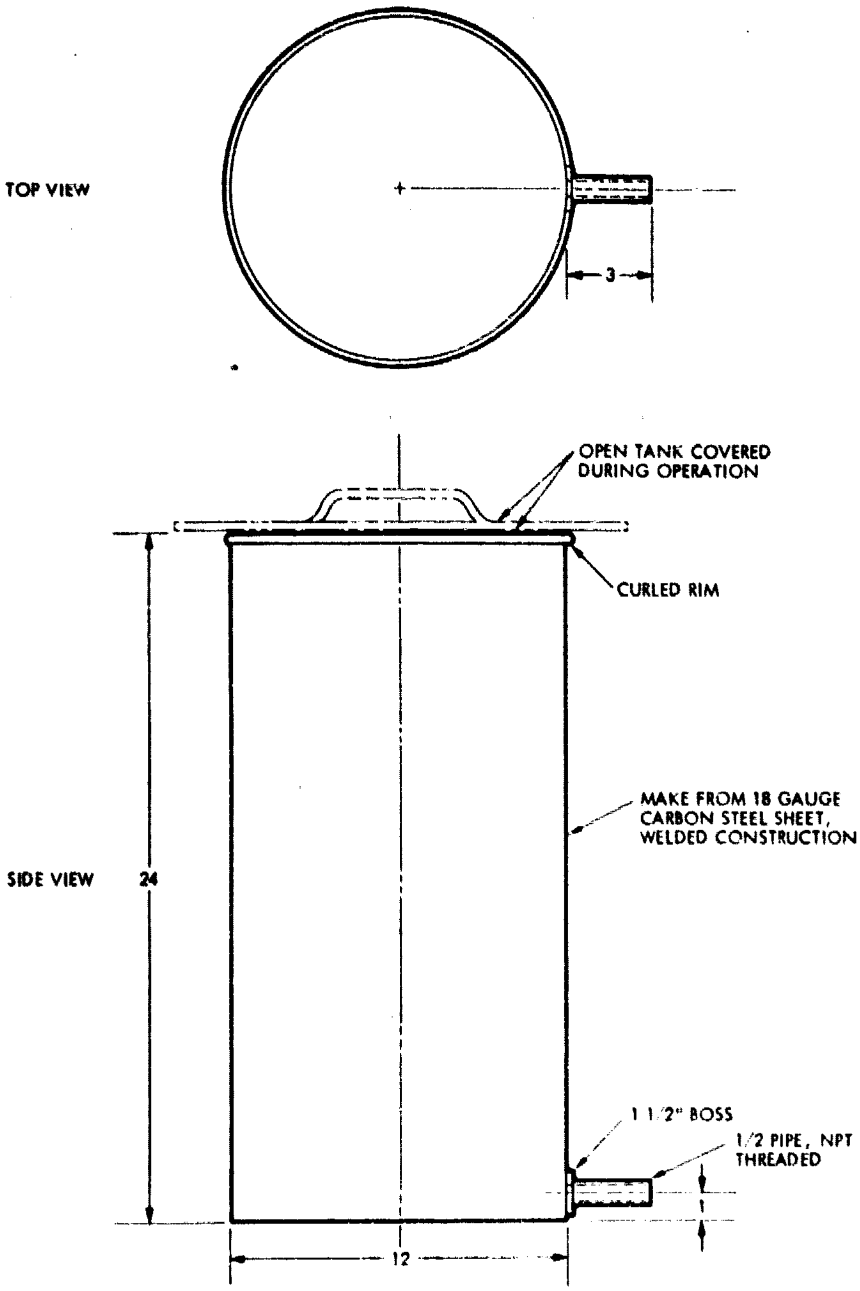


Figure 18. Wastewater Neutralizing Tank – Mini-Pilot Plant



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 19. Caustic Solution Supply Tank Mini-Pilot Plant

