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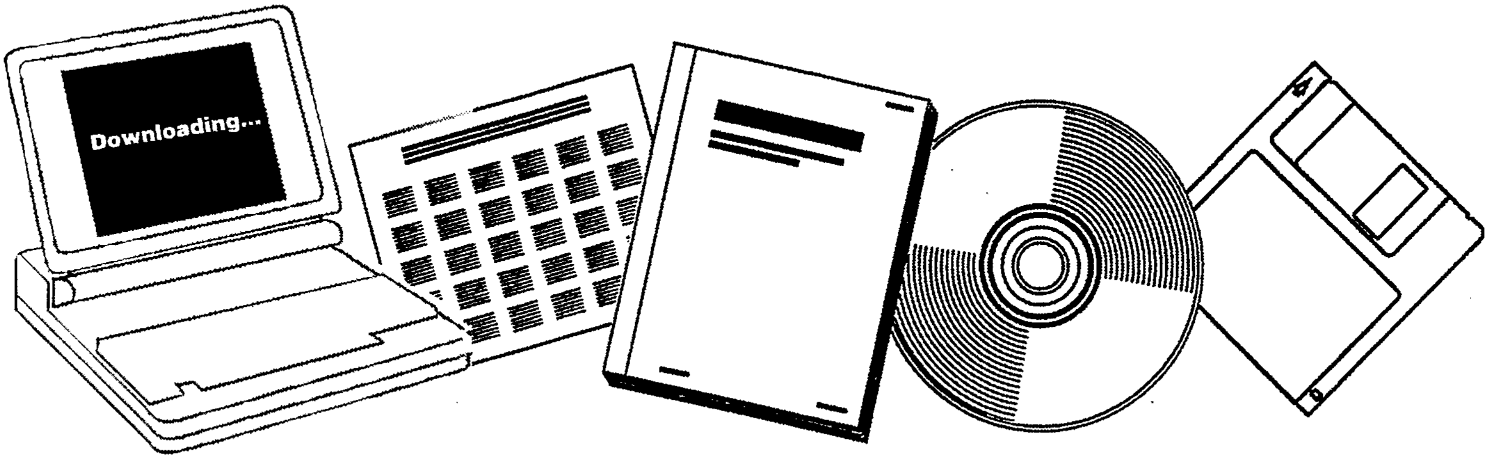
# TECHNICAL EVALUATION SERVICES COAL CONVERSION AND UTILIZATION-LIQUEFACTION. RESEARCH AND DEVELOPMENT REPORT NO. 82, INTERIM REPORT NO. 5

PARSONS (RALPH M.) CO., PASADENA, CALIF

JUL 1976



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# TECHNICAL EVALUATION SERVICES COAL CONVERSION AND UTILIZATION - LIQUEFACTION

## PROJECT LIGNITE (PDU - STAGE)

RESEARCH AND DEVELOPMENT REPORT NO. 82
INTERIM REPORT NO. 5

July 1976

Under Contract No. E(49-18)-1234

*Prepared for*
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
WASHINGTON, D. C. 20545

*Prepared by:*
THE RALPH M. PARSONS COMPANY
100 West Walnut Street
Pasadena, California 91124

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# ABSTRACT

This report presents an evaluation of Project Lignite activities as performed at the University of North Dakota (UND), Grand Forks, North Dakota under ERDA Contract E(49-18)-1224. This evaluation was performed by The Ralph M. Parsons Company under Modification Number 6 of ERDA Contract E(49-18)-1234.

The evaluation includes a discussion and analysis of PDU performance to date and summarizes the results of supporting laboratory studies. Also included are an outline of future work planned, identification of potential problems, prospects for commercial operability, an assessment of SRL economics, and recommendations regarding future activities and programs to achieve ERDA objectives with existing facilities at UND.

Currently, the PDU is operating at baseline conditions processing 50 lbs per hour of North Dakota lignite and producing about 58% SRL product on a MAF basis. The liquefaction products are being used for startup of the solid-liquid separations unit.

Future PDU activities are aimed at completion of process variable studies. These studies are scheduled for the latter part of this year so that the unit can achieve an orderly shutdown by termination of contract in March 1977.

Recommendations are given by Parsons on the PDU activities needed to obtain adequate data for scale-up and evaluation of the economic potential of the SRL process.

# SECTION 1

# INTRODUCTION

In accordance with Modification No. 6 to Energy Research and Development Administration (ERDA) Contract E(49-18)-1234, Technical Evaluation Services, we have prepared a technical and economic review of Project Lignite. This review was based on participation in project Advisory Committee Meetings, visits to the process development unit (PDU) operations, and review of Project Lignite reports.

The objectives of the work performed by The Ralph M. Parsons Company are as follows:

(1) Summarize work required as defined by tasks and schedule in the University of North Dakota (UND) contract.

(2) List the work accomplished and in progress by task.

(3) Summarize conclusions from existing data generated on the UND contract.

(4) Evaluate the SRL process from both technical and economic standpoints.

(5) Outline the future work planned and recommend the most effective experimental program to provide adequate data to scale-up the SRL process and evaluate the economic potential of the process. Include comments regarding additional data required to determine operability and scale-up feasibility.

(6) Comment on prospects for practical commercial operability.

(7) Comment on the assumptions made and results obtained by the UND Economics Department in its evaluation of a commercial SRL plant.

The tasks and schedule included in the UND contract were initiated on March 28, 1972 and the program was scheduled to run for a five year period ending March 1977.

We understand that ERDA has evaluated the current project status and funding is being provided to carry the project to the March, 1977 date in order to allow sufficient time for the proposed process development unit (PDU) test program.

We consider the operation of the 50 pound per hour PDU and the technological and commercial potential assessments to be the most important parts of the current program. The laboratory autoclave work provides background support data.

The Project Lignite objectives are defined by the following UND paragraphs which are excerpts from the UND Contract No. E (49-18)-1224.

## 1.1 OBJECTIVE

Work to be performed under this contract shall be directed toward development of one or more processes for upgrading typical Northern Great Plains lignite into fuel gas, liquid fuels, chemicals, and related products.

## 1.2 STATEMENT OF WORK

The contractor will perform research and development work to determine technologically obtainable and practical economic yields of useful products from treatment of lignite. The specific development projects will be small-scale continuous operation of steps in the overall refinery scheme that need technical clarification before large-scale testing. The current project is intended to culminate in a design of a pilot plant for demonstration of the refinery concept if approved in advance by the Contracting Officer.

### 1.2.1 PHASE I

Investigation of the process for solubilizing coal and recovering a solid refined product. The work will include methods of dissolving lignite in the presence of hydrogen, carbon monoxide, and mixtures of carbon monoxide and steam.

### 1.2.2 PHASE II

Carbonization studies of typical lignite to determine yields of liquids, solids, and gas. Methods will be developed for upgrading each of the major products.

### 1.2.3 PHASE III

Hydrogenation-distillation studies on extracts obtained from Phase I will be made using various catalysts to determine the effect of catalysts on yield and products obtained.

### 1.2.4 PHASE IV

The contractor will conduct studies on continuous low-pressure hydrogenation of lignite to determine product distribution and yield under a range of operating conditions.

## 1.3 REPORT ORGANIZATION

This report includes an evaluation of the Project Lignite activities conducted to date, recommendations for improvements as appropriate, and a recommended future experimental program to achieve ERDA's Project Lignite objectives.

A summary of the material contained in this report is presented in Section 2. Recommendations for future program work are given in Section 3. Section 4 provides a review of the current status of Project Lignite activities and an analysis of the test data on Phases I, II, III, and IV. The SRL Process is evaluated in Section 5 from a technical and economic point of view.

Appendix A includes the results of metallurgical tests on PDU equipment failures performed by The Ralph M. Parsons Company. Appendix B includes a compilation of the results of Project Lignite activities to date as published in the Project Lignite progress reports.

# SECTION 2

# SUMMARY AND CONCLUSIONS

## 2.1 SUMMARY OF ALL ACTIVITIES TO DATE

The Project Lignite work to date has been aimed at achieving successful operation of the PDU and development of adequate data to justify the design of a pilot plant; also to provide a basis for evaluation of commercial potential. Laboratory studies using a batch autoclave have been completed and the results of these studies plus recommendations from Pittsburg and Midway Coal Mining Company (P&M) have led to the design, construction and operation of a PDU. Operation of the PDU was begun during the first quarter of calendar 1975.

The PDU was designed to process 50 lbs/hr of lignite at 30% moisture to produce solvent refined lignite (SRL). The unit has been described in detail in ERDA report FE-1224-T-1 dated September, 1974. A block flow diagram and the projected material balance used for the PDU design are shown in Figure 1 and Table 1 included in this section.

As of June 1976, the PDU has completed approximately 20 runs, each consisting of about one continuous week of operation without shutdown. During the period from initial startup in January 1975 to June 1976, a total of about 850 hours of PDU operation has been logged in. The laboratory studies conducted in support of PDU operation utilized a batch autoclave. Since 1972 approximately 300 runs were made.

During 1975, numerous mechanical equipment problems were encountered and corrected on the PDU. The major problem during this period was repeated failure of stainless steel components. For example, the preheater coil failed on three separate occasions and was replaced with a new one each time. Metallurgical tests performed under Parsons direction indicated that the failure mechanism was due to chloride stress corrosion of the stainless steel (see Appendix A). We recommended that for the benefit of continuity of PDU operations and until the failure mechanism was fully understood, all high pressure components subjected to the chloride attack be replaced by Incoloy 800. New components fabricated of this material were installed in January of 1976. Since that time no equipment failures due to chloride attack have been observed. In general, the PDU is now considered mechanically sound.

Since the installation of the new Incoloy 800 equipment, the PDU has logged in approximately 11 runs of about 1 week duration each for a total of about 500 hours. Current PDU operations objectives are to achieve solvent balance with nominal "baseline" conditions set at 2500 psig, 750°F preheater outlet, 1.4 liquid hourly space velocity and 334 gas hourly space velocity, 1.9/1 weight ratio of solvent to lignite. For these liquefaction conditions, only one of two 20 foot by 4 inch diameter dissolver reactors is being employed.

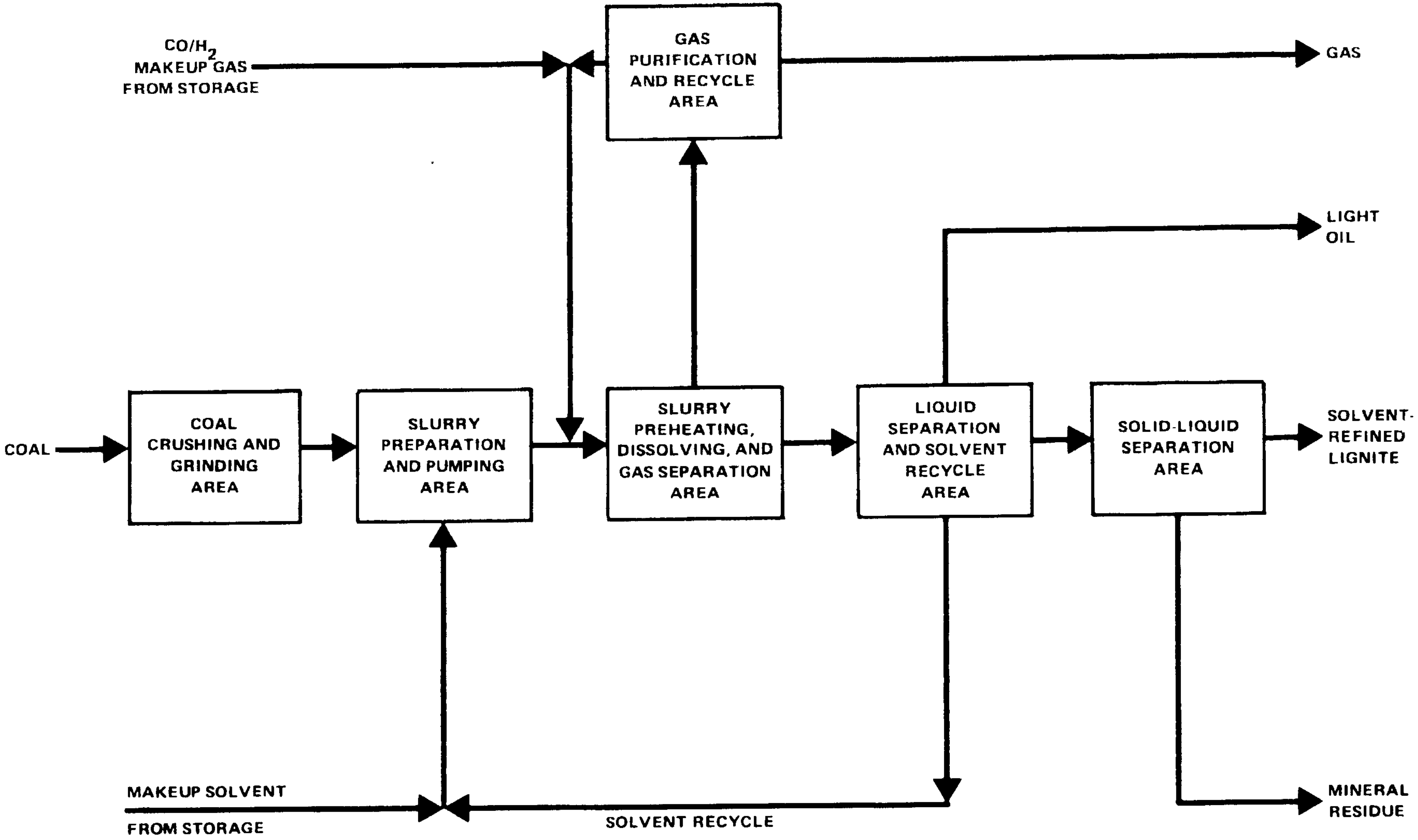


Figure 1 - PDU Block Flow Diagram

Table 1 - PDU Projected Material Balance

Basis: Moisture, Ash Free Lignite: 31.00 lb/hr
Moisture : 15.50 lb/hr
Ash : 3.50 lb/hr
Total : 50.00 lb/hr

| IN | lb/hr |
|---|---|
| Coal and Solvent | 143.00 |
| Hydrogen and Carbon monoxide | 18.39 |
|  | 161.39 |

| OUT | lb/hr |
|---|---|
| Gas to Recycle | 5.68 |
| Mineral Residue | 5.98 |
| SRL (Product) | 14.86[a] |
| Light Oil | 0.41 |
| Water | 5.16 |
| Wash Solvent | 2.45 |
| Process Solvent | 93.00 |
| Heavy Oil | 2.00 (add to SRL) |
| Vapor to Thermal oxidizer | 31.85 |
|  | 161.39 |

[a]

|  |  |
|---|---|
| 14.34 | SRL |
| 0.42 | Uncoverted Coal |
| 0.10 | Ash |
| 14.86 | Product |
| 2.00 | Heavy Oil |
| 16.86 | Product |

Data generated from the PDU have been utilized to guide the program from initial startup, through shakedown runs, and currently, to select process conditions for achieving solvent balance. For example, at baseline conditions used in run M-5C, over 90% conversion was obtained with a 58 wt% yield of SRL. This data was published in a paper presented by Max Souby at the Gulf Coast Lignite Conference held June 2, 3, and 4, 1976 at the University of Texas at Austin. These results closely parallel the projected material balance in Table 1.

Based on PDU operations over the last several months, we judge the PDU equipment as designed, adequate to achieve the intended results.

PDU operations are now aimed at gathering sufficient data for completing the heat and material balance around the liquefaction unit excluding the solid-liquid separations unit. PDU operations are routine with a better than 90% service factor.

In regard to the quality and quantity of the data generated by the PDU, we cannot provide comments at this time since there have been no publication of PDU data in any of the progress reports received to date. We will evaluate the PDU data when it is available and as authorized by ERDA.

Autoclave runs made as part of laboratory studies in support of PDU operations are complete. Approximately 200 runs were used to select the PDU start-up solvent, effects of recycle, liquefaction processing conditions, and effects of coal feed pretreatment and storage conditions. Also studied in the laboratory was upgrading of SRL by catalytic hydrogenation. These data were accumulated from about 90 autoclave runs conducted by the UND Chemistry Department under subcontract from Project Lignite. These runs examined effects of catalyst type, pressure, temperature, and solvent. The results indicated that conditions for SRL upgrading to low sulfur liquid fuels were 2500 psig, tetralin solvent, presulfided HT-100 catalyst supplied by Harshaw, 840°F and a reaction time of two hours. No further laboratory tests are contemplated at this time.

## 2.2 CONCLUSIONS FROM THE DATA GENERATED

### 2.2.1 PDU

The PDU as designed is capable of processing 50 lbs/hr of lignite through the liquefaction train, producing about 55 to 58 wt% SRL on a MAF basis. This is similar to the design basis as selected from laboratory data and P & M recommendations. At baseline conditions of 2500 psig, 750°F preheater outlet, 1.4 liquid and 334 gaseous hourly space velocities, respectively, and 1.9/1 solvent to coal weight ratio, the PDU is reportedly able to achieve solvent balance. Detailed material balance data is currently being compiled by Project Lignite for publication. These conditions will be used for generating sufficient vacuum bottoms for shakedown operations for the solid-liquid separations unit.

### 2.2.2 LABORATORY STUDIES

The autoclave work performed during the past 4 years, consisting of about 200 runs for Phase I and about 100 runs for the remaining Phases, yielded the following results:

A. Phase I - Solubilizing of Coal

1. Coal Pretreatment Studies.

- Effect of cation addition
- Effect of dehydration
- Effect of phenol extraction

All of these tests indicated that pretreatment was either ineffective or produced undesirable effects.

2. Evaluation of Solvents. These studies indicated that carbon black feedstock (FS-120) was best for PDU startup.

3. Solvent Recycle Tests. These studies indicated that, after as many as five passes, no evidence was observed of solvent degradation.

4. Lignite Storage Tests. These studies indicated that, after 70 weeks, air-free environments showed no effect on lignite liquefaction properties. Air storage did show a slight decrease in reactivity.

5. Effects of Reducing Conditions. These tests indicated that CO gave the best results but that syngas (50% $H_2$/50% CO) gave nearly the same results. The syngas was selected since recovery and use of pure CO for PDU operation are impractical.

6. Miscellaneous Parameters. Filtration temperature of 400°F was selected for laboratory preparation of SRL samples to facilitate solids-separations without undesirable solvent flashing.

Reaction time for the autoclave work was selected at 30 minutes. Longer times reduced yields of liquid products.

Particle size of lignite was selected at -100 mesh for laboratory studies. Tests made at larger particle sizes showed no significant effect on liquefaction results and directionally indicated that -0.25 inch particles could be used for PDU operation.

B. Phase II - Carbonization of Lignite

Autoclave runs made by precarbonizing lignite prior to liquefaction indicated that this pretreatment impaired the lignite reactivity. No further work is planned for this phase.

C. Phase III - SRL Upgrading

Autoclave tests conducted by the UND Chemistry Department under subcontract to Project Lignite were aimed at hydrogenation of SRL to premium low sulfur liquid fuels. The study results indicated that overall conversion and denitrogenation was best with presulfided Ni-Mo-$Al_2O_3$ catalyst, using tetralin solvent, 2500 psig hydrogen pressure 700°F, and two hours reaction time in the autoclave. At these conditions, conversions of SRL of 88% to distillable products were acheived.

### D. Phase IV - Direct Hydrogenation of Lignite

Direct hydrogenation involves contacting pulverized lignite with hydrogenation gas in the presence of a catalyst A few exploratory runs were made with the autoclave in a preliminary look at effects of catalyst and solvent. The results were inconclusive and no further work is currently planned.

## 2.3 OUTLINE OF FUTURE WORK PLANNED

Future work on Project Lignite is aimed primarily at completion of PDU operations. Some batch autoclave work will be carried out in support of PDU operations as required. The following is a summary outline of runs to complete in the scheduled PDU program which will close out in December to permit an orderly shutdown of the project by its termination date of March 1977, subject to an ERDA decision to extend the project period and funding:

### 2.3.1 BASELINE RUNS FOR PRODUCTION OF SRL PRODUCT

- Includes operation of the solids-liquid separations unit.

### 2.3.2 PARAMETER RUNS

- Solvent/coal ratio (2 runs)
- Gas Composition (6 runs)
- Pressure (4 runs)
- Temperature (3 runs)
- Liquid and gas hourly space velocities (6 runs)
- Gas/solvent ratio (2 runs)
- Coal variety (14 runs)

Each of the above runs is scheduled for about 2 days continuous operation.