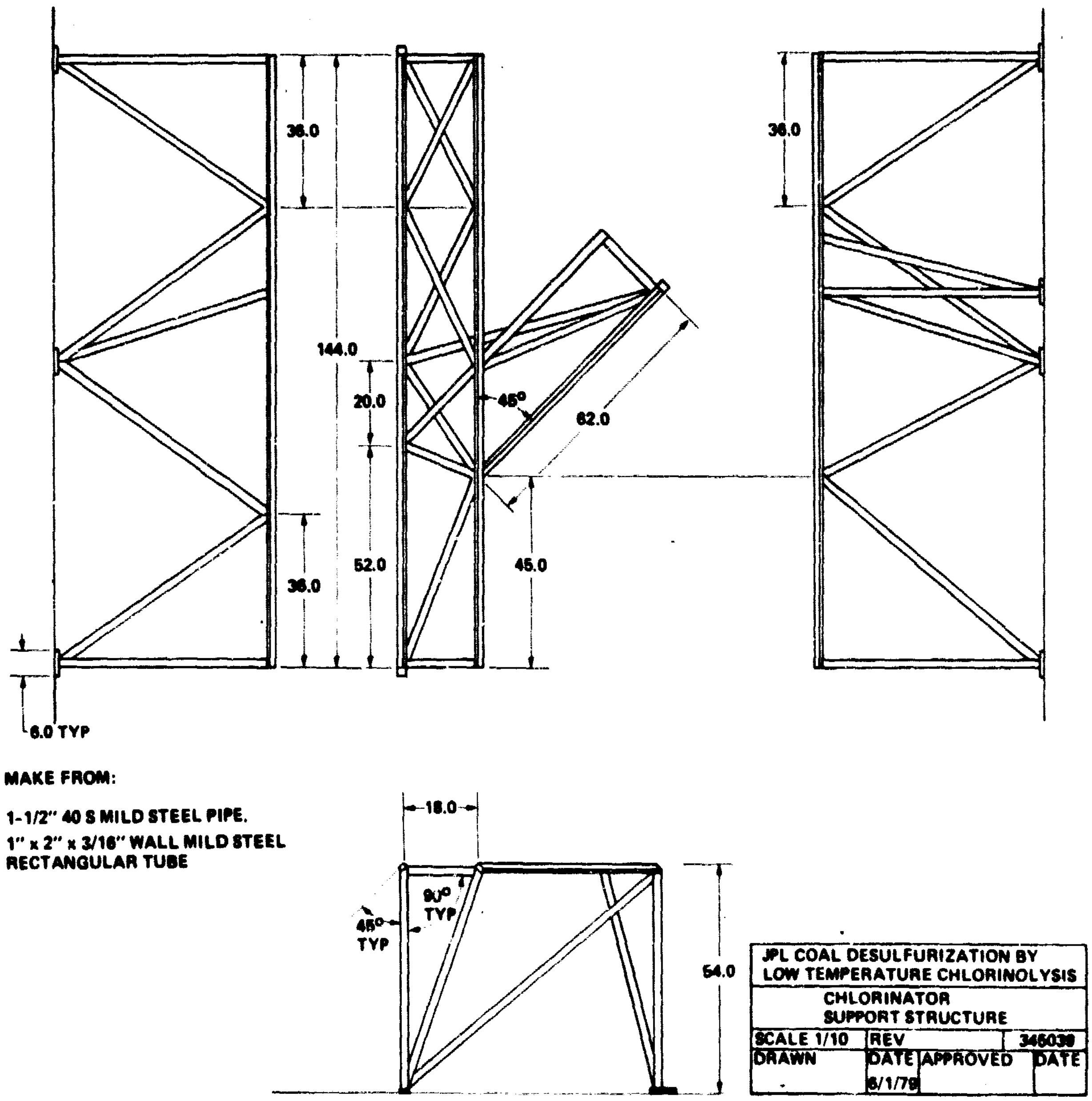
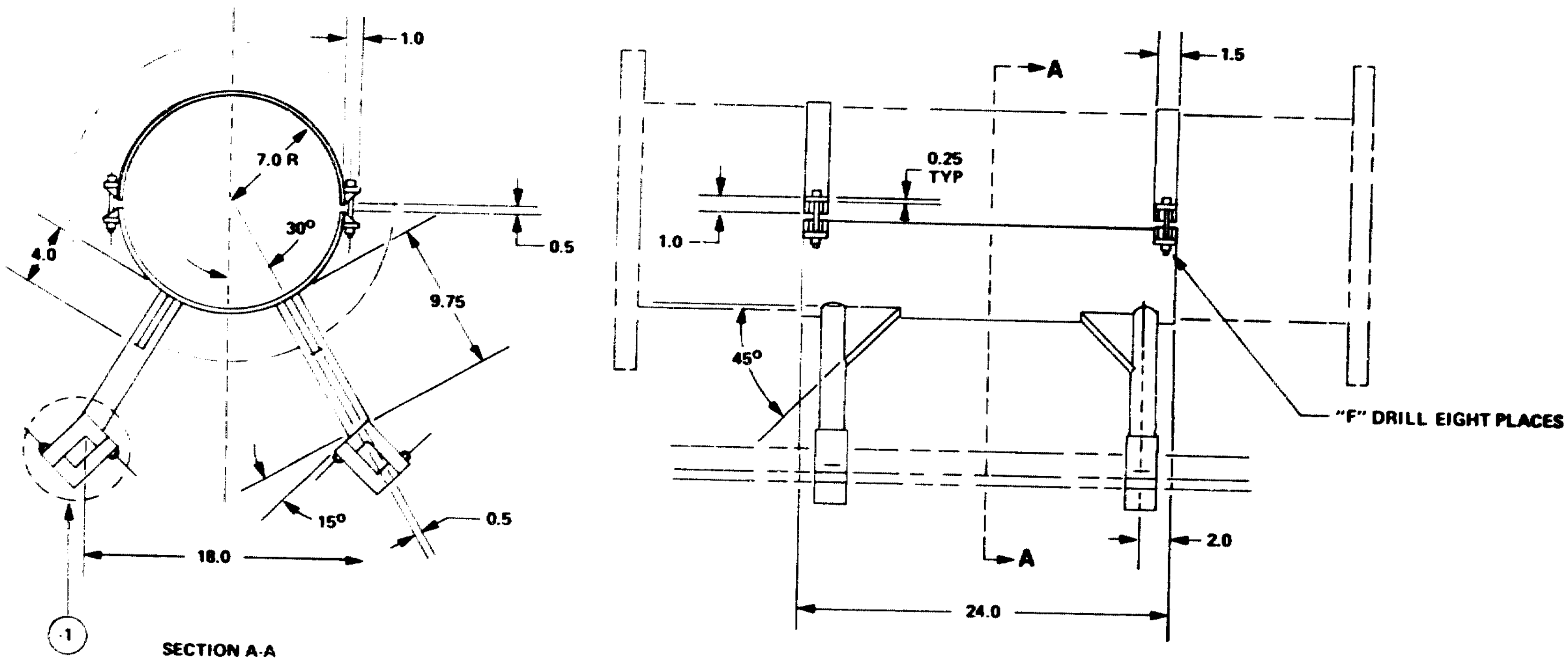


Figure 20. Chlorinator Support Structure - Mini-Pilot Plant



MAKE STRAPS & CRADLE FROM MILD STL PLATE 1/4" THK. CRADLE PLATE DIM. BEFORE ROLLING, 21 X 24 X 1/4 INCHES.

MAKE LEGS FROM 1-1/4-INCH MILD STL PIPE 40S.

OTHER ITEMS MILD STL AS REQUIRED.

JPL COAL DESULFURIZATION BY LOW TEMPERATURE CHLORINOLYSIS			
CHLORINATOR SADDLE – MINI-PILOT PLANT			
SCALE 1/5	REV	345037	
DRAWN	DATE 6/25/79	APPROVED	DATE 6/26/79