## 2.4 IDENTIFICATION OF POTENTIAL PROBLEMS AND PROGRAM GAPS

One of the primary potential problem areas in the current PDU program is production of SRL. Since the solids-separations unit is not yet operational determining baseline conditions and performing parameter studies will depend for the most part on analysis of the vacuum tower bottoms or spot inspection of SRL samples from laboratory filtration.

Another potential problem is the lack of data from gas recycle operation. It would be important to assess the impact of component buildup in the recycle loop as it effects the projected gas treatment requirements for a commercial size plant.

In reviewing the current PDU program, there are no provisions for operations on a 7 day basis. Startup and shutdown each week could contribute to operability problems which would perhaps not occur on a steady state production run of, say, 4 weeks duration.

## 2.5 PROSPECTS FOR PRACTICAL COMMERCIAL OPERABILITY

The SRL process must prove out the following process steps from both a technical and economic standpoint in order to achieve good prospects for practical commercial operability:

(1) Coal/solvent slurry preparation and pumping and preheating.

(2) Coal dissolving and solid-liquid separation.

(3) Achieving an acceptable SRL product quality to meet existing specifications for such components as ash, sulfur, and nitrogen and functional product performance.

## 2.6 ADDITIONAL DATA REQUIRED

To determine operability and scale-up feasibility, additional data are scheduled to be developed during the PDU parameter study to be conducted during the latter part of the PDU program as discussed in Subsection 2.3.2

## 2.7 ECONOMICS

An evaluation of UND's economics for a 30,000 T/D SRL plant was made. The results of the evaluation indicated that the costs estimated for Unit 12 - coal liquefaction and filtration, should be increased from $41 million estimated by UND, to about $45 million based on mid-1973 major equipment costs. This is based on recent work we have done on large scale liquefaction facilities using large diameter heavy wall vessels.

Our evaluation also indicated that if the UND estimate of oxygen requirements is correct, then the oxygen plant cost should be increased from $23 million to about $35 million. This is because the oxygen plant costs in OCR R&D Report No. 82 Interim Report No.1 are based on the largest plant available. Therefore multiple plants will be required to handle the increased capacity factor of 2.83 estimated by UND.

Regarding the plant total cost, we recommend an escalation factor for the period mid 1973 to mid 1975 which is 20% greater than that used by UND. This would increase the UND total plant cost from $460 million to approximately $615 million including the increases estimated for Unit 12 and the oxygen plant.

In the development of product selling price, we would estimate for planning purposes, about $1.90/MMBTU for mid-1975 in contrast to the $1.53/MMBTU by UND based on a 12% discounted cash flow rate of return (DCF). In addition to the increase in total plant cost, the selling price increase was a result of economic factors as described below. For example, for this preliminary evaluation, we recommend a four year construction schedule, annual maintenance cost at 4.0% of fixed capital, plant overhead and general expenses of 60% of total labor, annual property taxes and insurance of 2.75% of fixed capital. Also state and federal income taxes of 52%, and investment tax credit of 10% would be recommended.

Analysis of the SRL economics indicates that the liquefaction section (Unit 12), has the most influence on investment cost and is also the most susceptible to process improvement. This is based on the Unit 12 major equipment cost which is estimated at about 43% of the total plant major equipment for a commercial SRL plant processing 30,000 T/D of lignite.

# SECTION 3

# RECOMMENDATIONS

The objective of ERDA's Division of Coal Conversion and Utilization for Project Lignite is to obtain adequate data for scale-up and evaluation of the economic potential of the SRL process. The following is our recommended program for achieving ERDA's objective:

## 3.1 PDU BASELINE OPERATIONS

Operate the PDU at the following preliminary "baseline" conditions using one 20 foot long reactor:

(1) 750°F preheater coil outlet temperature

(2) 2500 psig dissolver pressure

(3) 50% CO/50% $H_2$ syngas

(4) Solvent to coal weight ratio of 1.9/1

(5) Liquid hourly space velocity of 1.4

(6) Gas hourly space velocity of 334

## 3.2 HEAT AND MATERIAL BALANCE

Through heat and material balances, determine SRL conversion, product yields, and solvent balance.

## 3.3 PDU PRODUCTION RUN

Start a production run for about four weeks continuous operation in order to gain experience with the unit and collect operating data and product samples. During the production run, determine the following:

(1) Complete heat and material balances

(2) Conversion

(3) Hydrogen consumption

(4) Product yields

(5) Product properties

(6) Heat duties around the dissolver

## 3.4 MATERIAL PROPERTIES

(1) ASTM distillation of liquid products (vacuum or atmospheric)

(2) Viscosities; as SSU or kinematic measurement

(3) Gravities

(4) Penetration: If material not suitable for viscosity measurement

(5) Acid and/or base numbers

(6) Pour point

(7) Elemental analyses

(8) Heat capacities

(9) Equilibrium K values

(10) Trace product yields: Such as HCN, $NH_3$ COS, $CS_2$, $H_2CO_2$, and $H_2CO$ as an example

(11) Trace metal and organometallics present in the liquid products

## 3.5 ECONOMIC APPRAISAL

Utilizing the data from the production run, develop a revised economic appraisal of the SRL process potential on a commercial scale of 30,000 T/D of lignite feed.

## 3.6 PDU OPERATIONS

We recommend that the PDU test program be operated on a 7 day a week, shift schedule. This will assist in expediting the planned program, minimize downtime from existing weekly startup and shutdown operations, and avoid mechanical and process complications caused by cycling the unit weekly through startup and shutdown.

## 3.7 PROCESS VARIABLE STUDY

Following the production run, a process variable study should be conducted to assess the impact of processing conditions on the economic appraisal. The following key factors are most susceptible to process improvement with the greatest influence on economics.

(1) Dissolver pressure

(2) Dissolver temperature

(3) Liquid and gas hourly space velocity

(4) Solvent/coal ratio

(5) Syngas composition

(6) Gas/solvent ratio

(7) Coal feed variety

## 3.8 METALLURGICAL TESTS

Concurrent with the above work, metallurgical tests should be conducted to determine materials of construction requirements for the liquefaction equipment in a commercial plant. Specifically, it must be determined if 316 stainless steel is satisfactory as has been used at the Wilsonville SRC facilities. Alternatively do special alloys need to be employed such as Incoloy 800 now in use in the PDU? Supporting experiments should be carefully performed to determine the cause of the recent PDU experience with chloride stress corrosion of stainless steel components. This will permit an assessment of the economic impact of this occurrence on planned tests in high-cost pilot plant facilities as well as the commercial viability of the SRL process.

## 3.9 PDU PROGRAM EXTENSION

The current PDU program is specifically aimed at completing PDU operations with the lignite liquefaction section. In order to fully evaluate the technical and economic viability of a commercial scale SRL process, we recommend that the Project Lignite PDU program be extended to include both solids liquid separations and SRL hydrogenation. This will provide operating data and subsequent evaluation of these two operating steps. The program extension will permit functional testing of the products from the SRL process.

## 3.10 PLANNED EXPERIMENTS

We recommend that Project Lignite develop a carefully planned experimental design for the test work to ensure the most effective utilization of program schedule and funds. It is of primary importance that data reduction and correlation procedures be defined at an early stage in the test program.

## 3.11 PILOT PLANT OPERATIONS

We recommend that following the completion of the PDU program, and subject to confirmation of potential commercial viability the SRL process be evaluated on a pilot plant scale at existing facilities such as Wilsonville or Tacoma.

Subject to confirmation at established check points, we strongly advise that the above recommendations be aggressively pursued to completion in order to achieve the full development of the Project Lignite program.

# SECTION 4

# STATUS AND ANALYSIS

We have reviewed the data developed under Project Lignite since the start of the ERDA contract by task. This section summarizes the status and analysis of the work accomplished in Phases I, II, III, and IV. For reference we have included the details of the results of metallurgical tests on PDU equipment failures in Appendix A and PDU operations and laboratory studies in Appendix B.

## 4.1 PHASE I LIGNITE SOLUBILIZATION

### 4.1.1 PDU OPERATION

The PDU was designed to process 50 lbs/hr of lignite at 30% moisture to produce a solid product of solvent refined lignite (SRL). The unit has been described in detail in ERDA Report FE-1224-T-1 dated September, 1974. A block flow diagram and projected material balance used for the PDU design are shown in Figure 1 and Table 1, respectively, included in Section 2. PDU startup was in early 1975. The history of PDU operations is summarized in Table 2.

During 1975, many mechanical problems were encountered which prevented achieving steady state operation.

Recently the PDU has corrected the mechanical problems and is now operating at baseline conditions of 2500 psig, 750°F preheater outlet temperature, 1.4 liquid and 334 gaseous hourly space velocities respectively, 1.9/1 solvent to coal ratio. At these conditions only one of the two 20 foot long by 4 inch diameter dissolver reactors is being used. Solvent balance has been achieved and vacuum bottoms is being accumulated for shakedown runs on the solids-liquid separation unit for production of SRL.

From January 1975 to June 1976, the PDU has made approximately 20 runs each, about one week of continuous operation. A total of about 850 hours of PDU operation has been logged in. Current operations are routine and parameter studies are scheduled to commence in the near future.

Preliminary results from the PDU indicate the unit is capable of achieving 55 to 58% conversion to SRL on a MAF basis as predicted by the laboratory studies and consistent with the design basis.

### 4.1.2 LABORATORY STUDIES

A series of laboratory studies was conducted with a batch autoclave in support of the PDU operations. These studies were made over the past 4 years and represented about 200 runs. The following summarizes the results of the studies as reported by UND. When it was felt that the data warranted it, we developed correlations and performed data analysis.

Table 2 - Status of PDU Operations

| Period | PDU Operations | Purpose | Remarks |
|---|---|---|---|
| Jan/Feb/Mar, 1975 | Shakedown Runs | Train Operators | No Coal Feed |
| Apr/May/June, 1975 | Shakedown Runs | Train Operators | First and Second Preheater Coil Failure |
| July/Aug/Sept, 1975 | Shakedown Runs | Checkout of Mechanical Equipment | Third Preheater Coil Failure |
| Oct/Nov/Dec, 1975 Jan, 1976 | New equipment installations | Installation of Incoloy 800 preheater coil and dissolvers | Unit down |
| Feb/Mar/April/ May, 1976 | Shakedown Runs | Checkout of New Equipment | Insufficient solvent recovery. No material balance. |
| June, 1976 | Baseline Conditions Selected | Collect Product for Solid/Liquid Separations Unit Startup | Solvent balance[a] achieved. Data being collected to make complete heat and material balance. |

[a] Baseline conditions at solvent balance: 2,500 psig, 750°F preheater coil outlet temperature, 1.9/1 wt ratio solvent to coal, 1.4 liquid hourly space velocity, 334 gaseous hourly space velocity, syn gas (50% $H_2$/50% CO), 1-20 foot dissolver vessel.

## A. Effect of Cation Addition

The test results indicated that naturally occurring cations present in the recently mined lignite appear to provide enough catalytic action to give sufficiently high yields of liquid products. Addition of cations did not indicate significant improvements in reactivity for production of desired liquid products.

## B. Evaluation of Liquefaction Solvents

The results of the solvent evaluation study indicated that carbon black feedstock (FS-120) was best for PDU startup operation based on performance, availability, and cost.

## C. Solvent Recycle Series

One of the key elements in determining the viability of the SRL process is the suitability of the solvent used in the process for recycle in order to provide for a self sustaining operation. Therefore, prior to PDU operation, a series of batch autoclave runs was made in which solvent used in the run was recovered and recycled for subsequent tests to simulate solvent recycle.

For test purposes, recycle solvent was recovered by distillation from the solvent-slurry mixtures from each run. The recovered solvent was collected from a number of runs at the same conditions in order to provide sufficient solvent for subsequent tests. Table 3 illustrates the number of runs made, the number of solvent passes for each run, and the reference to the Project Lignite Progress Report where the data were tabulated.

The data referenced in Table 3 were analyzed in order to determine if solvent recycle, as performed in the series of batch tests, resulted in any observable deleterious effects with regard to product yields and properties. Table 4 is a compilation of all the recorded data and summarizes product yields and solvent properties as a function of the number of solvent passes. Table 4 also illustrated the data variability based on the calculated standard deviation. For example, for the fourth pass, the product solvent wt% carbon was 88.13 ± 0.18. The 0.18 is the calculated standard deviation for the 3 autoclave runs.

The results of the data analysis are presented in Figures 2 and 3. Inlet solvent properties showed a trend towards increasing hydrogen content and decreasing sulfur content with each successive pass. However, the change in these properties was relatively small and showed evidence of leveling out after about 5 passes. Other properties and product yields did not show any significant change with the number of passes tested.

One property not correlated, but observed by Project Lignite personnel, indicated that filtration of the products tended to improve while slurry viscosity tended to increase with increasing number of passes.

Table 3 - Data Source Index
Recycle Solvent Studies

| 1st SERIES OF TESTS | RUN NO. | REFERENCE (PROGRESS REPORT NO.)[a] |
|---|---|---|
| 1st Pass Runs | 527 | 25 |
| | 529 | 25 |
| | 533 | 26 |
| | 536 | 26 |
| | 537 | 27 |
| | 546 | 28 |
| | 547 | 28 |
| | 548 | 28 |
| | 557 | 29 |
| | 560 | 29 |
| 2nd Pass Runs | 529 | 25 |
| | 534 | 26 |
| | 543 | 27 |
| | 551 | 28 |
| | 552 | 29 |
| | 558 | 29 |
| 3rd Pass Runs | 535 | 26 |
| | 544 | 27 |
| | 553 | 29 |
| | 559 | 29 |
| 4th Pass Runs | 545 | 28 |
| | 554 | 29 |
| 5th Pass Runs | 565 | 30 |

[a] Project Lignite Monthly Progress Report No.

Table 3 (Contd)

| 2nd SERIES OF TESTS | RUN NO. | REFERENCE (PROGRESS REPORT NO.)[a] |
|---|---|---|
| 1st Pass Runs | 573 | 32 |
| | 574 | 32 |
| | 575 | 32 |
| | 576 | 32 |
| | 577 | 32 |
| 2nd Pass Runs | 578 | 33 |
| | 579 | 33 |
| 3rd Pass Runs | 580 | 33 |
| | 581 | 33 |
| 3rd SERIES OF TESTS | | |
| 1st Pass Runs | 584 | 34 |
| | 586 | 34 |
| 2nd Pass Runs | 585 | 34 |
| | 588 | 34 |
| 4th Pass Runs | 587 | 34 |

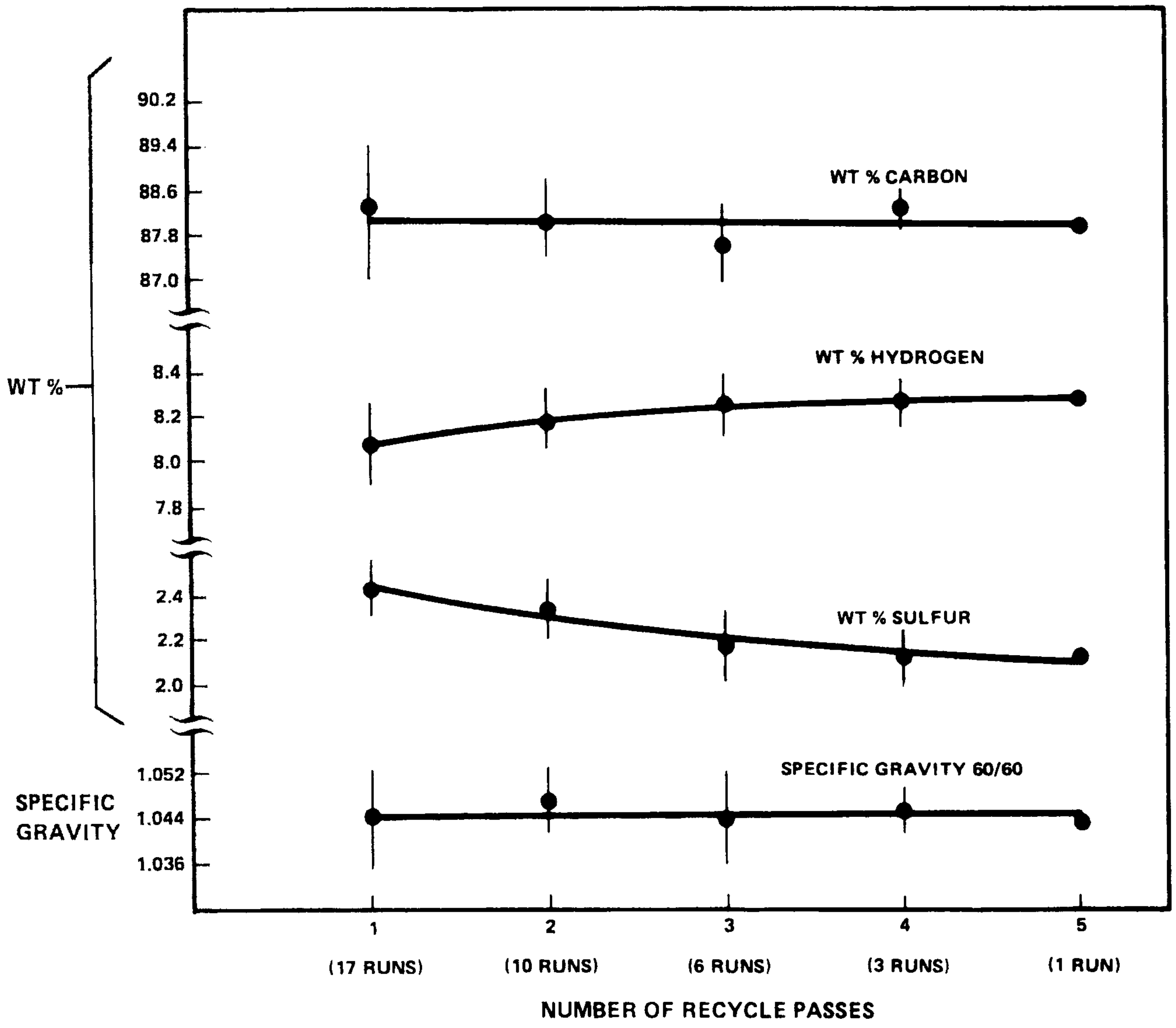
[a] Project Lignite Monthly Progress Report No.