Figure 21. Chlorinator Saddle – Mini-Pilot Plant

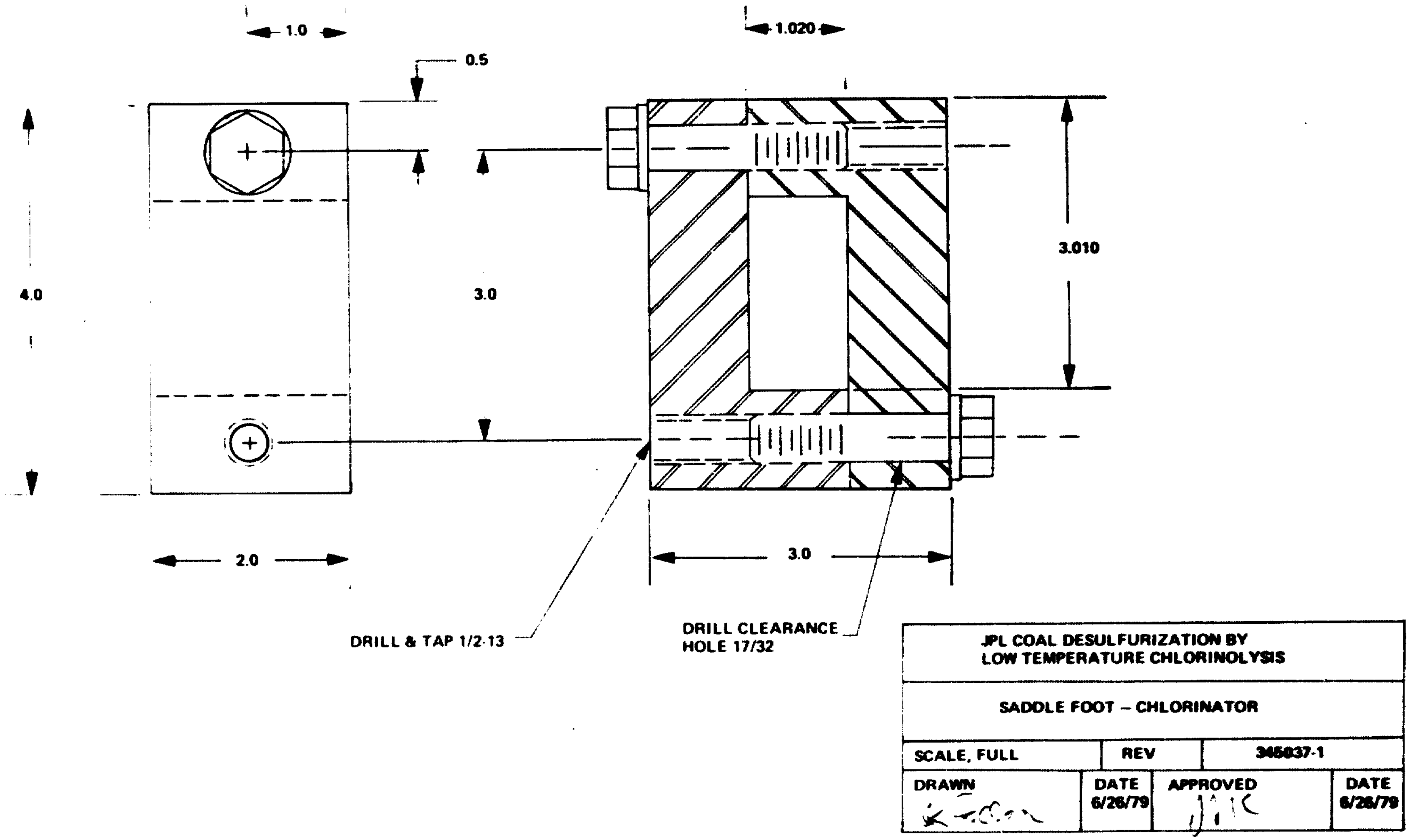


Figure 22. Saddle Foot-Chlorinator — Mini-Pilot Plant

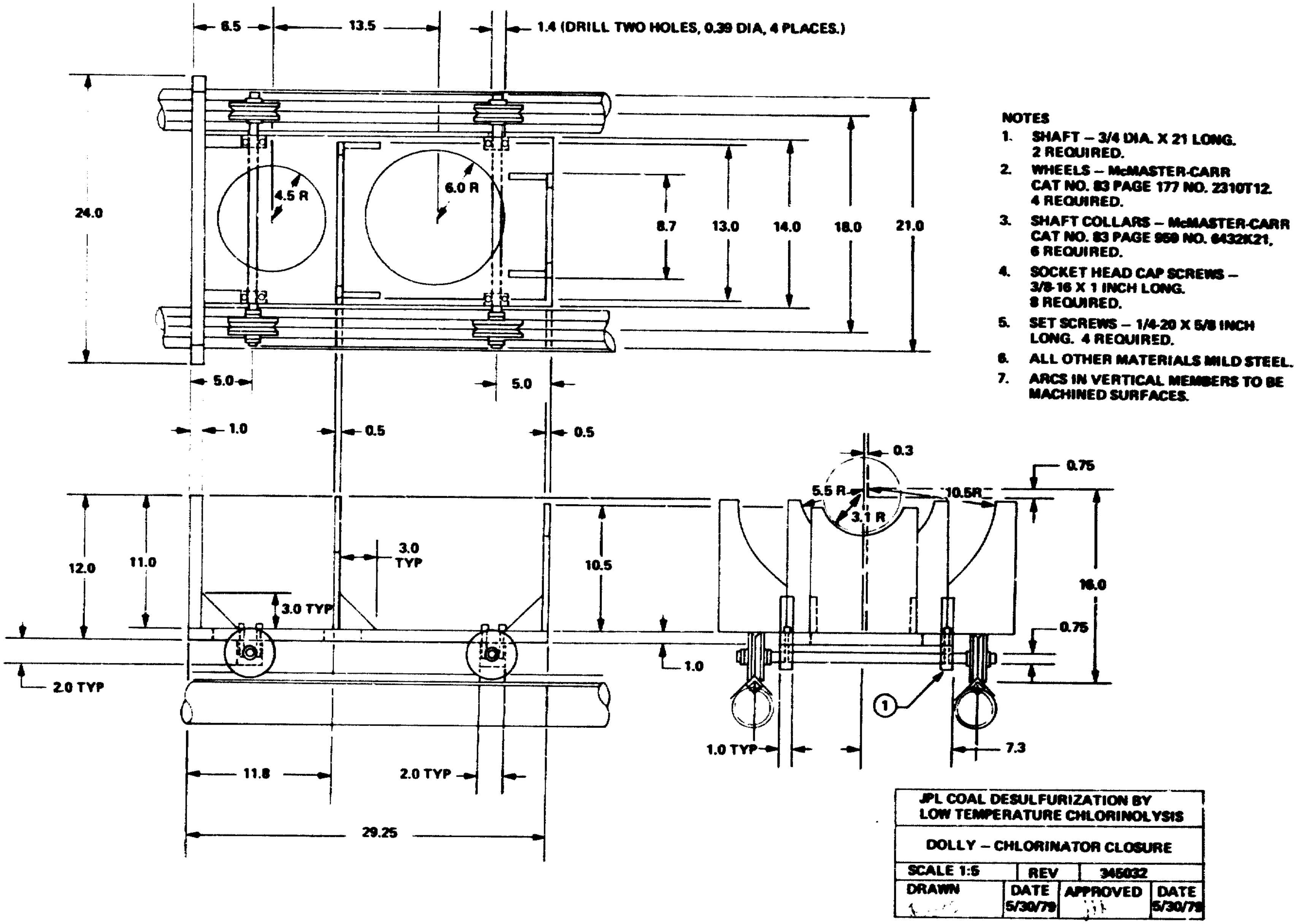
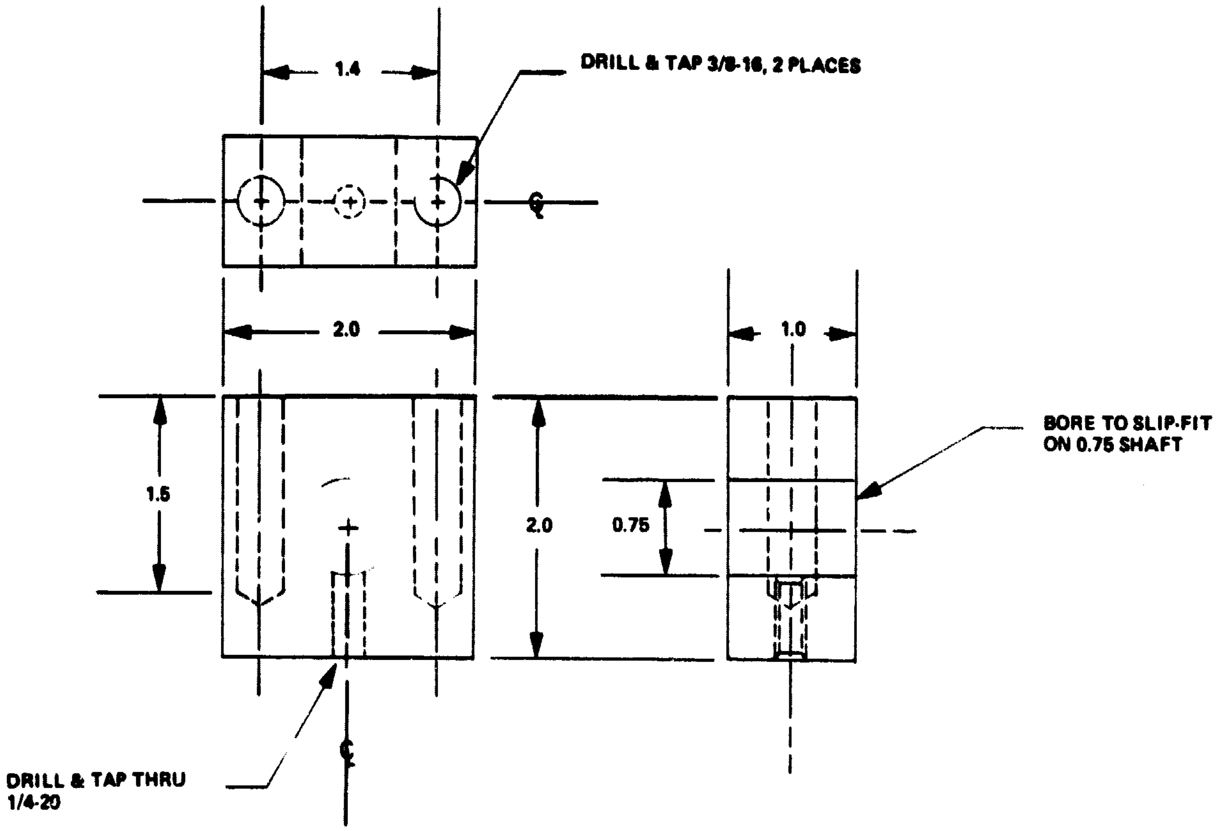


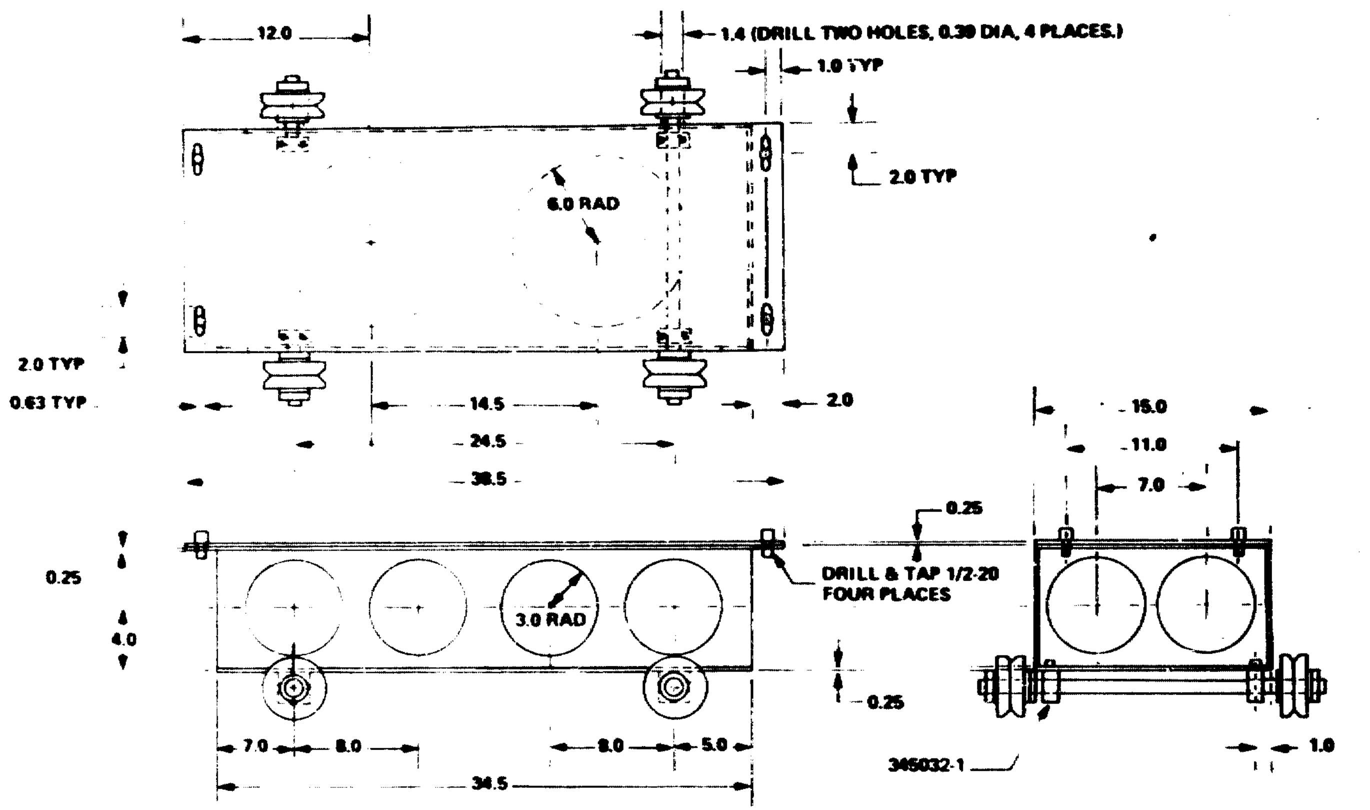
Figure 23. Dolly-Chlorinator Closure – Mini-Pilot Plant



MATERIAL: MILD STL
4 REQUIRED

JPL COAL DESULFURIZATION BY LOW TEMPERATURE CHLORINOLYSIS			
AXLE BLOCK — DOLLY			
SCALE FULL	REV	345032-1	
DRAWN	DATE 5/30/79	APPROVED	DATE 5/30/79

Figure 24. Axle Block-Dolly — Mini-Pilot Plant



NOTE –

1. SHAFT – 3/4 DIA. X 22 LONG, 2 REQUIRED.
2. WHEELS – McMASTER-CARR CAT NO. 83 PAGE 177 NO. 2310T12, 4 REQUIRED.
3. SHAFT COLLARS – McMASTER-CARR CAT NO. 83 PAGE 958 NO. 6432K21, 6 REQUIRED.
4. SOCKET HEAD CAP SCREWS – 3/8-16 X 1 INCH LONG, 8 REQUIRED.
5. SOCKET HEAD CAP SCREWS – 1/2-20 X 1 INCH LONG, 4 REQUIRED.
6. SET SCREWS – 1/4-20 X 5/8 LONG, 4 REQUIRED.
7. ALL OTHER MATERIALS MILD STEEL.