## Table 4 - Recycle Solvent Tests
## Summary of Results

| Number of Recycle Passes | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Number of Tests | 17 | 10 | 6 | 3 | 1 |
| YIELDS, Wt. % of MAF COAL | | | | | |
| Net Gas | 34.5 ± 3.4 | 34.7 ± 5.2 | 37.2 ± 4.4 | 33.3 ± 3.1 | 34.2 |
| Net Liquid | 64.2 ± 2.8 | 63.7 ± 3.0 | 63.1 ± 3.5 | 64.2 ± 2.4 | 64.4 |
| Unconverted | 10.8 ± 3.2 | 10.9 ± 1.0 | 10.3 ± 1.2 | 11.2 ± 1.3 | 10.7 |
| Net $H_2O$ + Ash | -10.2 ± 2.2 | -9.2 ± 2.4 | -10.6 ± 0.8 | -8.7 ± 2.1 | -9.3 |
| Coal/Solvent Visc, C.P.[1] | 3,979 ± 965 | 4,810 ± 1,360 | 4,549 ± 1,084 | 4,344 ± 704 | 5,864 |
| INPUT SOLVENT | | | | | |
| Ash, Wt. % | 0.02 ± 0.02 | .047 ± .025 | .025 ± .017 | 0.03 ± 0.01 | .01 |
| Carbon, Wt. % | 88.25 ± 1.3 | 88.04 ± 0.50 | 87.59 ± 0.90 | 88.22 ± 0.4 | 87.91 |
| $H_2$, Wt. % | 8.09 ± 0.19 | 8.18 ± 0.17 | 8.25 ± 0.15 | 8.25 ± 0.10 | 8.25 |
| S, Wt.% | 2.41 ± 0.13 | 2.33 ± 0.08 | 2.18 ± 0.08 | 2.12 ± 0.10 | 2.13 |
| Sp. Gr. 60/60 | 1.044 ± 0.007 | 1.047 ± 0.007 | 1.044 ± .006 | 1.045 ± 0.004 | 1.043 |
| Br Fld. Visc, C.P. | 41.4 ± 12.2 | 51.3 ± 16.1 | 42.6 ± 10.9 | 39.9 ± 7.7 | 39.0 |
| IR Ratio | 0.20 ± 0.007 | 0.20 ± 0.009 | 0.19 ± 0.011 | 0.19 ± 0.006 | 0.18 |
| PRODUCT SOLVENT[2] | | | | | |
| Ash, Wt. % | 0.024 ± 0.021 | 0.026 ± 0.017 | 0.045 ± 0.044 | 0.025 ± 0.007 | .01 |
| Carbon, Wt. % | 87.94 ± 1.37 | 87.94 ± 0.74 | 87.94 ± 0.39 | 88.13 ± 0.18 | 86.50 |
| $H_2$, Wt. % | 8.09 ± 0.46 | 8.27 ± 0.18 | 8.21 ± 0.15 | 8.23 ± 0.19 | 7.90 |
| S, Wt. % | 2.33 ± 0.10 | 2.22 ± 0.13 | 2.17 ± 0.15 | 2.15 ± 0.11 | 2.05 |
| Sp. Gr. 60/60 | 1.046 ± 0.007 | 1.043 ± 0.005 | 1.046 ± 0.005 | 1.041 ± 0.010 | 1.045 |
| Br Fld. Visc, C.P. | 45.7 ± 14.9 | 51.7 ± 22.9 | 42.0 ± 16.0 | 53.7 ± 17.0 | 46.0 |
| IR Ratio | 0.19 ± 0.008 | 0.19 ± 0.010 | 0.19 ± 0.005 | 0.19 ± 0.011 | 0.20 |
| SOLVENT RECOVERY | | | | | |
| Wt. %[3] | 101.8 ± 2.2 | 102.2 ± 1.5 | 100.5 ± 1.2 | 99.8 ± 0.6 | 101.9 |
| NET PRODUCT[4] | | | | | |
| Light Oil, Wt. % | 6.4 ± 1.3 | 5.2 ± 1.8 | 6.6 ± 1.3 | 6.3 ± 1.5 | 6.7 |
| SRL, Wt. % | 57.8 ± 3.4 | 57.8 ± 3.5 | 56.4 ± 4.1 | 57.9 ± 3.7 | 57.7 |

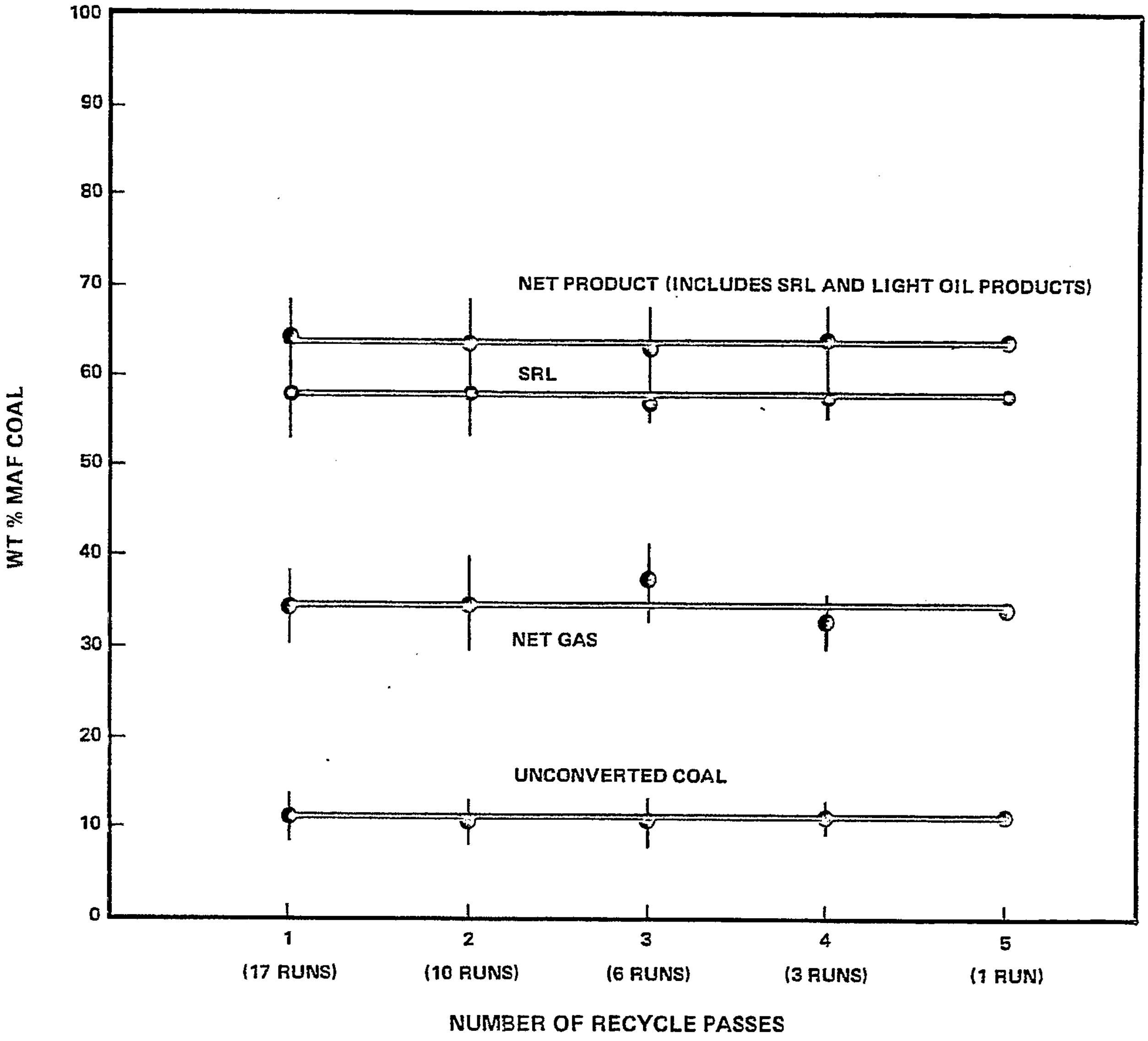
NOTES: 1) Measured at room temperature.
2) Product solvent used for next pass tests.
3) 100% recovery basis.
4) MAF coal.

± Numbers are standard deviations.



NOTES: SOLVENT PROPERTIES BASED ON INLET SOLVENT COLLECTED FROM PREVIOUS RUNS.
VERTICAL LINES ON DATA POINTS REPRESENT STANDARD DEVIATION.

Figure 2 - Recycle Solvent Tests - Solvent Properties



NOTE: VERTICAL LINES ON DATA POINTS REPRESENT STANDARD DEVIATION.

Figure 3 - Recycle Solvent Tests - Product Yield

### D. Effect of Lignite Storage

In order to assess the effect of storage conditions on lignite liquefaction, a batch autoclave study was undertaken by Project Lignite personnel to evaluate the effects of air, nitrogen, and water environments on a sample of freshly mined lignite. The air and nitrogen storage was maintained at 50% R.H. During the storage test period representative samples from each of the storage conditions were subjected to standard liquefaction procedures.

The test was terminated after a total storage time of 70 weeks. Table 5 shows the run numbers and references the Project Lignite Progress Report where the detailed data are summarized. The test results are summarized in Table 6 which illustrates the effects of storage time on product yields for water, nitrogen, and air storage.

Figure 4 contains a plot of product yields vs. storage time. Based on the data scatter, there was no obvious trend that could be attributed to the type of storage - air, nitrogen, or water. However there was evidence of a gradual deterioration of the lignite based on decreases in product yields over the 70 weeks.

### E. Effects of Reducing Conditions

The tests indicated that pure CO gave the best results. Syngas (50% $H_2$/50% CO) gave similar conversion with somewhat reduced yield of liquid products. It was concluded that syngas would be more attractive for PDU operations since use of pure CO would probably be impractical if gas recovery and recycle are utilized.

### F. Effect of Dehydration on Liquefaction

The results of lignite dehydration were to significantly reduce conversion. In addition, dehydration also resulted in lowering yields of liquid and gas products. Operational problems were increased because of reduction in filtration rates. Based on these findings, lignite dehydration prior to liquefaction does not appear to be an acceptable processing step.

### G. Miscellaneous Parameters

1. Filtration Temperature. Tests were conducted in the laboratory using the batch autoclave and laboratory batch filtration equipment. The test data indicated that a filtration temperature of about 400°F was best in order to suppress excessive solvent flashing and slow filtration rates caused by the increased viscosity of the slurry.

2. Reaction Time. Tests conducted in the autoclave indicated that greater than 30 minutes residence time results in reduced yields of liquid products and a corresponding increase in gaseous products. Therefore, 30 minutes was selected as the baseline residence time for the autoclave tests in order to maximize yield of liquids.

## Table 5 - Data Source Index
## Lignite Storage Tests

| | RUN NO. | REFERENCE (PROGRESS REPORT NO.)[a] |
|---|---|---|
| FRESH COAL | 504 | 21 |
| | 505 | 21 |
| | 525 | 25 |
| | 526 | 25 |
| WATER STORAGE | 515 | 23 |
| | 523 | 24 |
| | 540 | 27 |
| | 542 | 27 |
| | 564 | 30 |
| | 595 | 46 |
| $N_2$ STORAGE | 517 | 23 |
| | 518 | 23 |
| | 522 | 24 |
| | 539 | 27 |
| | 561 | 30 |
| | 592 | 37 |
| | 593 | 37 |
| | 613 | 46 |
| | 615 | 46 |
| AIR STORAGE | 516 | 23 |
| | 521 | 24 |
| | 524 | 24 |
| | 541 | 27 |
| | 562 | 30 |
| | 563 | 30 |
| | 594 | 38 |
| | 614 | 46 |

[a] Project Lignite Monthly Progress Report No.

## Table 6 - Lignite Storage - Summary of Results[a]

| Storage Conditions | Fresh Lignite | | | | | Water Storage | | | | | | | $N_2$ Storage | | | | | | | | | | Air Storage | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Weeks of Storage | 0 | 0 | 0 | 0 | 0 | 6 | 12 | 24 | 24 | 36 | 70 | 70 | 6 | 6 | 12 | 24 | 36 | 70 | 70 | 70 | 70 | 6 | 12 | 12 | 24 | 36 | 36 | 70 | 70 |
| Run No. | 504 | 505 | 525 | 526 | Avg of 19 Runs | 515 | 523 | 540 | 542 | 564 | 595 | 616 | 517 | 518 | 522 | 539 | 561 | 592 | 593 | 613 | 615 | 516 | 521 | 524 | 541 | 562 | 563 | 594 | 614 |
| Yields wt % MAF Coal | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Net Gas | 35.4 | 38.3 | 37.5 | 37.2 | 34.0 | 39.2 | 40.9 | 41.7 | 37.4 | 35.1 | 47.2[b] | 33.8 | 38.1 | 38.2 | 39.6 | 35.3 | 29.8 | 47.1[b] | 44.1[b] | 28.8 | 33.7 | 41.6 | 36.8 | 30.6 | 33.8 | 36.0 | 35.0 | 49.2[b] | 35.1 |
| Net Product | 66.0 | 66.7 | 66.2 | 63.4 | 64.6 | 64.6 | 67.0 | 72.4 | 69.1 | 70.1 | 57.3 | 66.7 | 65.8 | 61.5 | 65.4 | 67.5 | 72.2 | 63.6 | 61.5 | 67.7 | 61.4 | 62.7 | 67.3 | 70.3 | 64.8 | 61.7 | 65.3 | 58.9 | 57.6 |
| Light Oil | 20.7 | 28.0 | 7.1 | 6.7 | 6.6 | 14.1 | 11.9 | 12.0 | 10.3 | 17.2 | 18.4 | 22.3 | 16.4 | 16.5 | 12.6 | 14.5 | 14.7 | 23.5 | 18.3 | 16.6 | 19.7 | 16.0 | 11.9 | 10.7 | 14.7 | 18.2 | 14.6 | 13.8 | 20.5 |
| SRL | 45.3 | 38.7 | 59.1 | 56.7 | 58.0 | 50.5 | 55.1 | 60.4 | 58.8 | 52.9 | 38.9 | 44.4 | 49.4 | 45.0 | 52.8 | 53.0 | 57.5 | 40.1 | 43.2 | 51.1 | 41.7 | 46.7 | 55.4 | 59.6 | 50.1 | 43.5 | 50.7 | 45.1 | 37.1 |
| Unconverted | 8.9 | 8.8 | 13.0 | 12.4 | 11.4 | 10.7 | 8.7 | 6.9 | 7.0 | 9.2 | 9.3 | 7.4 | 9.0 | 13.4 | 9.1 | 8.3 | 9.8 | 6.2 | 7.4 | 11.8 | 6.7 | 8.8 | 9.3 | 10.4 | 10.4 | 11.0 | 10.6 | 7.3 | 12.4 |
| Water + Ash | -10.3 | -13.8 | -16.7 | -13.0 | -10.0 | -14.5 | -16.6 | -21.0 | -13.5 | -14.4 | -13.8 | -7.9 | -12.9 | -13.1 | -14.1 | -11.1 | -11.8 | -16.9 | -13.0 | -8.3 | -1.8 | -13.1 | -13.4 | -11.3 | -9.0 | -8.7 | -10.9 | -15.4 | -5.1 |
| Solvent Recovery | 99.4 | 91.8 | 102.9 | 101.2 | 102.0 | 94.1 | 96.0 | 101.4 | 98.8 | 94.9 | 93.6 | 87.7 | 95.5 | 94.3 | 97.1 | 94.8 | 95.5 | 95.3 | 93.2 | 91.5 | 83.1 | 95.3 | 97.1 | 99.6 | 95.6 | 91.8 | 96.9 | 91.8 | 88.7 |

[a] Autoclave Test Conditions:
Time: 30 min.
Avg Temp: 750°F
Avg Press: 3,000 psig
Gas Charged: $CO/H_2$

[b] These yields not used for correlations due to anomalies in the data.

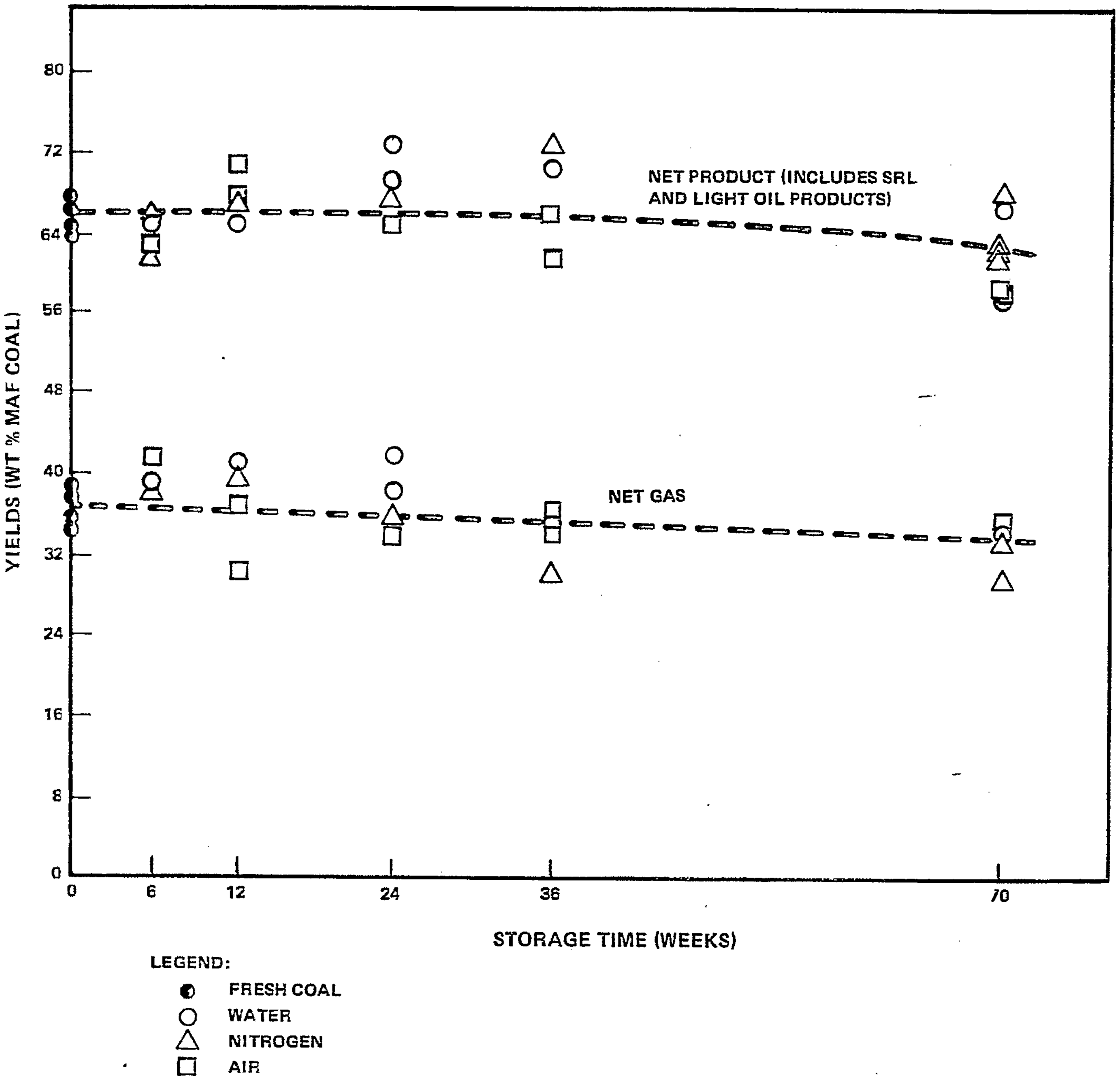


Figure 4 - Lignite Storage Product Yields

3. Particle Size of Lignite. Tests made with lignite at -100 mesh and -0.24 inch gave comparable results and indicated that within the size range tested, particle size is not a significant factor.

4. Phenol Pretreatment of Lignite. Since coals are known to swell when treated with phenol, it was reasoned that phenol pretreatment of lignite might remove certain coal constituents and thereby improve liquefaction characteristics. Laboratory tests conducted to examine this effect, indicated little or no improvement in liquefaction yields. Therefore, this processing step was considered unnecessary.

## 4.2 PHASE II - CARBONIZATION OF LIGNITE

This work was undertaken in the laboratory in an effort to study the effect of carbonization of lignite on product yields. Bench-scale attempts were made in which product char produced from carbonization was further processed utilizing conventional liquefaction. The result was that overall product yields were significantly reduced when compared to lignite liquefaction without prior carbonization. Therefore, it was concluded that lignite overall reactivity is impaired by the carbonization treatment. These results were the basis for concluding this phase of the scope of work. No further carbonization tests are planned.

## 4.3 PHASE III - SRL UPGRADING

This work, conducted as a subcontract from Project Lignite to the University of North Dakota Chemistry Department, was aimed at hydrogenation of SRL to premium fuels. The initial tests were to establish baseline conditions. The test results indicated that baseline conditions for catalyst screening were: 75 gms of SRL, 3.75 gms of catalyst, 150 milliliters of Tetralin, initial hydrogen pressure of 2,500 psig, reaction temperature of 700°F, and residence time of two hours.

The best catalyst, in terms of overall conversion and denitrogenation was presulfided Ni-Mo-$Al_2O_3$. About 90% of the SRL could be converted to yield 10% gases and 80% distillable liquids. Almost equally high conversion was obtained with SRC when using the reaction conditions developed primarily for SRL conversion.

## 4.4 PHASE IV - DIRECT HYDROGENATION OF LIGNITE

Direct hydrogenation of lignite, in contrast to liquefaction, involves contracting of pulverized lignite with hydrogenation gas such as $CO/H_2$ in the presence of a catalyst. Conditions for this operation would be low pressure, fixed, or fluid bed at moderate temperatures. To date, only a few exploratory autoclave runs have been attempted in an effort to take a preliminary look at the effects of catalyst and solvent on lignite hydrogenation. The results obtained were inconclusive. No selection has as yet been made and no further work is currently planned.

# SECTION 5

# EVALUATION OF THE SRL PROCESS

## 5.1 TECHNICAL

The results of recent PDU operations have been used to select a reasonable set of baseline processing conditions. These are 2500 psig, 750°F preheater outlet, solvent to coal weight ratio of 1.9/1, syngas of 50% CO/50% $H_2$, and about 1.4 liquid hourly space velocity in the dissolver reactor. After the PDU completes the parameter study, optimum SRL processing conditions can be selected and equipment designs and estimates firmed up in order to complete the economic assessment of a projected commercial size plant.