REV A	FRONT AXLE RELOCATE, 5.0 TO 7.0			
JPL COAL DESULFURIZATION BY LOW TEMPERATURE CHLORINOLYSIS				
DOLLY – PRESSURE FEEDER				
SCALE 1:5	REV A	345033		
DRAWN	DATE 6/2/79	APPROVED	DATE 6/4/79	

Figure 25. Dolly-Pressure Feeder — Mini-Pilot Plant

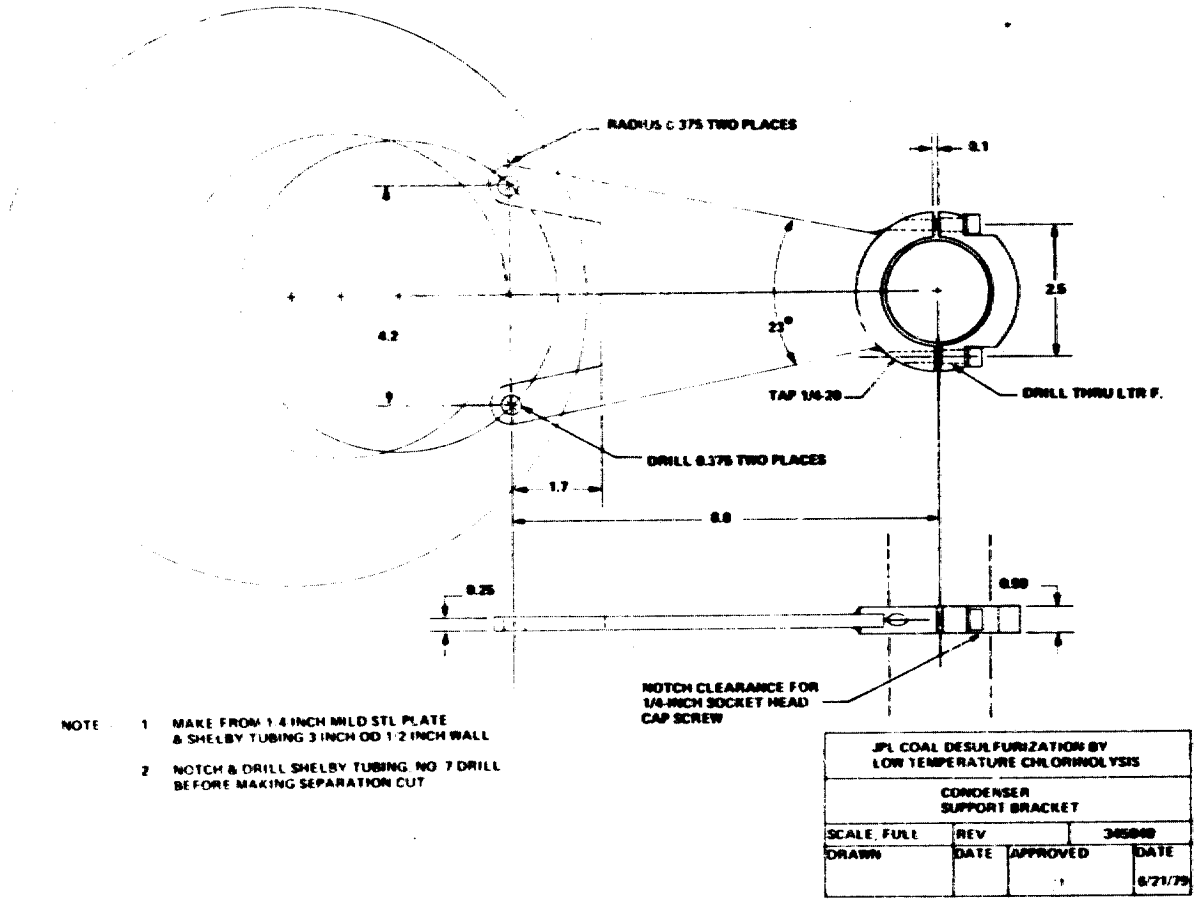


Figure 26. Condenser Support Bracket — Mini-Pilot Plant

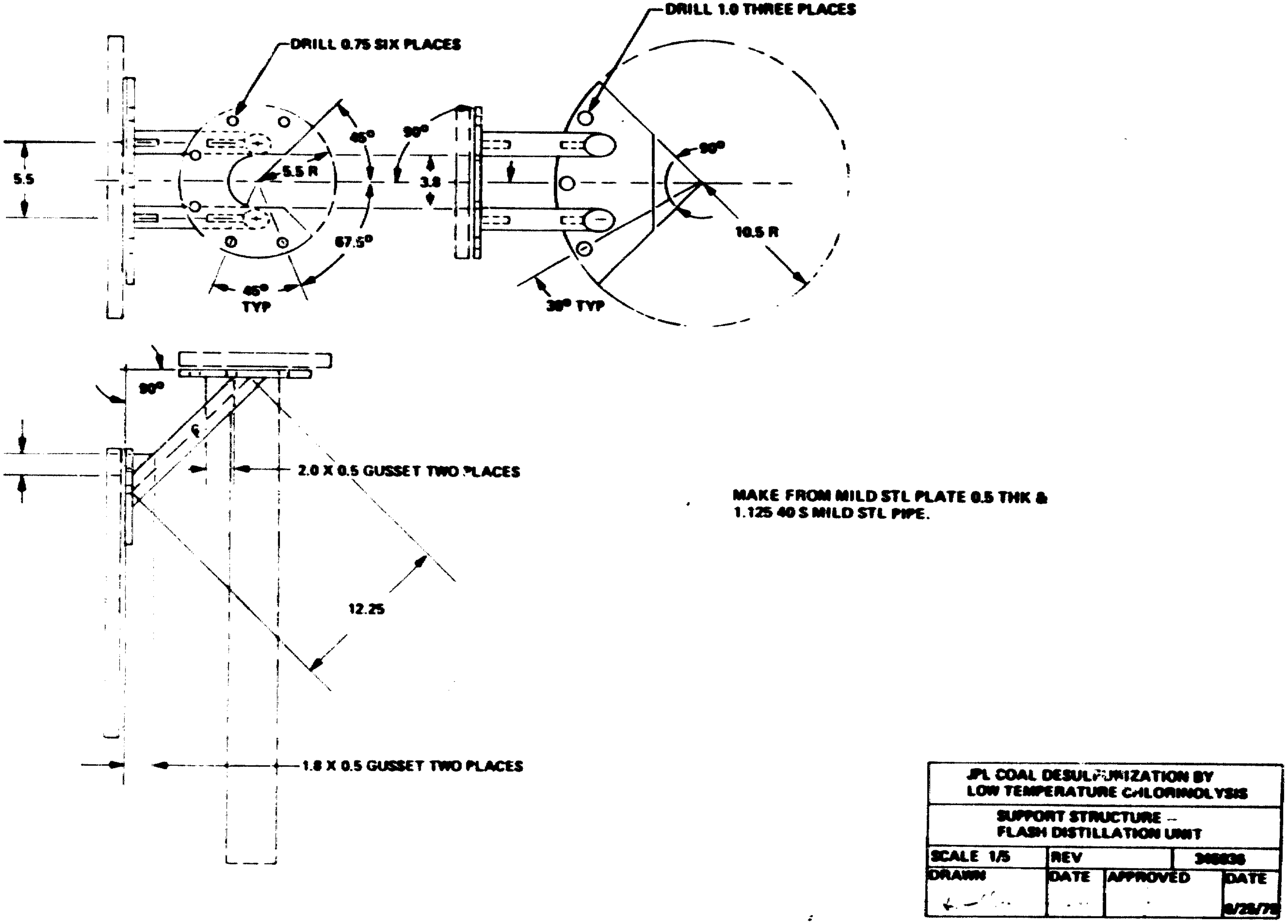


Figure 27. Support Structure-Flash Distillation Unit — Mini-Pilot Plant

to establishing steady-state operating conditions. Phasing of feed materials may be required to avoid problems of caking, etc. Mechanical operation of the equipment is described as follows:

The dry pulverized coal is fed to the chlorinator via a pressure screw feeder designed to operate up to 100 psig back-pressure. Water and solvent are transported from holding tanks to the chlorinator via metering pumps at pressures up to 100 psig. The coal slurry is continuously agitated in the chlorinator with a variable speed Chemineer agitator equipped with ten radial impellers to provide coal suspension and plug flow. 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 injected 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 heat transfer to a cooling coil to maintain temperature control.

The chlorinated coal slurry discharges to the flash distillation unit where live steam injection is used to flash the organic solvent to a condenser and condensate is collected in a solvent recovery tank. Any HCl off-gas from the condenser is collected in a 5 gallon caustic solution scrubber. With water as solvent, the flash distillation unit serves as a pass-through unit only.

The coal slurry from the flash distillation unit is discharged to a holding tank for periodic transfer to the slurry feed tank of the horizontal belt vacuum filter. As the 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 drops into a cake hopper as the belt turns over a pulley wheel.

The coal is then periodically transported to the dechlorinator coal feed hopper. The acid filtrate solution from the vacuum filter is neutralized with caustic soda before discharge from the process.

The chlorinated coal is fed by a twin-screw feeder into the dechlorinator where it is dechlorinated at temperatures of 350 to 500°C. The dechlorinator is electrically heated to provide the required temperature. Retention time of coal in the calciner is governed by the angle of inclination of the dechlorinator and the feed angle and rotational speed of flights. Off-gases consist primarily of a mixture of steam, HCl and nitrogen purge gas. A caustic scrubber will collect the HCl in the off gas. In a commercial unit, the HCl will be recovered for recycling to a Kel-chlor plant.

Coal from the dechlorinator is discharged to a product coal storage 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.

PLANNED OPERATION