## 5.2 ECONOMICS

From an economic standpoint, the parts of the SRL process that have the most influence on investment costs are as follows:

Coal Liquefaction: For a commercial size plant, as discussed in Report 82 for the SRC process, the coal liquefaction section (Unit 12), containing equipment for coal dissolving and filtration, represents nearly 30% of the major equipment costs and is almost double the estimated cost of any other section of the plant. One of the prime contributors to this cost is the dissolver vessels. For the SRL process, current PDU operations have established reasonable baseline liquefaction conditions which are similar to SRC. However parameter studies expected to get underway in the near future could zero in on lower severity processing conditions in order to facilitate reducing the cost of the liquefaction section.

Materials of Construction: The occurrence of stress corrosion cracking in the PDU preheater coil and downstream equipment associated with coal liquefaction has resulted in the replacement of stainless steel components with expensive Incoloy 800. This occurrence might have been caused by startup problems with chlorides present as a result of the chlorinated solvent used to clean out the equipment. However, until the mechanism has been defined, it would be risky to assume that stainless steel would suffice for a commercial plant.

### 5.2.1 COMMENTS ON UND ECONOMICS

We have reviewed the economics prepared by the Economics' Department of UND for the SRL process. The basis for the review was the report included in Quarterly Report No. 7 entitled "An Economic Evaluation of a Plant for the Solvent Refining of Lignite."

## A. Capital Investment

The development of investment costs by UND was based on factoring from Parsons Report No. 82 for a 10,000 T/D Illinois No. 6 feed coal modified SRC plant to a plant to process 30,000 T/D of Lignite and produce SRL. We present the following comments on the factors developed by UND as presented in Table C-1, page C-4 of Quarterly Report No. 7:

- Major equipment costs for the coal liquefaction section (Unit 12) was estimated by UND at about $41 million, on a mid-1973 pricing basis for a 30,000 T/D SRL plant. This estimate was made by using a multiplier of 1.855 times the Unit 12 major equipment costs of about $22 million in Report 82 for SRC. The multiplier of 1.855 was developed by UND by using an exponential scaling factor of 0.6 on a capacity factor of approximately 3. Subsequent to the publication of Report 82, we have completed technical and economic studies for large scale SRC facilities which update the information in Report 82. For the large scale SRC facilities, the liquefaction section was designed for processing 20,000 T/D of dried coal. This is essentially the same rate as would be required for processing 30,000 T/D of lignite containing about 30% moisture and therefore the results are applicable for estimating the SRL facilities. For the large scale SRC facilities, we have increased the dissolver vessels from 10' diameter in Report 82 to 12.5' diameter and reduced the liquid residence time from 60 minutes in Report 82 to 15 minutes. In addition, the dissolver pressure was increased from 1200 psig in Report 82 to 2200 psig which is similar to current PDU operations. As a result of these design changes, the 6 parallel dissolvers in Report 82 were reduced to 3 parallel dissolvers for processing twice the flow rate of coal. Utilizing this information, we estimate the coal liquefaction section (Unit 12) of a 30,000 T/D SRL plant at about $45 million based on mid-1973 pricing.

- Another major cost item we would comment on is the oxygen plant-Unit 24. UND uses a factor of 1.87 which is derived from using an exponent of 0.6 on a capacity factor of 2.83. Since the oxygen plant cost in Report 82 is based on 2000 T/D size - the largest available, we would recommend that the cost be increased by about a factor of 3 in order to handle the 5558 T/D of oxygen estimated by UND. This would result in a cost of Unit 24 of about $35 million instead of the $23 million reported by UND.

- The other factors used for the various sections are for the most part around 2.0 which is essentially a capacity factor of 3 raised to the 0.6 power for such sections as coal slurrying and pumping, gas treatment, gasification, utilities, and offsite facilities. This is a reasonable judgement especially since, for the most part, these sections are not multiple trains but single units scaled up in size.

Another point worth mentioning is that the UND economics are based on excluding costs for hydrogenation of fuel oil and naphtha products as well as fuel gas sulfur removal. Costs for these as presented in Report 82 for SRC total $6.1 million and we could estimate for the SRL 30,000 T/D plant, about $12 million - roughly 10% of major equipment costs.

### B. Selling Price Determination

In the development of the product selling price by UND, the total fixed capital investment was corrected for escalation from mid 1973 (Report 82 basis) to mid 1975. We would suggest in total, a fixed capital investment of $615 million rather than the UND figure of $460 million as shown in Table 4 page C-1 of their Quarterly Report No. 7. In addition, a three year construction period appears optimistic. The demonstration plant in Report 82 was based on 4 years for fund drawdown purposes.

The product selling price determined by UND estimated operating labor based on an equation developed by Wessel for chemical plants as described on page C-3, paragraph 2 of Project Lignite Quarterly Technical Progress Report No. 7. In Parsons opinion, use of this equation results in lower labor costs than obtained by a direct estimate for each unit as was used for Report No. 82. Maintenance cost was then estimated by equating maintenance labor to twice operating labor. The overall result would put maintenance at 3.15% of fixed capital investment instead of 4.0% used by Parsons. Plant overhead and general expense was calculated by UND at 45% of total labor. In Parsons opinion, this is low since we would estimate payroll burden alone at about 35%. We would suggest plant overhead and general expenses at about 80% of total labor for a preliminary type estimate. Property taxes and insurance used by UND in Parsons opinion are considered low and estimated at about 1.75% of fixed capital. We would suggest property taxes and insurance at about 2.75% of fixed capital. UND used $3.50/ton for the cost of lignite which may be somewhat optimistic dependent on location.

Considering a 20 year project life, state and federal income taxes of 52%, investment tax credit of 10%, and a 12% DCF after taxes, Parsons would estimate the product selling price for a 30,000 ton per day plant producing 11,050 ton per day of products at about $1.90/MM Btu in contrast to the $1.53/MM Btu estimated by UND.

# APPENDIX A

# RESULTS OF METALLURIGICAL TESTS ON PDU EQUIPMENT FAILURES

Page

1. Project Lignite Preheater Coil Metallurgy, Dr. J. B. O'Hara to Dr. D. E. Severson, July 18, 1975. A-2
2. Project Lignite Pilot Plant Materials Problems, Dr. J. B. O'Hara to Dr. D. E. Severson, August 26 1975. A-11
3. Project Lignite Pilot Plant Materials Problems, Dr. J. B. O'Hara to Dr. D. E. Severson, September 29, 1975. A-36

July 18, 1975

Dr. D. E. Severson
Department of Chemical Engineering
University of North Dakota
Grand Forks, North Dakota 58201

SUBJECT: Project Lignite
Preheater Coil Metallurgy
Reference: ERDA Contract E(949-18)-1775

Dear Dr. Severson:

This letter transmits three copies of an interim report and recommendations for action on the subject of the Project Lignite preheater coil failures. It summarizes the results of discussions as well as test work and analysis that we have carried out on the coil failure materials. The discussions have included those of our Mr. N. H. Berlin during his participation of the July 10, 1975 Project Lignite Advisory Committee meeting in Grand Forks, as well as subsequent discussions between your Messrs. Max Souby and W. Barney and our Messrs. N. H. Berlin, W. J. Lochmann and L. T. Overstreet. Mr. Lochmann heads our Materials Selection group and Mr. Overstreet is a Principal Materials Selection Engineer.

Copies of Mr. Overstreet's report are attached; included are recommendations based on analysis of metal samples from the first group sent to us from Coil No. 2 which had failed.

Additional metal samples have since been received and are in the process of being analyzed. Preliminary results indicate that chloride stress corrosion cracking also is occurring in the high pressure separator and piping to Cooler E-3. The presence of deep pits and, possibly, acid attack in the piping to E-3 are indicated. We recommend that you carefully and promptly review the personnel safety exposures which result from this metals attack.

The above factors suggest that higher molybdenum stainless steel alloys than are presently being contemplated may be required in areas of high chloride concentrations.

Because of the high potential for chloride stress corrosion cracking and pitting in this system, we strongly recommend that areas where stainless steel is now being used, or contemplated being used, should be carefully evaluated with regard to risk of future failures. We also recommend that the reasons for the metals' failure be defined and rationalized with the experience to date of the Tacoma, Washington SRC pilot plant.

We are preparing reports containing additional results and conclusions and will expect to transmit these to you within the next several weeks.

We will be pleased to discuss this subject with you as you wish.

Very truly yours,

The Ralph M. Parsons Company
ORIGINAL SIGNED
J. B. O'HARA

J. B. O'Hara
Project Manager

JBO:eb
Enclosures

cc: Dr. J. O. Batchelor, ERDA, Washington
Mr. N. P. Cochran, ERDA, Washington
Mr. E. Schmetz, ERDA, Washington

INTEROFFICE CORRESPONDENCE Date July 18, 1975

To Norton Berlin

From L. T. Overstreet

SUBJECT Job 5435-1 First Report on Metallurgical
Problems -- Project Lignite,
Coal Conversion Pilot Plant,
University of North Dakota

---

Analysis of coil sections from Heater E-1 from the second coil failure as provided by Dr. W. Barney, has been completed. Additional samples are being analyzed from Coil Number 3 and piping after the high pressure separator. A formal report covering all aspects of this investigation will be written upon completion of remaining samples. This report can be considered a preliminary progress report.

Conclusions Transgranular, multibranched cracking typical of chloride stress corrosion cracking of austenitic stainless steel has occurred in the coil sections near the inlet.

Chloride is concentrating at the second coil from the inlet as chloride bearing water flashes through the dew point (about 400-450°F).

Chloride cracking will continue to occur in 18Cr-8Ni stainless steel coils unless nearly all chloride (probably less than a few ppm) can be removed.

Chloride cracking will probably continue to occur in 18Cr-8Ni stainless steel even after stress relief if total stress from all sources including residual and operational such as hoop and bending stresses exceed about 10,000 psi.

Changing to Incoloy 800 will increase nickel content enough to eliminate chloride stress corrosion cracking if residual cold working is removed by stress relief. Incoloy 800 should be able to withstand operational stresses without stress cracking.

Recommendations Coil Number 5, made of Incoloy 800 should be stress relieved at 1650°F ± 25°F for four hours after fabrication. Weld filler metal for joining Incoloy should be Rolled Alloys 330 or 333. We do not recommend the higher nickel electrodes such as Inconel 182 because of the high sulfur content of the coal and solvent.

We would like to examine other areas of the failed coils to determine whether chloride pitting or acid attack may be occurring.

Microstructure Analysis Microstructure of the coil is fine grain with evidence of flow lines and numerous twinned grains indicating the material is still in a state of cold work.

Etching from 10 seconds to two minutes in electrolytic oxalic acid did not produce a "ditch" structure in grain boundaries. Therefore, we do not feel the material we examined was sensitized as defined by ASTM A-262, Detecting Susceptibility to Intergranular Attack in Stainless Steels. As the spectrographic analysis shows, carbon content is low which would account for the lack of sensitization. Other areas of the coil could be in a state of localized sensitization if the fabricator had applied heat to facilitate bending, especially of 90 degree bends of higher carbon content.

Transgranular cracks came from inside the tubing. Very little evidence of pitting was found on the inside surfaces. Many of the cracks were extremely straight for most of their length suggesting that crack propagation was fast through a high tensile stress field.

Some cracks progressed longitudinally with the tube axis, then turned and progressed transversely indicating a complex residual tensile stress configuration.

No cracks were found on the inside radius of the coil. Most of the transverse cracks were located at the ten o'clock and two o'clock positions near the outside radius of the coil.

Analysis of Deposits The two long sections of coil were filled with distilled water, heated to 100°F for 1/2-hour and the water analyzed for chloride, sodium and pH. Results are attached. Enough chloride definitely is present to promote cracking. The acid responsible for lowering the pH has not been identified. Low pH will accelerate chloride stress corrosion cracking.

Sodium was checked to determine whether caustic cracking was a possibility. However, the low pH makes caustic stress corrosion cracking unlikely.

L. T. Overstreet

LTO:hh

Attachment

CC: J. B. O'Hara
W. J. Lochmann

METALLURGICAL TESTING CORPORATION
15750 SALT LAKE AVENUE, CITY OF INDUSTRY, CALIFORNIA 91745

Area Code 213
964-1294
283-2020

TO: RALPH M. PARSONS COMPANY

Attn: Leslie T. Overstreet

DATE July 14, 1975
YOUR P.O. NO 2-5435-1
MATERIAL 316 Stainless Steel
SPECIFICATION

Laboratory No. 75-101M

## METALLURGICAL EXAMINATION

One (1) sample of 316 stainless steel tubing was submitted for metallurgical examination. The sample was sectioned and specimens were prepared for several tests. The results were as follows:

## CHEMICAL ANALYSIS

The spectrographic analysis of the sample gave the following results

| | |
|---|---|
| Carbon-------------------- | .02% |
| Manganese----------------- | 1.98% |
| Silicon------------------- | .55% |
| Phosphorous--------------- | .019% |
| Sulfur-------------------- | .014% |
| Chromium------------------ | 16.78% |
| Nickel-------------------- | 13.53% |
| Molybdenum---------------- | 2.25% |
| Copper-------------------- | .15% |

The material was 316 stainless steel tube and the concentration of its components meet the specification of AMS 5573E (tube).

Warm, distilled water, Chloride free was placed inside the tubes, held for about half hour. The water is collected and then analyzed as follows:

RESPECTFULLY SUBMITTED

METALLURGICAL TESTING CORPORATION

tjr

METALLURGICAL TESTING MTC CORPORATION

Area Code 213
964-1294
283-2020

1575.0 SALT LAKE AVENUE, CITY OF INDUSTRY, CALIFORNIA 91745

TO: RALPH M. PARSONS COMPANY

Attn: Leslie T. Overstreet

DATE July 14, 1975

YOUR P.O. NO. 2-5435-1

MATERIAL 316 Stainless Steel

SPECIFICATION

---

Laboratory No. 101M (Page 2 Cont.)

| | Long Tube | Short Tube |
|---|---|---|
| Chlorides (Cl-) | 536 PPM | 379 PPM |
| Sodium (Na+) | 76 PPM | 59 PPM |
| pH | 5.5 | 6.0 |

The analysis indicates also a large concentration of Calcium ions.

Two specimens were prepared for microscopic examination of the longitudinal and cross section tube as requested.

Two photomicrographs were taken, one at a 50X magnification and the other at at 200X magnification.

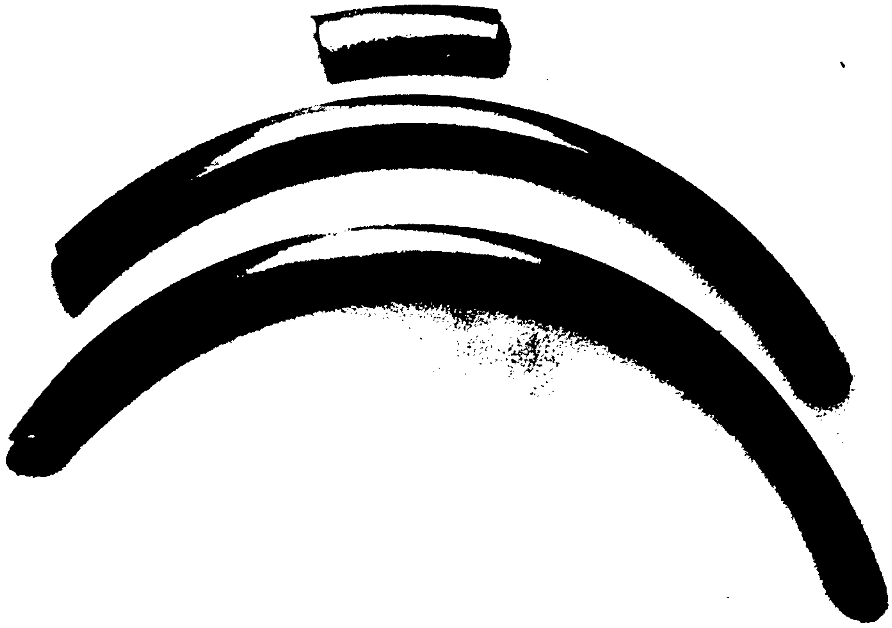
Balance of samples, metallurgical mounts and photomicrographs, were returned to the customer for additional evaluation.

RESPECTFULLY SUBMITTED

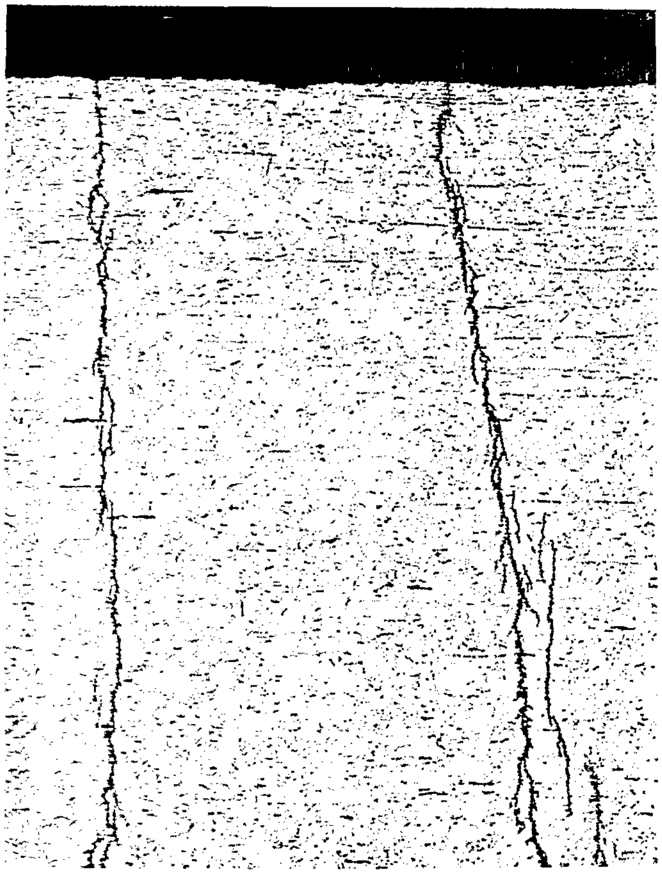
James P. Sandy

METALLURGICAL TESTING CORPORATION

tkr



No. 1 As-received samples. Short section at top was used for analysis. Numerous transverse cracks can be seen along the top edge of the short sample and the bottom tube.



No. 2 Transgranular cracking from inside the tube. No evidence of sensitization. 50x Oxalic acid etch; 2 minutes.

No. 3 Complex transgranular cracking near the intersection of a transverse and longitudinal crack. 200x, Oxalic acid, 2 minutes.

August 26, 1975

Dr. D. E. Severson
Department of Chemical Engineering
University of North Dakota
Grand Forks, North Dakota 58201

SUBJECT: Project Lignite
Pilot Plant Materials Problems
Reference: ERDA Contract E(949-18)-1775

Dear Dr. Severson:

This letter transmits three copies of our metallurgical report regarding the five samples sent to The Ralph M. Parsons Company from the Project Lignite pilot plant. These samples were obtained after preheater coil No. 3 had failed and included samples of material after the reactor that had failed during pilot plant operations.

In general, the metallurgical tests confirmed chloride stress corrosion as well as acid attack on some samples. Recommendations include using an Incoloy 800 preheater coil in place of 316 SS used previously.

We are currently preparing to analyze samples of material after the dissolver vessel. A report on these findings should be available within the next several weeks and will be transmitted to you.

We will be pleased to discuss this matter with you as you wish.

Very truly yours,

THE RALPH M. PARSONS COMPANY
ORIGINAL SIGNED
J. B. O'HARA

J. B. O'Hara
Project Manager

JBO:rs

CC: Dr. J. O. Batchelor, ERDA, Washington
Mr. N. P. Cochran, ERDA, Washington
Mr. E. Schmetz, ERDA, Washington

# METALLURGICAL ANALYSIS OF STAINLESS STEEL SAMPLES FROM PROJECT LIGNITE COAL CONVERSION PILOT PLANT UNIVERSITY OF NORTH DAKOTA

August 14, 1975

Prepared by

L. T. Overstreet
Principal Materials
Application Engineer
THE RALPH M. PARSONS COMPANY
Pasadena, California

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## SCOPE

Five stainless steel samples were sent to The Ralph M. Parsons Company for analysis from the University of North Dakota, Project Lignite Pilot Plant. Two samples were sections of helical coil from heater E-1; one sample from the inlet end had failed by cracking. The sample from the outlet end had not failed. The other three samples consisted of piping and a thermocouple from the high pressure separator area.