A parametric investigation of continuous flow mini-pilot plant operating conditions will be carried out to determine the optimum conditions for chlorination, hydrolysis, solvent distillation, spray wash-vacuum filtration and dechlorination. A minimum of three high sulfur bituminous/sub-bituminous coals will be selected for the evaluation. The range of operating conditions include:

Chlorination

Solvents - water, methylchloroform

Solvent/coal - 2/1

Coal feed - 1 to 3 kg/hr

Chlorination (Continued)

water/coal - 0 to 0.3 (with methylchloroform)

pressure - 0 to 75 psig

temperature - 50 to 130°C

chlorine injection - 5 to 20 SCFH

coal size - 50 to +200 mesh

retention time - 30 to 120 minutes

Solvent Distillation

steam

pressure - 0 to 75 psig

temperature - 100 to 130°C

Spray Wash and Vacuum Distillation

water/coal - 1/1, 2/1

temperature - 20 to 100°C

Dechlorination

temperature - 350 to 400°C

time - 5 to 60 minutes

purge - steam, N_2

A preliminary and partial sample plan for mini-pilot plant tests is included in Table 21.

Table 21. Sample Plan for Mini-Pilot Plant Tests

Operating Conditions: Coal types (to be designated), mesh size-100 to +200 sampling at various time intervals. Solvent distillation at 100°C and addition of water equivalent to amount of solvent. Vacuum filtration of coal with spray water wash (water/coal ratio 2). Dechlorination of coal at 350°C to 400°C.

Run No.	Solvent*	Coal Feed Rate, Kg/hr.	Water/Coal	Slurry Flow Rate, Kg/hr.	Retention Time, Min.	Temp. (°C)	Press. (Psig.)	Cl_2 Feed (% Stoich.)
1	Methyl Chloroform	2	0.0	6	73	65	0	110
2	"	2	0.3	6.6	65	65	0	110
3	"	2	0.3	6.6	65	65	30	110
4	"	2	0.3	6.6	65	65	75	110
5	"	2	0.3	6.6	65	100	Optimum	110
6	"	4	0.3	13.2	27	Optimum	Optimum	110
7	Water	2	-	6	60	65	0	110
8	"	2	-	6	60	100	0	110
9	"	2	-	6	60	130	0	110
10	"	2	-	6	60	100	30	110
11	"	2	-	6	60	100	75	110
12	"	2	-	6	60	130	30	110
13	"	2	-	6	60	130	75	110
14	"	4	-	12	30	Optimum	Optimum	110

APPENDIX A

APPENDIX A

Table A-1. Operating Procedure for Chlorination Bench-Scale Batch Reactor System

A. Start-up

1. Preheat the reactor with live steam for at least thirty minutes before charge and drain the condensate.
2. Weigh the slurry tank and both solvent recovery tanks and connect the slurry tank and secondary solvent recovery tank back to the system.
3. 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 the lines below valves V5 and V6 by joining them into a loop.
4. Fill the scrubber with 10 liters of 2N sodium hydroxide solution.
5. Close the drain plug (V2) in the reactor. Make sure that O-ring is seating properly.
6. Turn on the steam generator for 20 minutes preheating period. Make certain that water line to steam generator is open (Valve V27). Thermostat setting 250°F. Keep the main steam valve (V22) closed.
7. 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.
8. Turn on recorders in the instrument panel.
9. Conduct the pressure check for leaks.
   - Turn on the pressure recorder.
   - Adjust the pressure control valve to close at 40 psi above expected operating pressure.

Table A-1. (Continued)

9. (Continued)

- Pressurize the reactor with nitrogen via chlorine line. Open the nitrogen tank valve, 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 several 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, pressure control valve is open (not sealing). Correct if necessary. Check for leaks in other places by the procedure outlined above
- Disconnect the loop connecting valves V5 and V6 and check each line for valve leaks. Reconnect back to a loop.
- Open valves V8 and V9 and check if any flow of gas occurs. This would reveal a small leak in the pressure control valve.
- Make certain that pressure release valve was adjusted to open at higher pressure than the one used during pressure checks!!
- Close valves V8 and V9. Open the pressure control valve. Check for leaks in valves V7 - V11 and in connections.
- Close the nitrogen tank valve and valves V15, 16, 17, 37, 14, and V38.

Table A-1. (Continued)

9. (Continued)

- Slowly release the pressure from the equipment via valve 10.

10. 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.
11. Close the opening and reconnect the burst diaphrapm stack.
12. Purge the equipment with nitrogen at 2-5 psi. 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.
13. Close nitrogen tank valve and valves V15, V16, V37, V14 and V38. Let the pressure equilibrate with outside.
14. Close valve V10 and pressure control valve.
15. Readjust the pressure relief valve to open at 80 psig, if readjustment is necessary.
16. Open valve V4.
17. Turn on the agitator to prescribed stirring rate (CCA 250 rpm).
18. 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.
19. Turn on the fans.

Table A-1. (Continued)

B. Operation

1. Open the steam valves (V22 and V24) 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.
2. Vent excess pressure from the reactor by opening pressure control valve and valve V10.
3. Close the steam valves V22 and V24.
4. Close valves V3, PCV and V10.
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 V24). 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 direct steam injection. 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.
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.

Table A-1. (Continued)

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 valve V3 pressure control valve and valve V10. Valve V10 should be adjusted so that gas flow through the scrubber is not too vigorous.
11. Add the prescribed amount of water to the reactor. 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.
12. Close valve V45. Disconnect the compression sprayer.
13. Reconnect the line between solvent recovery tank and valves V5 and V6.
14. Open valves V5 and V6.
15. Adjust the steam flow and temperature so that temperature inside the reactor reaches boiling point of solvent as fast as possible and vigorous solvent distillation is achieved. After most of solvent is distilled off, temperature inside the reactor will rise until the boiling point of water is reached. Temperature inside the reactor should be kept slightly below the boiling point of water (ca 95°C) for about 20-30 min. until last traces of the solvent are removed.

Table A-1. (Continued)

C. Shut-down

1. Close the steam flow (valves V22 and V24).
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 (otherwise solvent recovery tank may burst). 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.

D. 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.

Table A-1. (Continued)

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

E. Emergency Procedures

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.

      a, Steam generator failure.

         Abort the run. Repair.

      b, Excessive pressure develops inside the system.

         1. Slow down the steam rate.

         2. Abort the run. Stop the steam flow.

   B. During chlorine addition.

      a, Temperature rises beyond prescribed limits

         1. Turn on cooling water to the reactor.

         2. Slow down the rate of chlorine addition.

         3. Close the chlorine tank valve and other chlorine line valves.

Table A-1. (Continued)

b, Pressure rises beyond the prescribed limits.

Relieve the pressure by opening valves V3, Pressure Control Valve, and V10. 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 line valves. Vacate the building.

c, Chlorine leaks to outside atmosphere develop.

1. If small and easily repairable (e.g. by tightening of flange screws or fitting) repair immediately.
2. When sizable, stop chlorine flow and try to release the pressure inside the reactor by venting through a scrubber. If not possible, vacate the building until the pressure inside the reactor equilibrates with the outside. Then purge the system with nitrogen while venting through a scrubber.

APPENDIX A

Table A-2. Operating Procedure for Solvent Distillation Bench-Scale Batch Reactor System

The basic operating pattern was the same for all runs.

(1) Pressure was reduced to ambient and maintained at 1 atm throughout the distillation.

(2) 4 kg of distilled water was added to the coal-methylchloroform water slurry.

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

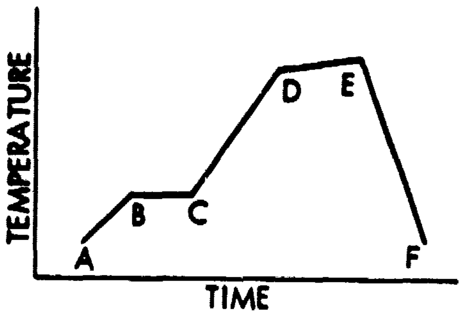
(4) The steam flow was increased to 1700-2900 g/hr (usually 2700 g/hr). The lower flow of methylchloroform vapors at these temperatures allowed the increase in steam flowrate, because the danger of coal entrainment and carryover was past.

(5) The temperature was held above 93°C for 20 to 50 minutes, typically 20 (except 5 minutes through run 10). The maximum temperature was always above 94°C, with a median temperature of 99°C. The exceptions were: run 25; 89°C; and run 39, 83°C. The purpose of this temperature hold was to remove the methylchloroform dissolved in the slurry water and that portion retained in the coal.

(6) The reactor was allowed to cool, usually with the aid of a cooling water coil, to 70°C or below. At this temperature the slurry wouldn't splatter as it was drained.

Table A-2. (Continued)

Temperature Time Profile:



A - commence steam heating

B - begin azeotropic plateau

C - end azeotropic plateau

D - 200°F = 93°C

E - steam off/cooling coil on

F - drain reactor

The entire distillation, A-F, required about 170 min, if it started at the usual initial temperature of 46°C. Runs 7 and 25, which commenced at 62°C, required 88 and 148 min respectively.

The azeotropic distillation, B-C, took 20 min when it was observed. Actual temperatures were 65.5, 67, 64.5, 63.3, and 63.3°C in runs 7, 19, 21, 28, and 31 respectively.