This report contains metallurgical observations, discussions of causes of corrosion and recommendations.

## SUMMARY

Type 316 SS heater coils are cracking from chloride stress corrosion cracking. Cracks have been most severe in areas of high residual stress from cold working and at points where a chloride concentrating mechanism such as flashing water has been operative.

Cracks have been fewer and less severe (not as deep) in hotter areas such as the heater outlet (about 800°F) and the High Pressure Separator (about 550°F).

Chloride stress corrosion cracking has occurred wherever tensile stresses have been present. Cold work has provided the chief source of tensile stress, but stresses from welding and, possibly, operational stresses (internal hoop stress and bending of piping installation or from thermal expansion) are also present.

Chloride stress corrosion in the Type 316 SS heater tube has not been accompanied by pitting. On the other hand, cracks in Type 304 SS have always started as pits. The only pitting occurring in Type 316 SS was in a sensitized region which contained no cracks.

Localized corrosion in the form of pitting and washing away of a small area of thermocouple and straight piping to E-3 was the result of acid attack.

Lowering of stresses by stress-relief and alloy changes are the primary recommendations for eliminating the chloride cracking problem.

## RECOMMENDATIONS

1. Coil No. 5, made of Incoloy 800, should be fabricated according to the procedure stated in this report.

2. After fabrication, all austenitic stainless steel piping should be given a stabilizing/stress relief at 1650°F ± 25°F for four hours.

3. The minimum alloy for heater coils and pilot plant piping should be Type 316 SS. Type 304 SS does not have enough pitting resistance for this pilot plant environment.

4. A low-chloride solvent should be considered -- less than 1 ppm.

5. If possible, a corrosion test spool containing short lengths of alloys such as those discussed under "Conclusions", should be joined in sections to form a length of pipe and installed at the point of greatest acid attack between the High Pressure Separator and Cooler. This test spool would give the relative resistance of these alloys under the high velocity flow conditions. In addition, insertion of a corrosion test rack containing coupons of a series of alloys in Separator, S-1, would give corrosion rates at lower velocities.

6. Identify the corrosives in S-1. Special attention should be given to the possible existence of organic acids.

7. Change from using trichlorethane cleaning agents to acetone or MEK.

8. The new High Pressure Separator, S-1, may be subject to chloride stress corrosion cracking if residual plus operating stresses are high. We would be happy to check this possibility if design information is forwarded to us.

## CONCLUSIONS

With a feed containing a high water and chloride content, the possibility of chloride stress corrosion cracks exists wherever there are significant tensile stresses. Stresses above about 10,000 psi (1) promote cracking in 18 Cr, 8 Ni stainless steels.

Using a stress-relieved austenitic stainless steel coil will help if the tensile stresses caused by operating conditions are low.

While very little pitting was seen on the inside surfaces of Coil No. 3, this coil had experienced only 50 hours of operation. It is anticipated that pitting would significantly affect coil life if high chloride containing feed were continued for long periods of operation. If a lower chloride content solvent can be used, Type 316 SS should give adequate coil service life. If the FS-120 solvent containing 50 ppm chloride is continued, higher molybdenum containing stainless steels may be required to realize long service life.

Coils No. 4 and No. 5 may be better in resisting chloride stress corrosion cracking, but may still pit because of high chloride in the feed. Austenitic stainless materials such as Incoloy 825, RA333, Carpenter 20 Cb-3 and Hastelloy G have high molybdenum contents and exhibit superior resistance to chloride pitting. One of the better alloys for chloride resistance is Allegheny Ludlum Alloy 6X (20 Cr, 24 Ni, 6.5 Mo) (2) but its availability in different forms and sizes is limited.

Some ferritic or duplex austenitic-ferritic alloys have high resistance to chloride stress corrosion cracking, but may lack pitting resistance unless both chromium and molybdenum contents are high. Type 329 SS and Carpenter 7 Mo are not considered to have enough molybdenum to resist chloride pitting in crevices (under scale). Ferritic alloys should be limited to temperatures below 700°F because of their susceptibility to 885°F embrittlement.

Unless water can be removed almost completely, it is doubtful that a reduction of water from twenty-five per cent to one or two per cent would eliminate chloride stress corrosion cracking or pitting. The lowered water content would cause higher chloride concentrations and probably cause more localized attack.

It is perplexing that chloride cracking is occurring at the hot end of the heater coil. Possibly, cracking is occurring at lower temperatures as the outlet goes through temperature cycles on start-up or shutdown. Also, it is possible that enough salt exists in the water phase to raise the water flash point at the outlet end of the coil.

## HEATER E-1, COIL NO. 3

Two samples for metallurgical examination were taken from the two turns of inlet tubing from Coil No. 3 (Photograph No. 1). One, Sample A, was from a crack near the straight section of coil; the other, Sample B, was taken near the broken end of the coil. This coil had been in service only about 50 hours before it failed.

Both samples contained chloride stress corrosion cracks similar to those found and reported in our First Report on Metallurgical Problems of July 18, 1975.

Photograph No. 2 of Sample A shows the inside surface containing a primary crack completely through the tube wall and several secondary cracks nearby in the sample taken near the straight section of the coil. Again, presence of flow lines and grain twins are evidence of cold working.

No evidence was found of sensitization in either sample.

Three samples for metallurgical examination were taken from the outlet turns of Coil No. 3 (Photograph No. 3, Samples C, D and E).

Photographs No. 4 and 5 contain incipient cracks at points where tensile stresses would be expected. The cracks at the outlet end of Coil No. 3 are typical of chloride stress corrosion cracks. Given longer operating times these small cracks would probably have propagated through the tube wall.

Photograph No. 6 is from a sample taken from an area of the coil which appears to be slightly more scaled on the outside surface than the other areas of the coil. The microstructure contains grain boundary carbides, shows some grain growth and an absence of numerous twins and cold flow lines. Somewhat surprising, no cracks were found in this area but cracks were present in relatively nearby areas at Sample D.

Oxalic etching will reveal grain boundary carbides but further tests are required to prove whether the material is sensitized (3). Such tests were not conducted on this sample. Grain boundary carbides could indicate sensitization or stabilization if sufficient time at high temperatures allowed replenishment of alloy in grain boundaries. Therefore, the lack of cracking in this area could have been the result of stabilization which resisted intergranular cracking and the result of lowered stress upon heating to temperatures of 1200°F or more.

It is difficult to determine when this heating occurred. If heating to temperatures of 1200°F was the result of the fire, some evidence of transgranular cracks should have been present as in the rest of the coil. If heating was a result of heat applied to ease fabrication, then the material could have become stabilized and stress relieved and no cracks would be found as appears to be the case.

The importance of the microstructure and lack of cracks in Photograph No. 6 is that similar conditions should exist in Coil No. 4 which has been stress-relieved for a long period which should stabilize the grain boundaries against intergranular corrosion or cracking as well as relieve cold work stress.

Photograph No. 4 was taken at the inside surface under the fillet weld joining the tube to the collar. Cracks were very localized to the zones just under the welds which indicates that residual welding stresses were responsible for promoting cracking.

## THERMOCOUPLE

A 1/8-inch diameter by 5-inch long thermocouple from High Pressure Separator, S-1, was sectioned at the tip and at a hole about mid-length where it appeared to have eroded (Photograph No. 7). The entire surface was covered with shallow pits and some transverse cracks were present.

Chemical analysis confirmed a 304 SS composition.

Microstructures revealed several interesting points. The tip of the thermocouple was a cast structure with no evidence of stress corrosion cracking. Evidently the tip had been produced by a weld deposit.

The body of the thermocouple had flow lines and many twinned grains which appeared upon etching, indicating existence of cold work. Photograph No. 8 shows that two modes of metal deterioration had taken place: 1) deep pitting, and 2) transgranular cracking at the bottom of pits.

## PIPING FROM S-1 TO E-3

Piping consisting of a Type 304 SS 90° bend (Photograph No. 9) and a Type 304 SS straight section (Photograph No. 12) from High Pressure Separator, S-1, to Cooler, E-3 were chemically analyzed and examined for cracks and pits. Both pieces had been removed because of leaks.

A transverse section through the 90° bend revealed pits on the inside radius of the bend which gradually became deeper and thinner until they became cracks (Photograph No. 10) on the inside surface of the outside radius of the bend. A longitudinal section indicated presence of pits on the inside radius and flow lines (Photograph No. 11). Flow lines indicate the bend was in a state of cold work. Cold work plus bending stresses from operation determined the location and size of cracks in the bend.

The straight section shown in Photographs No. 12 and 13 is of interest because no evidence of cracking was found. Instead, a very localized area of metal loss was found next to the brass swedge lock fittings (Photograph No. 14). The appearance of metal thinning accompanied by smaller pits suggest attack by some type of acid which was just slightly above the dew point in S-1 but subsequent cooling by the length of line between S-1 and E-3 brought the acid to its dew point, or the heat sink of the swedge lock fitting and cooler tube sheet caused a "fin effect" to bring the acid to its dew point.

The type of acid responsible for corrosion could be the subject for further investigation. Possible acids could be sulfurous, sulfuric, hydrochloric or carboxylic (4) acids of the naphthenic type. Acids such as formic and carbonic would not be suspected, although may be present, because 304 SS is normally not subject to attack in these acids.

If the acid is an organic-naphthenic then 316 SS and other molybdenum bearing stainless steels will provide good corrosion resistance. If acids are the strong inorganic types, stainless steels of higher nickel and chrome content may be required.

While the use of high alloys can be accomplished at reasonable expense in a pilot plant, such alloys may be prohibitive in large scale plants. Therefore, it would be desirable to know the responsible corrodent if possible. Such information would allow a better understanding of the corrosive process and enable the selection of materials for large scale plants based on optimum resistance and expense.

## OPERATING CONDITIONS CORRELATED TO CORROSION

An attempt was made to correlate operating conditions with the location of severest cracking in which leaks occurred. If a linear distribution of temperature is assumed from inlet of 300°F to outlet of 800°F, cracking and leaks have consistently occurred near the inlet where temperature is in the range of about 350°F to 450°F. It is suspected that chlorides are concentrating in this temperature range because of "salting out" of chlorides as water is flashed.

At about 1800 psig system pressure, there would have to be about 23% water in the feed to produce a flash point of about 450°F if an ideal solution is assumed. This correlates with the figure of about 25% water in the coal, if coal is assumed to be the major portion of the feed. However, because the mixture is a complex composite of solids, oils, gases, salts and water, there is no way of precisely calculating the water flash point; it is probably coincidence that the known water content correlates so closely with the water content needed to produce a partial pressure of the right magnitude to give a flash point near 450°F.

Moreover, the existence of cracks at the outlet of Coil No. 3 and in the high pressure separator area suggests that water as a liquid may be entrained and carried along to higher temperature areas or that the salt content is sufficient to raise the flash point to higher temperatures.

Another possibility exists in that cracking in higher temperature areas may be taking place only during start-up or shutdown as these areas temporarily concentrate chloride.

## PROCEDURE FOR FABRICATING AN INCOLOY 800 HEATER COIL

Material for heater coil shall conform to ASME SB-163 or SB-407 Alloy 800 Grade 2. ASME Code stresses shall be adhered to for design.

Material shall be purchased by the fabricator in straight lengths sufficient to form a continuous coil with a minimum of welds. Coupling or socket welds shall be used for joining tube sections.

1. Form by cold (350°F maximum) bending with mandrels, pipe bending forms or other suitable tools and machines to provide a helical coil to dimensions shown on the drawing.
2. Forming shall provide a smooth coil conforming to the specified radius at all points. Surface of the coil shall be free of dents, scratches, weld gouges, weld spatter or other defects.
3. All bends such as those near the inlet and outlets shall be formed using bending tools. They shall not be formed by hammering, bending in a vise, or any other method which would squeeze the tube, leave dents or scratches or create a radius of less than three inches.
4. Welding shall be by the Gas Tungsten-Arc Process using Rolled Alloys RA330 bare electrode. No preheat shall be used.
5. Welding shall be performed by welders qualified in accordance with Section IX of the ASME Code.
6. All welds shall be 100% Radiographed.
7. All welding shall be performed prior to heat treatment.
8. The fabricated coil shall be placed in an oven at 1650°F ± 25°F and held for four hours. Cooling shall be in still air.
9. The furnace atmosphere used in heat treating shall conform to Huntington Alloys Bulletin, T-40 (5), and shall be free of sulfur or ammonia compounds and slightly reducing. The coil shall be free of paint, oil, and other foreign substances just prior to insertion in the furnace.

## REFERENCES

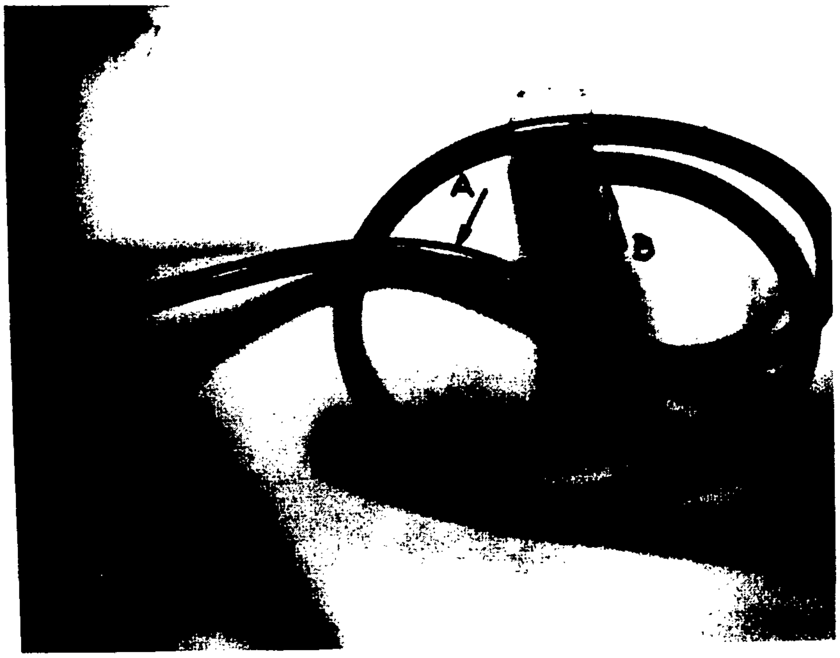
1. "Effect of Composition and Heat Treatment on Stress Corrosion Cracking of Austenitic Stainless Steels." E. E. Denhard, Jr., CORROSION, Vol. 16, 1960.

2. "New Molybdenum Stainless Steels for Corrosion Resistance: A Review of Recent Developments." R. F. Steigerwald, MATERIALS PERFORMANCE, September, 1974.

3. "Detecting Susceptibility to Intergranular Attack in Stainless Steels." ASTM A-262-70. AMERICAN SOCIETY FOR TESTING AND MATERIALS, 1973.

4. "Corrosion of Refinery Equipment by Naphthenic Acid." MATERIALS PROTECTION, September, 1963.

5. "Engineering Properties of Incoloy Alloy 800." Bulletin T-40, Huntington Alloys, Huntington, West Virginia.

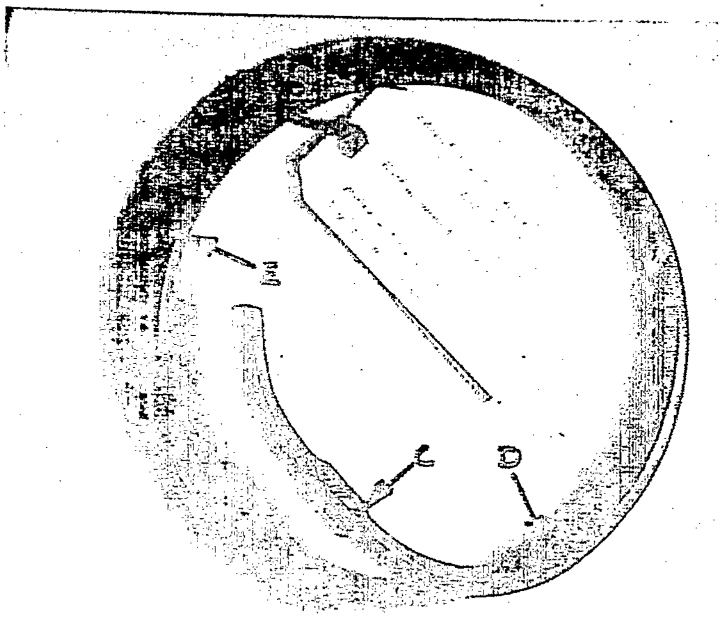


No. 1

1. INLET END OF COIL NO. 3. Sample A was taken at a crack through the pipe which ran about a quarter of the way around the circumference. Sample B was taken near the end which broke off from the coil. Inlet is the straight section toward Sample A.

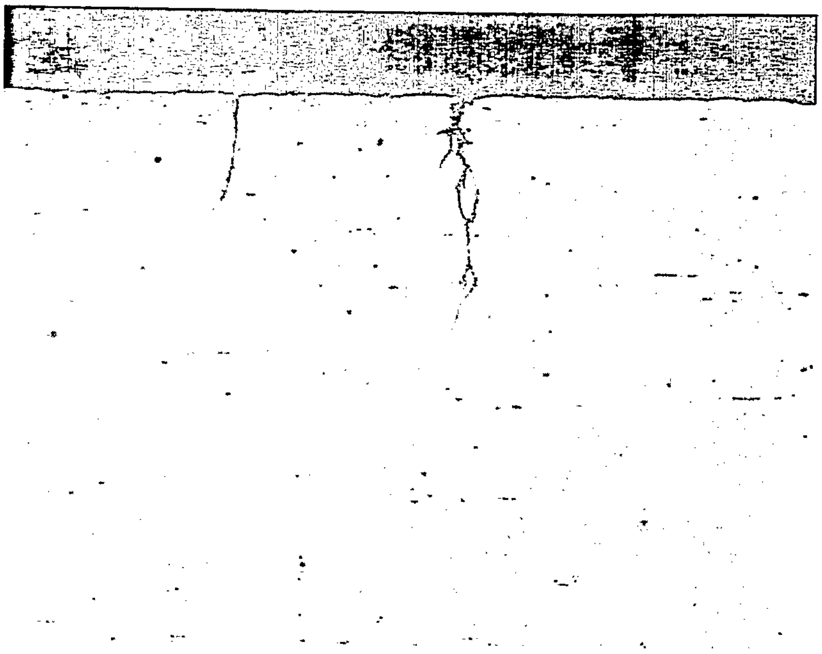
No. 2

2. 100X OXALIC ACID. Microstructure at Sample A shows primary crack through pipe wall and numerous secondary cracks initiating on the inside surface. Grains have been stained to enhance contrast and bring out flow lines.



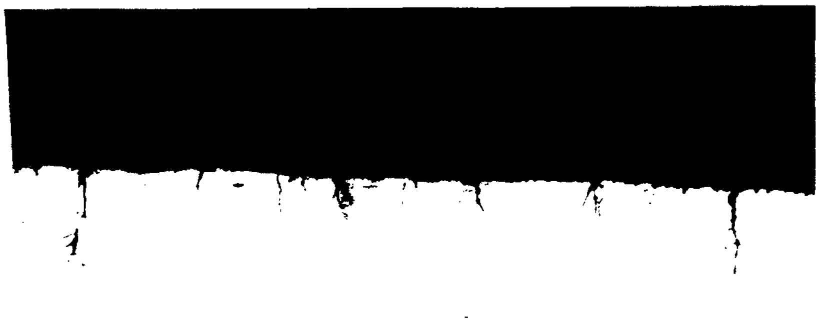
No. 3

3. OUTLET END OF COIL NO. 3. Sample C was taken at the fillet weld, Sample D at a dent on the inside radius and Sample E at a scaled zone.



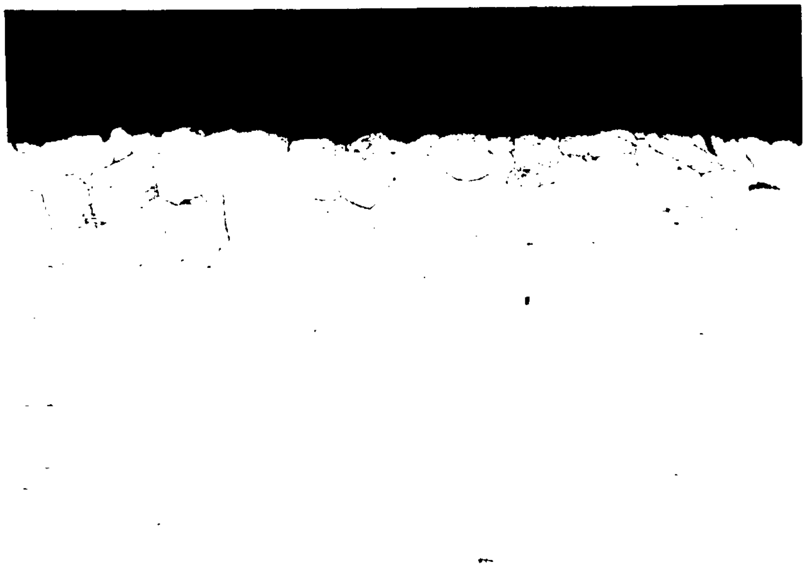
No. 4

4. 100X OXALIC ACID. Microstructure at Sample C. Localized area of transgranular cracks is on inside surface under fillet weld of collar to pipe.



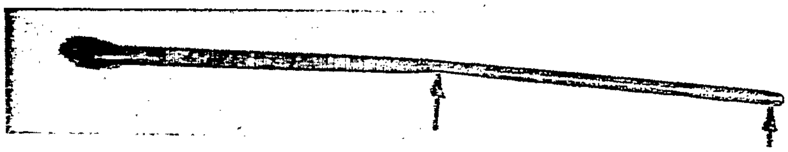
No. 5

5. 100X OXALIC ACID. Sample D. Cracks are on inside surface in dented area.



No. 6

6. 200X OXALIC ACID. Sample E inside surface is slightly pitted. Some grain growth has occurred and sensitization has taken place.



No. 7

7. THERMOCOUPLE FROM HIGH PRESSURE SEPARATOR, S-1. Samples for microstructural analysis were taken at arrows. Tip of thermocouple made by depositing a weld bead. Hole was probably caused by acid splashing in a localized area possibly off of internals in the vessel. Material is 304 SS.

No. 8

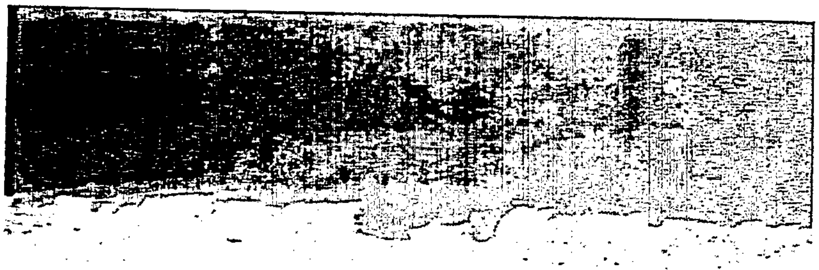
8. 100X OXALIC ACID. Sample is from the tip of thermocouple. General pitting and transgranular cracking resulted from chloride and residual cold working stresses.

No. 9

9. 90° BEND ON OUTLET OF HIGH PRESSURE SEPARATOR, S-1. Arrow points to approximate location of leak. Material is 304 SS.

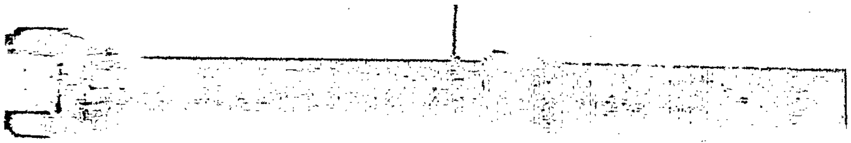
No. 10

10. 100X OXALIC. Transverse section of bend shows pitting extending into transgranular cracks. Other areas on the compression side showed only pits. Cracks were present on the inside surface on the outside radius of the bend.



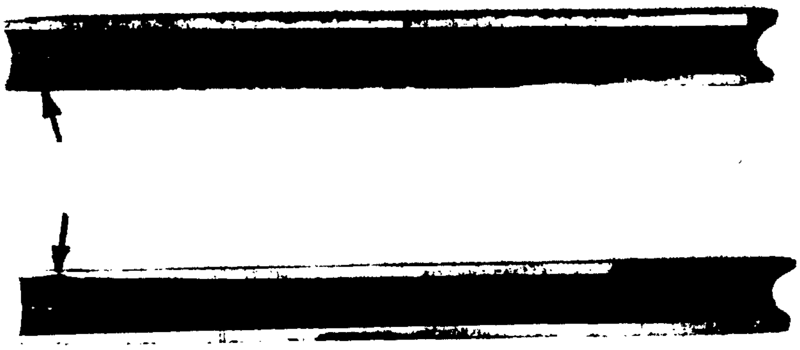
No. 11

11. 100X OXALIC ACID. A longitudinal section on the inside radius of the 90° bend shows only pitting. Cold flow lines denote cold working.



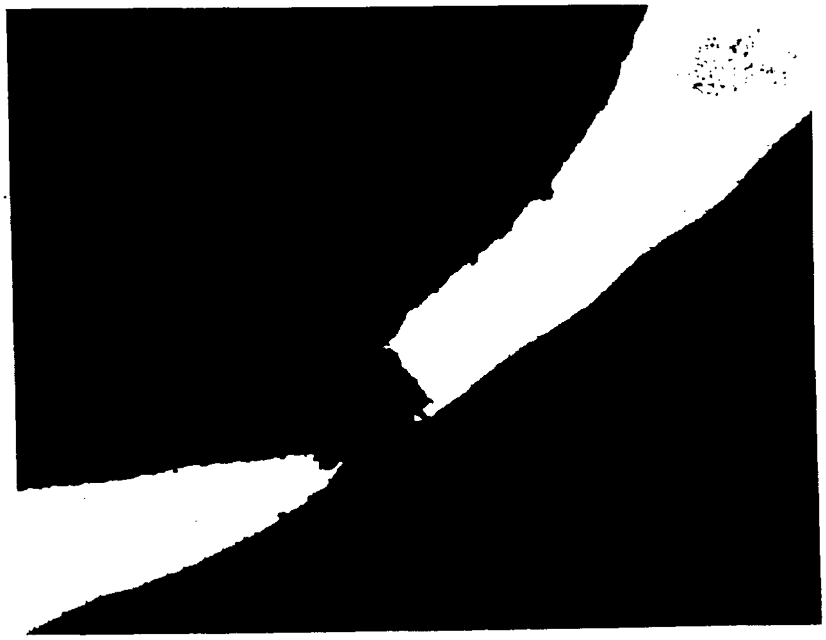
No. 12

12. STRAIGHT SECTIONS OF PIPE INTO COOLER, E-3. Leak occurred at arrow near swedglock fitting. Material is 304 SS.



No. 13

13. PIPE TO E-3 WAS SPLIT OPEN to show localized washing action which caused the hole. Pipe on the other side of the hole in the cooler was of normal thickness.



No. 14

14. 50X OXALIC. No cracking was found, only general washing and pitting.

# APPENDIX A

METALLURGICAL TESTING MTC CORPORATION
19739 SALT LAKE AVENUE, CITY OF INDUSTRY, CALIFORNIA 91745

Area Code 213
964-1294
283-2020

RALPH M. PARSONS COMPANY

DATE August 11, 1975

YOUR P.O. NO.

MATERIAL Stainless Steel

SPECIFICATION

REPORT OF CHEMICAL ANALYSIS

Laboratory No. 75-124M

| Sample Nos. | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| | THERMOCOUPLE | STRAIGHT PIPE TO E-3 | 90° BEND | COIL NO. 3 INLET END |
| Carbon---------- | .06% | .04% | .04% | .02% |
| Manganese------- | 1.38% | 1.62% | 1.61% | 1.48% |
| Silicon--------- | .49% | .53% | .60% | .37% |
| Phosphorous----- | .023% | .025% | .029% | .029% |
| Sulfur---------- | .017% | .015% | .018% | .018% |
| Chromium-------- | 18.15% | 18.29% | 18.09% | 17.90% |
| Nickel---------- | 9.70% | 8.76% | 8.32% | 11.19% |
| Molybdenum------ | .45% | .42% | .45% | 2.31% |
| Copper---------- | .32% | .43% | .48% | .28% |

Analysis indicates samples 1, 2, and 3 to be 304 Stainless Steel and sample number 4 to be 316L Stainless Steel.

## APPENDIX B

# memorandum

**TO:** Project Lignite Staff

**DATE:** July 24, 1975

**FROM:** W.G. Barney, Project Lignite

**RE:** Metal Failures

The following is a summary report of metal failures due to corrosion which have occurred during the conduct of Project Lignite in the period from initial start-up to the present.

## CHRONOLOGICAL ORDER

| Failure | Description |
|---|---|
| No. 1 | On April 15, 1975 a "weep" hole was detected in the side of a 90° bend between S-1 and E-3. The material is 1/2" x 0.083" wall type 304 stainless steel. |
| No. 2 | On April 29, 1975, the helical coil in E-1 was removed from service due to coke plugging. During subsequent attempts to remove the coke a section of the coil broke off. The coil is made of 9/16"OD x 5/16"ID, type 316 stainless steel. This coil has been arbitrarily designated as <u>E-1 Coil No. 1</u>. |
| No. 3 | On June 11, 1975, a second coil in E-1 failed in service. This coil is constructed of the same material as the first. It has been designated as <u>E-1 Coil No. 2</u>. |
| No. 4 | On June 30, 1975, several thermocouple wells were removed from service. These units were all fabricated by Project Lignite technicians and employ a well or sheath made from 1/8"OD type 304 stainless steel. They are used by insertion through tubing tees and crosses. They vary in length but have about 4-5 inch immersion. TR-3-5 and TI-3-12 which are located at each end of E-2 (now air cooled) were removed because of perforation of the sheath and resultant leakage. The perforation was due to erosion, erosion-corrosion and/or pitting. Several other units were removed and found to be in various states of attrition. They were: TI-4-7 (severly erroded), TI-1-10, TI-3-10, TI-2-10 TI-3-1, TI-1-5, TI-4-8, TI-2-1, TI-1-11, (may be replacement for previous leaker), TR-3-4, TI-4-1, and TI-2-6 (3/8"OD). |
| No. 5 | On July 8, 1975, a significant leak developed in the process fluid tube inlet to E-3 cooler. This was subsequently determined to be a longitudinal crack about 3/16" long. The material at this point is 1/2" OD x 0.083" wall, type 304 stainless steel tubing. |
| No. 6 | On July 9, 1975, a third coil in E-1 also failed in service. This coil is designated as <u>E-1 Coil No. 3</u> and is also constructed of type 316 tubing which is 9/16"OD x 5/16"ID. |

No. 7 At various times since installation, some electrical immersion heaters in E-1 have failed. In all instances there has been melting and spalling of the Incoloy sheath.

Of the seven general failures indicated, the loss of the E-1 coils is the most serious. There are several similarities and several differences in the service experience of the first three coils. They are outlined in the following summary. A fourth coil which has just been received from the fabricator is also described.

## E-1 COIL DATA

### Coil No. 1

Supplied by: Autoclave Engineers
Service hours: Approximately 400 hours total. 125 logged hours with coal
 68 logged hours with solvent only.
Coal source: Baukol-Noonan only
Service temperature: 750°F
Max. temperature: 1050°F
Service pressure: 1250 psig
Max. pressure: 1800 psig (hot)
 10,000 psig (cold)
Fluidized media: Spent cat cracker catalyst
Fluidizing media: Dried air (-40°F Dew point)
Coal solvent: FS120 and fractions of FS120 (Gulf)
Gas: Coil exposed internally to both $H_2$ and CO during service.
 Purge gas was nitrogen.
Slurry inlet: Bottom of coil
Tubing material: Type 316, Cold drawn 9/16" OD x 5/16"ID
Chlorides: New spent catalyst = 2.3 ppm
 Used (in E-1) catalyst = 1.7 ppm
 Ottawa sand = 7.4 ppm
 Solvent, FS120 = 38-54 ppm
 Coal = negligible
Fracture location: Bottom of coil
Slurry inlet temp. (all coils): 325°F

### Coil No. 2

Supplied by: Autoclave Engineers
Service hours: 250 total logged hours (approximately 200 hours with coal)
Coal source: About 95% North American
Service temperature: 750°F
Max. temperature: 820°F before failing
 900°F during failure
Service pressure: 1250-1500 psig
Max. pressure: 1800 psig (hot)
 hydrostat (cold)
Fluidized media: Ottawa sand
Fluidizing media: Dried air (-40°F Dew point)
Coal solvent: FS120 and fractions of FS120 (Gulf)

## Coil No. 2 Cont.

Gas: Coil exposed internally to both $H_2$ and CO during service.
Purge gas was nitrogen
Slurry inlet: Bottom of coil
Tubing material: Type 316, cold drawn 9/16"OD x 5/16"ID
Chlorides: See No. 1
Fracture location: Bottom of coil

## Coil No. 3

Supplied by: N.S. Stephens Co., Chicago
Service hours: Cold Solvent = 9 hrs.
Hot solvent = 28 hrs.
Hot solvent & coal = 13 hrs.
Coal source: North American (Zap)
Service temperature: 750°F
Max. temperature: 770°F during service
1400° - 1600°F after failure
Service pressure: 1500 psi
Max. pressure: 1450 psi hot, hydrostat cold
Fluidized media: Ottawa Silica Sand
Fluidizing media: Dried Air (-40°F D.P.)
Coal solvent: Gulf FS120 and recycle solvent (partially coal derived)
Gas: $H_2$ & $H_2$+CO. No $N_2$.
Slurry inlet: Top of coil
Tubing material: Type 316 annealed 9/16"OD x 5/16"ID
Chlorides: See No. 1
Fracture location: Approximately 60 inches in from inlet at top of coil.

## Coil No. 4

Supplied by: N.S. Stephens Co., Chicago
Tubing material: Type 316 annealed 9/16"OD x 5/16"ID
Heat treatment: Stress relief, following coil fabrication, by Lindberg Heat treat of Chicago. Coil held at 1625°F ± 25°F for four (4) hours followed by forced air cooling. Coil was supported in furnace by special basket.
Expected service conditions:

1. Coal to be dried to about 2% moisture before feeding-remainder of moisture to be removed in the slurry vessel.

2. Increase operating pressure to 3000 psi.

3. Hydrogen only will be used.

In attempting to ascertain the causes of failure, several samples were examined locally and others were sent to consultants. The following is a tabulation of sample disposition and status of subsequent evaluations:

## SAMPLE EVALUATIONS

| Sample | Disposition and Evaluation Reports |
|---|---|
| No. 1 | Sections of E-1 coils No. 1 and No. 2 were examined by Project Lignite staff. Evidence of stress corrosion cracking (SCC) was found and documented with photomicrographs. |
| No. 2 | Sections of E-1 coil No. 2 were sent to Ralph M. Parsons on June 25, 1975. A first report dated July 18, 1975, has been received from Parsons. |
| No. 3 | The 90° bend described under Failure No. 1 was given to Norton Berlin of Parsons on July 10, 1975. An oral report only has been received. |
| No. 4 | The tube failure section described under Failure No. 5 was given to Mr. Berlin also on July 10. An oral report has been received. |
| No. 5 | Thermocouple TI-4-7 was also taken to Parsons by Mr. Berlin. An oral report has been received. |
| No. 6 | The top, primarily straight, section of E-1 Coil No. 3 was shipped to Parsons July 14, 1975. No report has been received. |
| No. 7 | Section from bottom of E-1 Coil No. 3 was shipped to Parsons July 18, 1975. No report has been received. |
| No. 8 | Sections of E-1 Coil No. 2 were taken to Gulf R&D by D.E. Severson on June 26, 1975. Copies of a report addressed to Willard Bull dated July 9, 1975, have been received. |
| No. 9 | A straight section of tubing (9/16" x 5/16") was removed from the bottom of R-1A and also taken to Gulf by D.E.S. There was no failure at this point - the section was removed to determine the extent of SCC. No report has been received. |
| No. 10 | A 90° tubing bend was removed from between R-1B and S-1. The history is precisely the same as indicated for sample No. 9. No report has been received. |
| No. 11 | Portions of E-1 Coil No. 1 were sent to Autoclave Engineers. No report has been received and one is not anticipated because it is now apparent that the coil failures are not attributable to faults caused by the fabricator. |
| No. 12 | A failed immersion heater has been sent to the manufacturer, E.L. Weigand. |

## COMMENTS

Mr. R.P. Gulley of Gulf R&D indicated in a telephone conversation July 23, 1975, that Gulf would examine samples Nos. 9 and 10, and submit a report.

Ralph M. Parsons, under their job number 5435-1, is continuing to evaluate all samples sent to them and will report in writing.

The evidence is conclusive and the evaluations are unanimous in designating stress corrosion cracking as the cause of failure of the E-1 coils. "Chlorides" have been specified as the general corrodent by both Parsons and Gulf but neither named a more specific agent.

Other forms of corrosion are identified in the various oral and written reports received to date in explanation of Failures Nos. 1, 4 and 5.

E-1 Coil No. 4 is unique relative to coils 1, 2 and 3 because of stress-relief annealing after coil fabrication. Under the proposed operating conditions, Coil No. 4 will not experience the same service conditions as the first three coils particularly with regard to removal of water from the coal. The question of whether or not stress relief will mitigate coil attack, is thus left unresolved.

The metal failures within the PDU have been discouraging and have obviously impeded progress in the area of principal investigation. However compensatory knowledge can be obtained by correct causality evaluations of the failures.

## RECOMMENDATIONS

1. All material failures should be fully logged indicating when, where, and what.

2. All sections of the system which are removed from service due to failure should be tagged as soon as possible with identifying information: Date, location, nature of failure, and name of engineer ordering removal.

3. A somewhat expanded, more rigorous materials evaluation program should be incorporated as a function within Project Lignite. This would include acquisition of UND staff expertise to conduct studies and to coordinate services required of other consultants. Requests for moderate equipment expenditures should be anticipated.

4. Within the program outlined in No. 3 above or some alternative arrangement, a determination should be made concerning the serviceability of E-1 coil No. 4 under high coal moisture conditions. Preferably this should be done in service in the PDU but only if it is considered to be no more hazardous to personnel than other sections of the system.

5. Other suggested areas of inquiry of immediate concern are:

    a. Extent of SCC in present system.
    b. Evaluation of service potential for stainless steel separators.
    c. Evaluation of sheath deterioration on immersion heaters of E-1.
    d. Determination of construction details including, heat treatment for the proposed Incoloy 800 E-1 Coil (Coil No. 5).
    e. Provide the same information as in (d) above for the two hydrogenation coils now on order.

As previously indicated, this is an initial report. Several investigations are currently in process. Resulting reports will be submitted as the data becomes available.

WGB:djk

September 29, 1975

Dr. D. E. Severson
Department of Chemical Engineering
University of North Dakota
Grand Forks, North Dakota 58201

SUBJECT Project Lignite
Pilot Plant Materials Problems
Reference: ERDA Contract E(949-18)-1775

Dear Dr. Severson:

We have completed the metallurgical test work on the samples submitted to us from the Project Lignite pilot plant. This letter transmits three copies of our metallurgical report on the two samples of expansion loop between the dissolver vessels.

The results of these analyses indicate incipient chloride stress corrosion on the inside surface of the inside radius of both samples which were from high stressed areas of the expansion loop between the dissolvers. It is our considered opinion that future expansion loops should be made of higher nickel alloys such as Incoloy 825 and Carpenter 20 Cb-3.

Also included in this report are comments on recent findings regarding dissolver cracks and a recommended design to avoid this occurrence. We have also included comments on the separators S-1 and S-2.

It should be noted that the metallurgical findings and recommended use of materials such as high nickel alloys are specific to the Project Lignite pilot plant. Special measures can be employed for larger diameter vessels such as cladding or weld overlays which are not practical with small diameters.

This completes our current work on Project Lignite. Please advise if we can be of further assistance to you.

Very truly yours,

THE RALPH M. PARSONS COMPANY

ORIGINAL SIGNED
J. B. O'HARA

J. B. O'Hara
Project Manager

JBO:eb:rs
Enclosures

cc: Dr. J. O. Batchelor, ERDA, Washington
Mr. N. P. Cochran, ERDA, Washington
Mr. E. Schmetz, ERDA, Washington

INTEROFFICE CORRESPONDENCE Date September 11, 1975

To Norton Berlin

From L. T. Overstreet

SUBJECT Job 5435-1 University of North Dakota Pilot Plant
Continuing Materials Problems
Project Lignite

---

Two samples of expansion loop between Dissolvers R-1A and R-1B have been analyzed for metallurgical defects and corrosion. Both samples were from high stressed areas of the loop.