The cooling time, E-F, ranged from 15 to 89 min (runs 38 and 23) but was often 20 to 40 min. The slurry was easily handled at the drain temperature, usually 48°-68°C, but was as low as 24°C.

METHYLCHLOROFORM CONTENT OF COAL FILTRATE

The water off the coal was analyzed by gas chromatography at JPL.

Run 31: none (methylchloroform) detected

Run 43: 0.05%, probably 0.02% methylchloroform

This compares with the solubility of methylchloroform in water, 0.5 at 20°C. The GC detection limit is ~0.01%.

METHYLCHLOROFORM RECOVERY

The reactor charge was always 4,000g of methylchloroform. Typically 5-10% of the slurry was removed by sampling during chlorination, which removed 200-400g of methylchloroform. From 2154g to 3802g was recovered by distillation, averaging 3063g. This is 58 to 97% recovery, averaging 83%, in the distillate tank.

APPENDIX A

Table A-3. Operating Procedure for Coal Filtration and Wash of Bench-Scale Batch Reactor System

Operation Summary

During runs 1 through 27 the filter bed was a 200 mesh stainless steel screen supported by a coarse screen. For run 28 and successive runs, the 200 mesh screen was replaced by a 325 mesh screen, and that covered with a single piece of Whatman No. 1 filter paper. The reactor contents were poured on the filter. After the free water was removed, a half-inch coal cake remained.

For runs 36 through 44 the dirty rinse water from the reactor cavity, which coal content was added to the bulk coal, was the first wash of the filter cake. Four kg of distilled water, sprayed uniformly over the face of the cake provided the final wash in all cases. The suction was provided by a blower capable of developing 35-inches water column suction (1-1/4 psi). After about 2/3 to 4 hours of vacuum treatment, the filter cake was dry by this technique. On four runs, the analyzed moisture was 40 wt. %, 35 wt. %, 35.5 wt. % and 23.5 wt. %. On another run, the moisture content was 47.7 wt. %.

Table A-3. (Continued)

OPERATING PROCEDURE

I. FILTRATION

1. Clean and weigh the filtrate recovery tank and reinstall it.
2. Clean and reinstall the empty sodium bicarbonate 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. Disconnect the insulated pipe section feeding into the lid of the vacuum filter.
6. Lift off the lid and set it on the floor as the slack in the thermocouple cables will allow.
7. Place the 1/2-inch wide asbestos gasket on the inside lip in the vacuum filter.

   NOTE: Asbestos gaskets are delicate. Moistening them before use but after placement assures a better seal.
8. The coal cake cage consists of three screens:

   A is the smaller fine mesh screen with a rim T-shaped in cross-section.

   B is the larger fine mesh screen with the L-shaped rim.

   C is the coarse mesh support screen.

   Seat screen "C" on the 1/2" lip gasket and place the smaller inch wide gasket inside it. Seat screen "A" inside screen "C".

   NOTE: The fine screens themselves are delicate. Whenever they are filled with coal, the support screen must be beneath them and in contact.

Table A-3. (Continued)

9. Connect the intermittent line from the vent fitting of V36 to the filtrate recovery tank and close V44.
10. Turn on the exhaust blower. Pour the slurry onto screen "A" while closing V36 to the extent necessary to remove water from the coal slurry.
11. 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.
12. Maintain suction until the cake is dry, but no longer than 20 minutes.

APPENDIX A

Table A-4. Dechlorination Procedure
Bench-Scale Batch Reactor System

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 940g. (2.07 lb.) of sodium bicarbonate ($NaHCO_3$) 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.

SET-UP

1. Remove the pipe cap (with its associated fittings) from the south end of the furnace. This involves:
   a. Removing the conduit clamp which holds the tee against the U-channel brace.
   b. Unplugging the thermocouple.
2. The cone puller is a five foot tool made from 1/4 inch tube with hooked ends. Use it to remove the near-end coal containment cone.
3. Close the open end of the pipe with a piece of aluminum foil.
4. Determine the moisture content of coal to be dechlorinated.

Table A-4. (Continued)

PREHEAT

1. Close toggle valve 2 (which controls the nitrogen flow to the now-disconnected southern pipe cap) and open toggle valve 1 (which feeds nitrogen into the furnace exhaust pipe).
2. Start the nitrogen flowing at 30 SCFH.
3. Adjust the furnace temperature set points to 400°C.
4. Turn on the furnace at the main breaker.
5. Wait for the furnace to equilibrate. The lining 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 linings reach the set temperature.
6. Turn on the tube rotation motor and set the speed to "20" (4 RPM) about 10 minutes before the coal is to be loaded.

COAL LOADING-PROVISIONAL PROCEDURE

1. 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.
2. Determine the moisture content of the coal before use.
3. Pack the coal into the half-cylinder loader.
4. Stop the furnace tube from turning and remove the aluminum foil.
5. Insert the loader into the furnace until the crossbar handle is even with the U-channel brace. This should also be about the point of contact with the coal containment cone.

Table A-4. (Continued)

6. Invert the loader and remove it after the coal has fallen completely out. Note the time.
7. Note any HCl gas, steam evolution, nitrogen flow, and any entrainment of the dry coal.
8. Use the cone puller to replace the southern coal containment cone.
9. Screw the pipe cap onto the furnace tube and reconnect the associated pieces. Close Toggle Valve 1 and open Toggle Valve 2.
10. Turn on the multipoint thermocouple recorder. Set the chart speed on slow.

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).

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. Close Toggle Valve 2, open Toggle Valve 1.
6. Remove the pipe cap with its associated fittings.
7. Remove the coal containment cone.

Table A-4. (Continued)

8. Remove the coal with the scraper. Collect it in the stainless steel beaker into which constant flow of nitrogen is maintained via 1/4 inch stainless steel tubing inserted close to the bottom of the beaker. Nitrogen will minimize smoldering of hot coal.

9. Cool the coal to room temperature while maintaining the nitrogen flow into the beaker.

10. Close the open end of the pipe with aluminum foil and let it cool for another 30 min while keeping the nitrogen flow at 10 SCFM.

11. Shut off the nitrogen flow to the pipe.

12. Remove the scrubber tank from the system. Measure the solution volume and take a sample of about 250 ml for titration.

13. Drain the scrubber tank system and rinse it.

NOTES AND EMERGENCY PROCEDURES

1. Controls on the furnace may malfunction and furnace can overheat. Check periodically the control lights, 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. <u>Maintain the nitrogen flow</u> through the pipe while loading and unloading hot coal. Otherwise the coal may catch on fire or explode.

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

Table A-4. (Continued)

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 container. Put the fire down with CO_2 fire extinguisher.