Incipient chloride stress corrosion cracks were found on the inside surface of the inside radius of both the 90° bend and the 180° bend. No cracks were found on the inside surface of the outside radius or in straight sections of tubing.

We have studied the design of the High Pressure Separators S-1 and S-2 and Dissolvers R-1A, R-1B and have enclosed our comments.

## Expansion Loop

Samples from expansion piping between Dissolvers R-1A and R-1B were removed as noted in Attachment No. 1. Photographs No. 1 and No. 2 show numerous cold flow bands and extreme twinning indicating the presence of a high state of cold work. Cracks are transgranular with some tendency for branching but generally straight. Depth of cracks was about .030 inches. Location of cracks at the inside surface of the inside radius would suggest that bending stresses from expansion produced the necessary tensile stresses for cracking. However, we would have expected some cracking on the outside radius if bending from expansion created these stresses. Evidently, residual cold work and "spring-back" in forming the bends acted to oppose stresses caused by expansion and reduced tensile stresses on the outside radius.

Some slight pitting was noted but was generally less than a grain deep.

## Recommended Materials

Future expansion loops should be made of higher nickel alloys to resist chloride stress corrosion cracking. Incoloy 825 and Carpenter 20 Cb-3 would provide both pitting and cracking resistance. Depending on the amount of deflection absorbed by the loop, stresses could be lowered by increasing loop size and radius.

## Dissolver Cracks

Cracks occurring in the 3/4-inch piping to the grayloc hub resulted in leaks and shutdown of the pilot plant. Further inspection reportedly found cracks in the tapped area of the hub.

These cracks could have been caused by chlorides but consideration also must be given to possible thermal fatigue. Insufficient clearance between the screwed pipe and the bottom of the tapped hole in the hub could result in "bottoming." Rapid changes in temperature would have caused the pipe to change dimensions faster than the hub and large stresses would have promoted thermal fatigue cracks in the fillet weld and hub.

## Dissolver Design

The attached sketch shows a recommended method of socket welding the 3/4-inch pipe to the hub. Leaving a gap at the bottom of the socket should avoid bottoming. The pipe and socket/coupling should be made of Incoloy 825, Incoloy 800 or Carpenter 20 Cb 3. The dissolver itself should be made of the above materials if possible. However, long deliveries may require using 316 SS.

The large thickness of a 316 SS hub should be sufficient to lower general stress below that causing chloride stress corrosion cracking. Localized stress from welding may promote cracking at the pipe to hub weld and if 316 SS must be used for the hub, we recommend overlaying the joint with a high nickel chloride stress cracking resistant material such as RA-333.

The thermocouple pipes attached to the side of the dissolver also present a potential cracking situation from chlorides or thermal fatigue. These socket joints should provide a gap to avoid bottoming.

## Separators

Engineers at the Masoneilan company in Los Angeles were consulted to determine how the Separators S-1 and S-2 were constructed. The high pressure chambers and flanges are made with ASTM A 351 Grade CF8M which is a 316 SS casting. The small pipe spools at each end of the chamber are fabricated from A 269-Grade TP 316 pipe and cast CF8M flanges. These liquid level controllers are constructed to ASMB Section VIII but no radiography or liquid penetrant inspection is performed.

Possible chloride cracking in these separators will depend on stress level. Code construction means operational stresses will be less than one-quarter of the tensile strength of CF8M. With heavy wall thicknesses, multipass welds should have been used which will effect stress relief of initial weld passes. In addition cast stainless steel usually contains about 2% to 15% ferrite which inhibits chloride cracking.

We conclude that the main components of the separators will be resistant to chloride cracking because of ferrite and low stresses. However, small single pass welds, bottomed-out pipes and imposed stresses due to piping loads may cause localized cracking. We suggest that piping attachments be inspected for possible high stresses similar to the dissolvers.

L. T. Overstreet

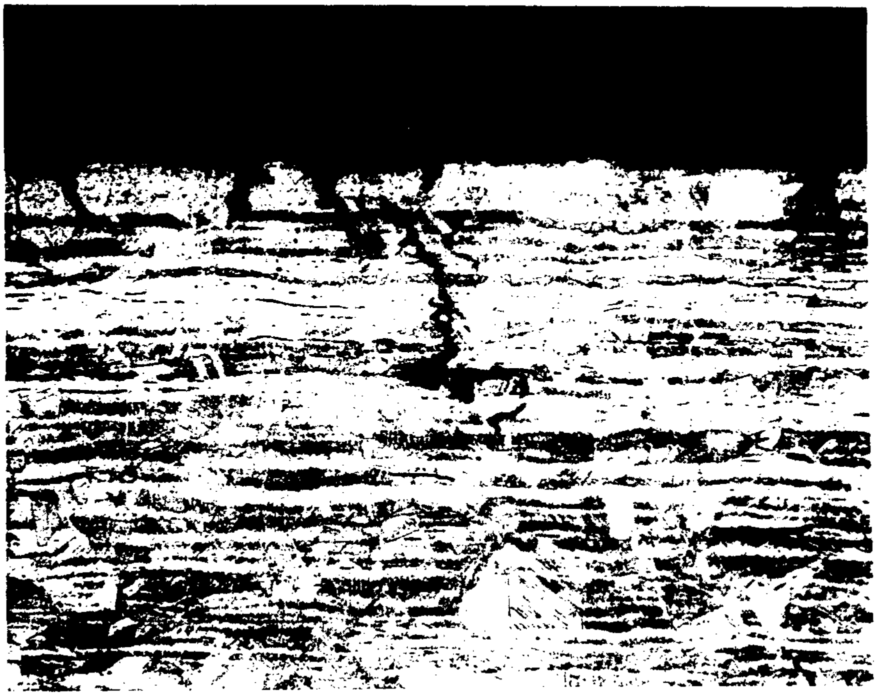
LTO:hh

Attachments

CC: W. J. Lochmann
J. B. O'Hara

Photograph 1

Cracks on inside surface of inside radius of the 90° bend. Grain twinning and banding indicate extreme cold working. Cracks exemplify the initial phases of chloride stress corrosion cracking. Oxalic acid, 100X.

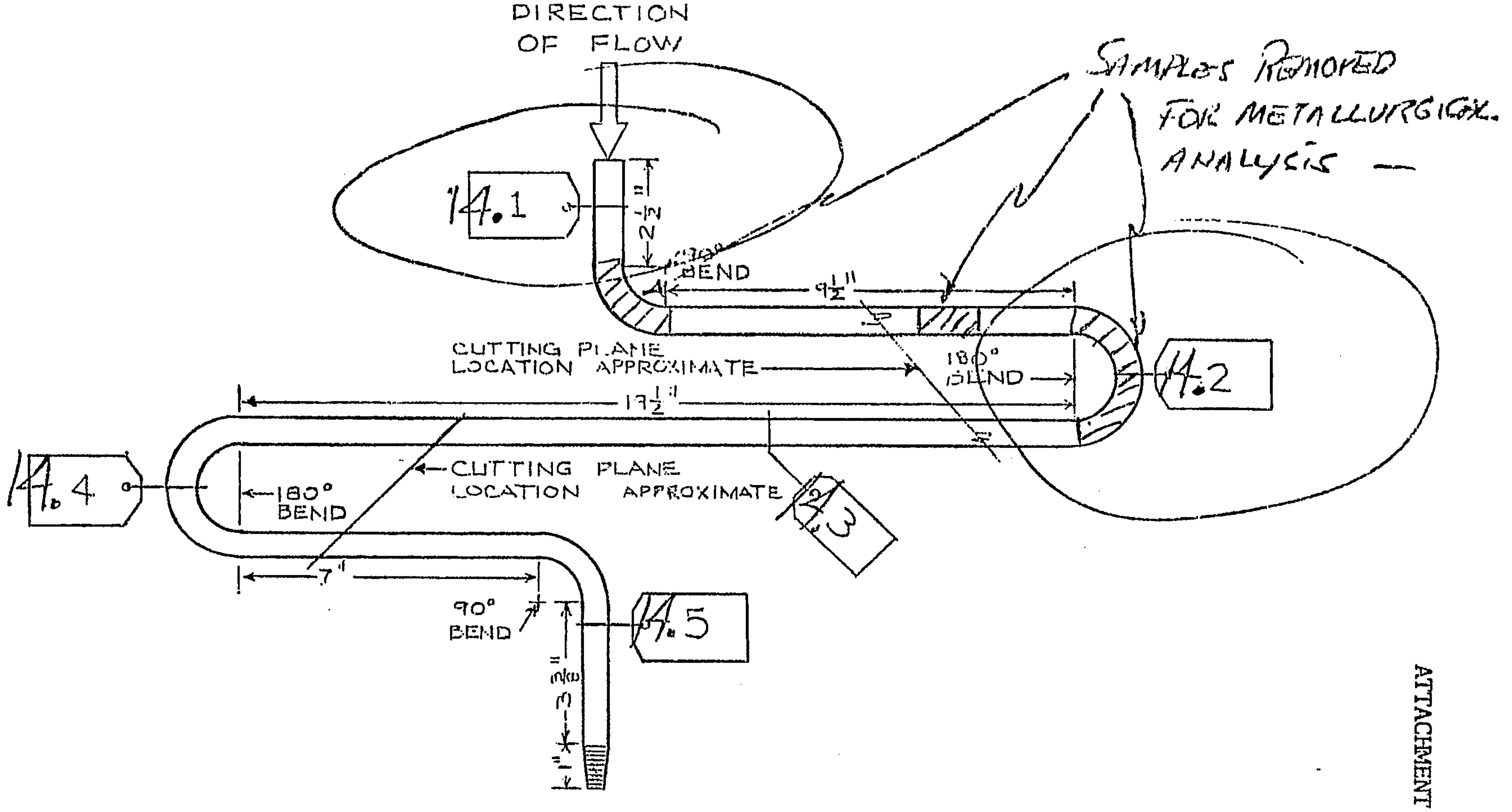


Photograph 2

Cracks in a similar area as Photograph No. 1 on the 180° bend. A state of high cold work is evident. Many cracks seemed to end as tangles of small branch cracks about .050" deep. Oxalic acid, 100X.

NOTES:

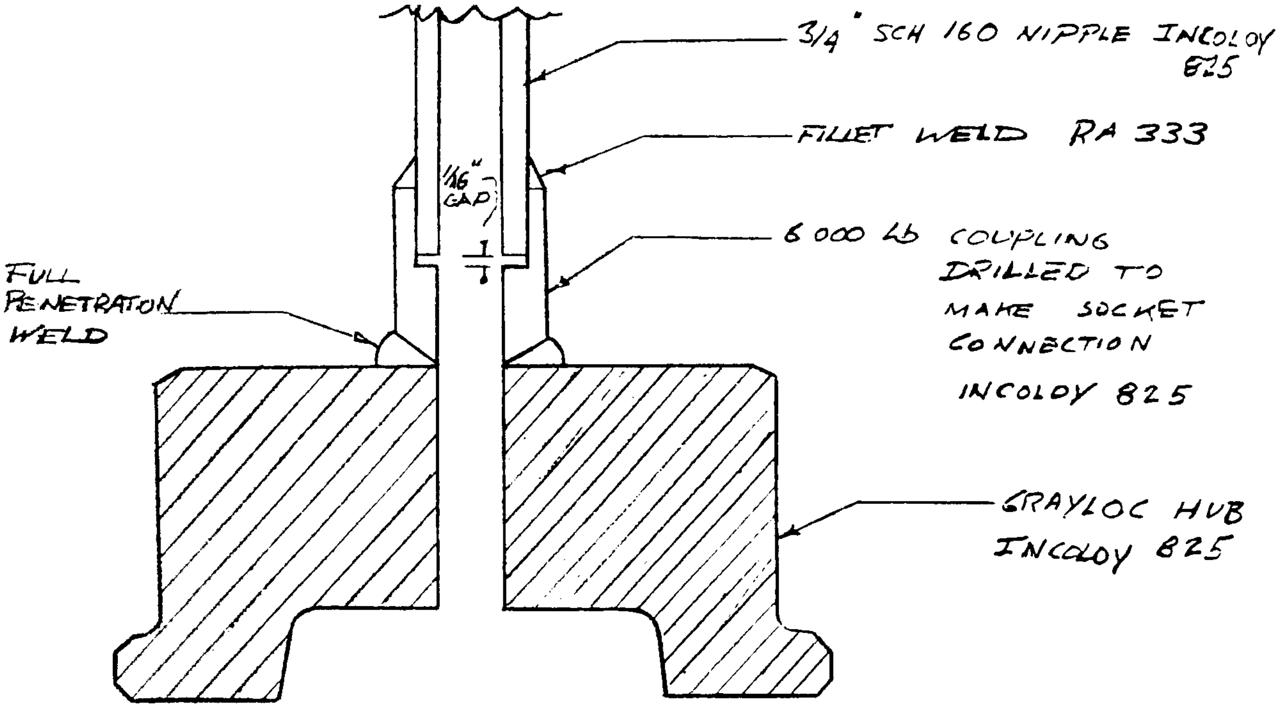
1. TUBING IS $\frac{1}{16}$" O.D x $\frac{5}{16}$" I.D 316 S.S.
2. ALL BENDS SHALL HAVE A 1" RADIUS



REMOVED FROM LINE CONNECTING TOP OF R-1A TO BOTTOM OF R-1B
LOCATED NEAR R-1B INLET

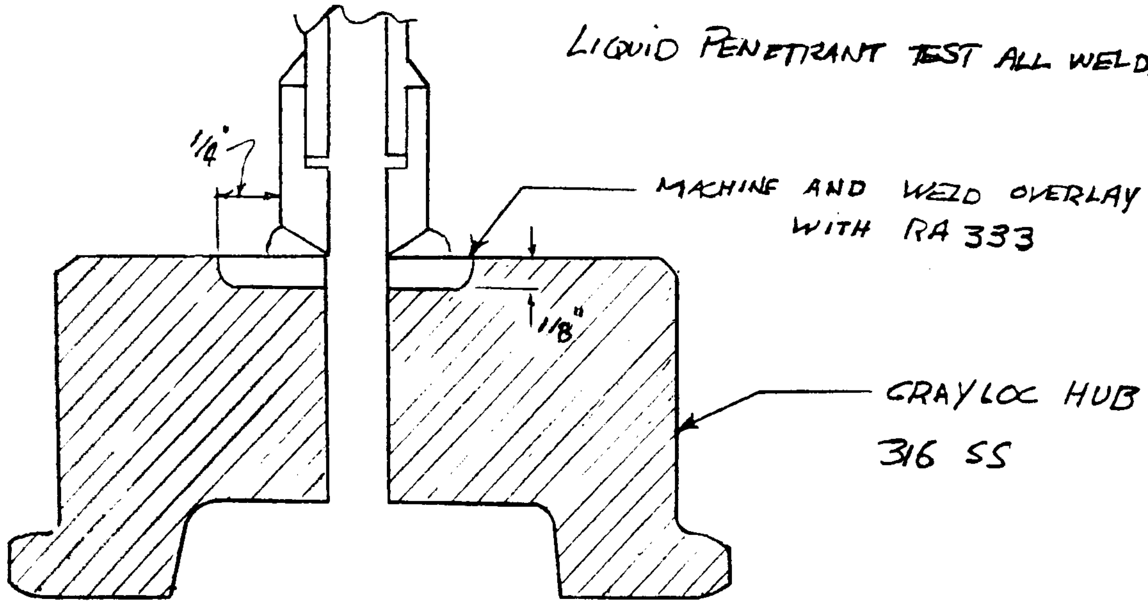
ATTACHMENT 1

ATTACHMENT 2



1ST CHOICE – USE INCOLOY 825 HUB

LIQUID PENETRANT TEST ALL WELDS



2nd CHOICE – USE 316 SS HUB WITH RA 333 WELD OVERLAY.

# APPENDIX B

## DISCUSSION OF RESULTS OF PROJECT LIGNITE ACTIVITIES

Contained in this appendix is a compilation of the results of Project Lignite activities to date covering both PDU operations and laboratory studies as published in 49 monthly and 7 quarterly progress reports over the last 4 years. The detailed results of laboratory studies conducted, analyzed, and interpreted by UND are summarized here for reference.

| Contents | Page |
|---|---|
| B.1 Phase I Lignite Solubilization | B-2 |
| B.1.1 PDU Operations | B-2 |
| B.1.2 Laboratory Studies | B-3 |
| A. Effect of Cation Addition | B-4 |
| B. Evaluation of Liquefaction Solvents | B-4 |
| C. Solvent Recycle Series | B-14 |
| D. Effect of Lignite Storage | B-14 |
| E. Effect of Reducing Conditions | B-14 |
| F. Effect of Dehydration Liquefaction | B-16 |
| G. Miscellaneous Parameters | B-19 |
| B.2 Phase II Carbonization of Lignite | B-21 |
| B.3 Phase III SRL Upgrading | B-22 |
| B.4 Phase IV Direct Hydrogenation of Lignite | B-25 |

# APPENDIX B

# DISCUSSION OF RESULTS OF PROJECT LIGNITE ACTIVITIES

Since 1972 to the present, Project Lignite has performed laboratory studies and operated a PDU for the development of the SRL process. The PDU design was based on the laboratory work and recommendations by P & M Coal Mining Co. Over 850 hours of PDU operations have been logged in and about 300 laboratory autoclave runs made in support of the PDU program. The results of the completed experimental work are discussed below.

## B.1 PHASE 1 LIGNITE SOLUBILIZATION

### B.1.1 PDU OPERATIONS

The Process Development Unit (PDU) construction was completed in December 1974 and initial startup in January 1975.

The design was based on processing approximately 50 lbs/hr of lignite to about 15 lbs/hr of SRL. The basic process steps incorporated in the PDU are illustrated in the block flow diagram in Figure 1 of Section 2. The PDU facility and operations are briefly described in the following paragraphs.

Lignite from the mine is brought in by rail car, split into representative samples, and stored in nitrogen purged bins. The coal is crushed and ground and stored in 55 gallon drums which are transported from the Coal Preparation Building to the PDU building for slurry preparation.

The slurry is prepared by blending the lignite with recycle lignite-derived solvent in a mix tank, pumped to reactor pressure (2,500 psig) and preheated in an electrically heated coil immersed in a fluidized solids sand bath.

After preheating to 750°F at 2,500 psig, the mixture enters the dissolver reactors which are equipped with interconnecting piping to provide a variety of residence times which includes, but are not limited to, 15 minutes to one hour. The reactor effluent flows to the gas separation equipment where non-condensible gases and light hydrocarbon vapors are separated from the slurry product in a series of five separation vessels where the pressure and temperature are reduced in stages. The effluent gases from the initial high pressure separation stage are processed through the gas recovery area to remove acid gases such as $CO_2$ and $H_2S$ in order to provide a means for recycling a portion of the $CO/H_2$ syngas back to the preheater inlet.

The product slurry is processed through a vacuum flash unit to recover solvent for recycle. The bottoms from the vacuum flash unit must be further processed to remove the ash residue and unconverted coal from the SRL product. Since the solid-liquid separation section is not yet operable, this separation is currently being performed in the laboratory by filtration of small batches.

A complete description of the PDU, with detailed flow diagrams and P&ID's, is contained in ERDA Report No. 106--FE-1224-T-1 dated September, 1974.

During the initial shakedown runs in the first half of 1975, operational and minor equipment problems were observed and corrected. However, during operations in June 1975, a sudden rupture of the preheater coil caused an unexpected shutdown. Analysis of this occurrence indicated chloride stress corrosion was the cause. Copies of our failure analysis reports are included in Appendix A of this report. This problem resulted in failure of 3 successive stainless steel preheater coils as well as failure of other downstream components including equipment associated with the dissolver reactors. As a result, replacement parts fabricated of Incoloy 800 were installed since this material is resistant to stress-corrosion cracking. This occurrence and associated delays due to new equipment installation resulted in very little productive information from the PDU, for the period of June to December 1975.

Installation of the new equipment was completed in January of 1976 and the PDU again started up in February, 1976. Since the startup, no further major equipment failures have occurred and the PDU has made about 11 runs each of about one week of continuous operation and logged in an additional 500 hours. PDU shakedown operations are complete and routine operation is in progress at baseline liquefaction conditions. Parameter studies are expected to commence in the near future.

### B.1.2 LABORATORY STUDIES

The laboratory studies were carried out for the most part in the Project Lignite laboratory with a batch autoclave. Since 1972 to present, about 200 autoclave runs were made covering the following items:

(1) Effect of Cation Addition

(2) Evaluation of Liquefaction Solvents

(3) Solvent Recycle Series

(4) Effect of Lignite Storage

(5) Effects of Reducing Conditions

(6) Effect of Dehydration Liquefaction

(7) Miscellaneous Parameters

- Filtration Temperature
- Reaction Time
- Particle Size of Lignite
- Phenol Pretreatment of Lignite

When it was felt that the data warranted it, we developed correlations and performed data analysis. For convenience the applicable autoclave runs are tabulated with reference to the Project Lignite Progress Reports. In addition Project Lignite R&D Report No. 106 Interim Report No. 2, when published, will contain the tabulated results of the autoclave runs. Table B-1, located in this Appendix, is an example of the data tables available.

## A. Effect of Cation Addition

The coal liquefaction process is generally believed to benefit from the catalytic effects of naturally occurring cations present in coal.

Therefore, a study was conducted to investigate the effects of cations on liquefaction yield parameters. The tests were conducted in the laboratory using the batch autoclave in which various cations such as Na, K, Fe, Ca, Co, Ni, Mo and a Ni-Mo catalyst were added to lignite prior to liquefaction. The lignite samples had undergone prior extraction of the naturally occurring cations in order to allow the effect of the added cations to be investigated.

The data collected from the autoclave runs, were tabulated in Project Lignite Progress Reports as referenced in Table B-2.

In general, at the high level of cation additions, all cations except Na and Ni resulted in low or intermediate yields of liquids. At all cation concentration levels tested, Mo appeared to catalyze extensive breakdown of the lignite to lower molecular weight components resulting in high yields of gas and light oils. Ni apparently limited conversion to desired liquid and light oil products with low yields of gaseous components.

The conclusion drawn from these tests by UND is that the naturally occurring cations present in the as-mined lignite appear to provide sufficient catalytic action to give high yields of liquid products. Addition of cations did not indicate any significant improvement in reactivity for production of desired liquid products.

## B. Evaluation of Liquefaction Solvents

For coal liquefaction, a solvent is employed to slurry the coal so it can be pumped and heated to reactor conditions. The solvent must also provide a vehicle for hydrogenation of the coal and dissolution of the liquified products.

## Table B-1 - Example Data Table
## Part 1: Effect of Storage on Lignite Reactivity - 24-36 Weeks
## Material Balance and Yield Data (Sheet 1 of 3)

| | 24-WEEKS STORAGE | | | | 36-WEEK STORAGE | | | |
|---|---|---|---|---|---|---|---|---|
| Run No. | 539 | 540 | 541 | 542 | 561 | 562 | 563 | 564 |
| **Test Conditions** | | | | | | | | |
| Time, hrs. | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Avg. Temp., °F | 750 | 750 | 750 | 750 | 752 | 752 | 752 | 752 |
| Max. Press., psia | 3070 | 2970 | 3110 | 3000 | 3075 | 3125 | 3125 | 3145 |
| Gas Charged | $CO/H_2$ | | | | | | | |
| Solvent | UNDCAO-74 | | | | | | | |
| Lignite | 73-2(B) | | | | | | | |
| | $N_2$ Strg | $H_2O$ Strg | Air Strg | $H_2O$ Strg | $N_2$ Strg | Air Strg | Air Strg | $H_2O$ Strg |
| **Material In, grams** | | | | | | | | |
| Coal & $H_2O$ | 323.1 | 318.0 | 323.5 | 321.9 | 323.5 | 324.2 | 324.4 | 316.9 |
| Solvent | 399.8 | 400.2 | 399.9 | 400.0 | 400.5 | 400.4 | 400.7 | 399.9 |
| Gas | 151.2 | 156.7 | 153.5 | 150.7 | 153.4 | 153.3 | 150.4 | 152.0 |
| Total | 874.1 | 874.9 | 876.9 | 872.6 | 877.4 | 877.9 | 875.5 | 868.8 |
| **Material Out, grams** | | | | | | | | |
| Filtrate | 458.5 | 448.8 | 429.3 | 450.1 | 447.0 | 413.3 | 427.9 | 437.2 |
| Filter Cake | 79.3 | 68.5 | 104.1 | 84.7 | 91.9 | 104.3 | 105.5 | 96.6 |
| Residues | 17.7 | 39.5 | 16.4 | 16.9 | 21.0 | 20.7 | 24.9 | 20.5 |
| Gas | 216.7 | 225.6 | 213.7 | 218.5 | 204.3 | 214.3 | 215.8 | 215.3 |
| $H_2O$ | 78.8 | 59.1 | 79.4 | 72.7 | 74.6 | 78.9 | 78.3 | 70.0 |
| Light Oil | 3.0 | 4.3 | 4.0 | 2.8 | 2.1 | 3.4 | 4.1 | 2.4 |
| Total | 854.0 | 845.8 | 846.9 | 845.7 | 840.9 | 834.9 | 856.5 | 842.0 |
| **% Recovery** | 97.7 | 96.7 | 96.6 | 96.9 | 95.8 | 95.1 | 97.8 | 96.9 |
| **Yields 100% Recovery Basis** | | | | | | | | |
| **Product, grams** | | | | | | | | |
| Light Oil | 29.1 | 22.0 | 29.5 | 20.6 | 29.4 | 36.6 | 29.2 | 34.5 |
| Solvent | 379.0 | 405.8 | 382.4 | 395.3 | 397.3 | 367.5 | 388.3 | 379.7 |
| Vac. Btms | 126.3 | 105.2 | 117.6 | 122.4 | 118.6 | 120.0 | 114.0 | 126.1 |
| Total Liquid | 534.4 | 533.0 | 529.5 | 538.3 | 545.3 | 524.1 | 531.5 | 540.3 |
| Net Liquids | 134.6 | 132.8 | 129.6 | 138.3 | 144.8 | 123.7 | 130.8 | 140.4 |
| Net Gas | 70.6 | 76.7 | 67.8 | 74.7 | 59.8 | 72.0 | 70.2 | 70.2 |
| Net $H_2O$ | -19.1 | -38.7 | -17.6 | -24.8 | -22.0 | -16.9 | -19.9 | -27.8 |
| Net Ash | -3.0 | -- | -0.6 | -2.3 | -1.6 | -0.5 | -1.9 | -1.0 |
| Unconverted Coal (MAF) | 16.7 | 12.6 | 20.8 | 13.9 | 19.5 | 22.1 | 21.2 | 18.4 |
| **Yields Wt% MAF Coal** | | | | | | | | |
| Net Gas | 35.3 | 41.7 | 33.8 | 37.4 | 29.8 | 36.0 | 35.0 | 35.1 |
| Net Liquid | 67.5 | 72.4 | 64.8 | 69.1 | 72.2 | 61.7 | 65.3 | 70.1 |
| Unconverted | 8.3 | 6.9 | 10.4 | 7.0 | 9.8 | 11.0 | 10.6 | 9.2 |
| Net $H_2O$ + Ash | -11.1 | -21.0 | -9.0 | -13.5 | -11.8 | -8.7 | -10.9 | -14.4 |
| **Total Liquid Composition (Wt%)** | | | | | | | | |
| Light Oil | 5.5 | 4.1 | 5.6 | 3.8 | 5.4 | 7.0 | 5.5 | 6.4 |
| Solvent | 70.9 | 76.1 | 72.2 | 73.5 | 72.9 | 70.0 | 73.1 | 70.3 |
| Vacuum Btms | 23.6 | 19.8 | 22.2 | 22.7 | 21.7 | 23.0 | 21.4 | 23.3 |
| **Net Liquid (Wt% MAF Coal)** | | | | | | | | |
| Net Light Oil | 14.5 | 12.0 | 14.7 | 10.3 | 14.7 | 18.2 | 14.6 | 17.2 |
| Net SRL | 53.0 | 60.4 | 50.1 | 58.8 | 57.5 | 43.5 | 50.7 | 52.9 |
| **Solvent Recovery** | | | | | | | | |
| Wt% | 92.6 | 98.0 | 92.3 | 95.8 | 95.0 | 87.3 | 94.8 | 92.0 |
| Wt% (100% Rec. Basis) | 94.8 | 101.4 | 95.6 | 98.8 | 95.5 | 91.8 | 96.9 | 94.9 |

## Table B-1 - Example Data Table
## Part 2: Effect of Storage on Lignite Reactivity - 24-36 Weeks
## Analytical Data (Sheet 2 of 3)

| | 24 WEEKS STORAGE | | | | 36-WEEK STORAGE | | | |
|---|---|---|---|---|---|---|---|---|
| **Run No.** | 539 | 540 | 541 | 542 | 561 | 562 | 563 | 564 |
| **Test Conditions** | | | | | | | | |
| Time | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Avg. Temp., °F | 750 | 750 | 750 | 750 | 752 | 752 | 752 | 752 |
| Max. Press., psia | 3070 | 2970 | 3110 | 3000 | 3075 | 3125 | 3125 | 3145 |
| Gas Charged | $CO/H_2$ | | | | | | | |
| Solvent | UNDCAO-74 | | | | | | | |
| Lignite | 73-2(B) | | | | | | | |
| | $N_2$ Strg | $H_2O$ Strg | Air Strg | $H_2O$ Strg | $N_2$ Strg | Air Strg | Air Strg | $H_2O$ Strg |
| **Analytical Data** | | | | | | | | |
| 1. Gas Analysis, Mol% | | | | | | | | |
| $H_2$ | 42.6 | 41.7 | 44.7 | 42.5 | 42.1 | 43.1 | 40.5 | 43.3 |
| $CH_4$ | 1.0 | 0.9 | 0.8 | 1.0 | 0.9 | 1.0 | 0.7 | 0.9 |
| CO | 23.0 | 16.6 | 23.0 | 20.7 | 22.3 | 22.4 | 23.5 | 18.6 |
| $C_2H_6$ | 0.5 | 0.4 | 0.3 | 0.6 | 0.4 | 0.4 | 0.4 | 0.4 |
| $CO_2$ | 32.5 | 38.6 | 30.8 | 34.5 | 33.8 | 32.8 | 34.5 | 36.2 |
| $H_2S$ | 0.4 | 1.8 | 0.4 | 0.7 | 0.5 | 0.3 | 0.4 | 0.6 |
| Gas Specific Gravity @RT | 0.774 | 0.791 | 0.761 | 0.796 | 0.777 | 0.773 | 0.775 | 0.746 |
| 2. Input Coal | | | | | | | | |
| Volatile Matter, Wt% | 27.88 | 29.82 | 29.37 | 32.67 | 29.21 | 32.39 | 32.11 | 29.80 |
| Ash, Wt% | 7.25 | 11.45 | 7.50 | 7.23 | 7.49 | 8.12 | 8.05 | 5.44 |
| Moisture, Wt% | 30.51 | 26.89 | 29.15 | 26.78 | 27.72 | 23.90 | 24.57 | 30.07 |
| Carbon, Wt% (1) | 63.56 | 59.48 | 62.32 | 61.52 | 64.90 | 63.14 | 63.14 | 66.16 |
| Hydrogen, Wt% (1) | 4.48 | 4.03 | 4.45 | 4.63 | 3.85 | 3.85 | 3.85 | 4.07 |
| Sulfur, Wt% (1) | 0.99 | 6.70 | 1.00 | 1.50 | 1.03 | 1.04 | 1.08 | 0.75 |
| 3. Input Solvent | | | | | | | | |
| Ash, Wt% | 0.06 | 0.06 | 0.05 | 0.05 | 0.04 | -- | -- | -- |
| Carbon, Wt% | 90.55 | 91.18 | 90.89 | 90.94 | 91.67 | 91.00 | 90.81 | 89.50 |
| Hydrogen, Wt% | 6.03 | 5.99 | 5.97 | 6.07 | 5.92 | 5.84 | 6.02 | 5.94 |
| Sulfur, Wt% | 0.61 | 0.62 | 0.65 | 0.62 | 0.55 | 0.59 | 0.58 | 0.53 |
| Specific Grav. 60/60 | 1.125 | 1.116 | 1.117 | 1.116 | 1.114 | 1.119 | 1.124 | 1.154 |
| IR Ratio | 1.7 | 1.8 | 1.8 | 1.8 | 1.77 | 1.77 | 1.77 | 1.77 |
| 4. Coal-Solvent Slurry | | | | | | | | |
| 5. Cake | | | | | | | | |
| Ash, Wt% | 24.07 | 33.41 | 20.51 | 21.23 | 21.54 | 20.40 | 19.31 | 15.15 |
| Carbon, Wt% | 64.57 | 60.44 | 69.23 | 67.11 | 67.91 | 69.07 | 67.95 | 72.71 |
| Hydrogen, Wt% | 4.25 | 4.02 | 4.46 | 4.60 | 4.35 | 4.60 | 4.71 | 4.83 |
| Sulfur, Wt% | 1.57 | 6.61 | 1.64 | 2.36 | 1.42 | 1.63 | 1.45 | 0.64 |
| Pyridine Sol., Wt% | 76.01 | 77.30 | 78.41 | 82.62 | 77.23 | 78.24 | 79.89 | 81.69 |

(1) Calculated on a moisture-free basis.

## Table B-1 - Example Data Table
## Part 2 (Contd): Effect of Storage on Lignite Reactivity - 24-36 Weeks
## Analytical Data (Sheet 3 of 3)

| Run No. | 539 | 540 | 541 | 542 | 561 | 562 | 563 | 564 |
|---|---|---|---|---|---|---|---|---|
| 6. Filtrate | | | | | | | | |
| Ash, Wt% | -- | 0.08 | 0.08 | 0.14 | 0.03 | 0.04 | 0.02 | 0.04 |
| Carbon, Wt% | 89.44 | 88.99 | 87.80 | 89.12 | 88.66 | 89.15 | 87.60 | 88.84 |
| Hydrogen, Wt% | 6.42 | 6.54 | 6.37 | 6.48 | 6.31 | 6.28 | 6.26 | 6.22 |
| Sulfur, Wt% | 0.53 | 0.53 | 0.49 | 0.49 | 0.46 | 0.44 | 0.41 | 0.39 |
| Blackness abs./g. @550 mu | -- | -- | -- | -- | 5.78 | 6.66 | 6.54 | 7.77 |
| 7. Vacuum Btms | | | | | | | | |
| Ash, Wt% | 0.10 | 0.57 | 0.24 | 0.55 | 0.17 | 0.14 | 0.20 | 0.12 |
| Carbon, Wt% | 85.39 | 83.47 | 83.96 | 84.07 | 85.92 | 85.26 | 85.76 | 84.70 |
| Hydrogen, Wt% | 6.15 | 6.55 | 6.03 | 6.36 | 5.88 | 6.04 | 5.80 | 5.81 |
| Sulfur, Wt% | 0.26 | 0.48 | 0.30 | 0.33 | 0.27 | 0.28 | 0.29 | 0.28 |
| Melting Point, °F | -- | -- | -- | -- | 297.4 | 288.1 | 308.5 | 286.6 |
| 8. Residue | | | | | | | | |
| Ash, Wt% | 15.70 | 33.16 | 8.46 | 6.29 | 7.60 | 4.83 | 7.77 | 3.39 |
| Carbon, Wt% | 72.95 | 60.87 | 78.35 | 81.93 | 79.17 | 85.26 | 80.91 | 76.66 |
| Hydrogen, Wt% | 5.23 | 4.56 | 5.76 | 6.02 | 5.25 | 6.11 | 5.73 | 5.31 |
| Sulfur, Wt% | 1.23 | 8.94 | 1.06 | 2.03 | 1.04 | 0.59 | 0.65 | 0.54 |
| Pyridine Sol., Wt% | 93.48 | 95.13 | 95.59 | 98.64 | 100.0 | 92.45 | 93.52 | 97.87 |
| 9. Light Oil | | | | | | | | |
| Carbon, Wt% | 80.73 | -- | 83.15 | 77.26 | 84.64 | 83.92 | 84.07 | -- |
| Hydrogen, Wt% | 9.32 | -- | 8.92 | 10.48 | 8.53 | 8.55 | 8.50 | -- |
| Sulfur, Wt% | 0.44 | -- | 0.45 | 0.60 | 0.39 | 0.47 | 0.54 | 0.44 |
| 10. Product Solvent | | | | | | | | |
| Ash, Wt% | 0.02 | 0.03 | 0.02 | 0.02 | 0.03 | 0.01 | -- | 0.02 |
| Carbon, Wt% | 91.27 | 90.37 | 90.19 | 90.78 | 90.38 | 90.85 | 88.81 | 87.69 |
| Hydrogen, Wt% | 6.66 | 6.50 | 6.28 | 6.54 | 6.46 | 6.35 | 6.21 | 5.93 |
| Sulfur, Wt% | 0.51 | 0.57 | 0.55 | 0.52 | 0.55 | 0.45 | 0.42 | 0.47 |
| Specific Grav. 60/60 | 1.105 | 1.102 | 1.106 | 1.105 | 1.119 | 1.114 | 1.114 | 1.113 |
| IR Ratio | 0.97 | 0.81 | 0.99 | 0.89 | 0.95 | 0.97 | 0.98 | 0.99 |

## Table B-2 - Data Source Index
## Cation Studies

| CATION | RUN NO. | REFERENCE (PROGRESS REPORT NO.)[a] |
|---|---|---|
| Sodium | 415 | 3 |
| | 425 | 5 |
| | 426 | 5 |
| Potassium | 423 | 5 |
| | 453 | 11 |
| Calcium | 416 | 3 |
| | 431 | 6 |
| | 456 | 12 |
| Iron | 424 | 5 |
| | 428 | 5 |
| Cobalt | 427 | 5 |
| | 429 | 6 |
| | 437 | 7 |
| Nickel | 432 | 6 |
| | 433 | 6 |
| | 435 | 7 |
| Molybdenum | 434 | 7 |
| | 436 | 7 |
| HDS-3A Cat | 438 | 7 |
| | 439 | 7 |
| HDS-3A | 520 | 24 |
| None | 421 | 4 |
| | 454 | 11 |
| | 455 | 11 |

[a] Project Lignite Monthly Progress Report No.

For the most part, anthracene oil has been generally used as solvent for laboratory tests. Due to limited supply of this material and the large volumes required for PDU unit startup operations, a study was conducted to evaluate commercially available solvents. The study utilized both coal-derived and petroleum-derived solvents tested in the batch autoclave under standardized lignite liquefaction conditions. Conditions selected for these tests were 30 minutes reaction time, 750°F, initial pressure 1,000 psig with 50% CO/50% $H_2$. Solvent performance was evaluated based on the following criteria:

(1) Product yields

(2) Characteristics of the SRL product

(3) Characteristics of the solvent recovered from liquefaction tests

(4) Ease of handling of the solvent

(5) Percentage of "standard" cut in as-received solvent

The standard cut in solvent distillation is the fraction obtained in the temperature range of 100 to 230°C at a pressure of 1.6 mm Hg. Light oil is the fraction from 0 to 100°C, and heavy ends that between 230°C to 255°C. For some tests, the raw or "as-received" solvent was used directly. In others, the standard solvent cut was used, and for some, the solvent was hydrogenated before use.

Table B-3 contains the list of solvents tested and corresponding autoclave run numbers with reference to Project Lignite Progress Reports where the data are tabulated.

For the coal derived solvents, using standard distillation cuts, yields of light oil were higher than when the heavy oils or as-received solvents were used. When hydrogenated, creosote oil as solvent resulted in higher light oil yields than when not hydrogenated, although hydrogenation had no apparent effect on light oil yields in the anthracene oil solvent tests.

Filtration characteristics for product liquids-solids slurry rated by Project Lignite personnel from best to worst in the following sequence depending on solvent used: creosote oil, light creosote oil, anthracene oils, middle-heavy creosote oils. Ease of handling of the as-received coal derived solvent on a best to worse series was: anthracene oil, light creosote oil, creosote oils, middle-heavy creosote oil.

For the petroleum derived solvents, low light oil yields were obtained with the carbon-black feedstock (FS-120), the aromatic concentrate, and #5 fuel oil when distilled to the standard cut. Some as-received solvents also gave low light-oil yields. These were the heavy aromatic

Table B-3 - Data Source Index
Liquefaction Solvent Studies

| COAL DERIVED | SOLVENT DESIGNATION | RUN NO. | DESCRIPTION | REFERENCE (PROGRESS REPORT NO.)[a] |
|---|---|---|---|---|
| Raw Creosote Oil | UNDRCO-73 | 463 | Topped-Heavy End Cut | 14 |
| | UNDRCO-72(2) | 447 | Standard - Solvent Cut | 9 |
| | UNDRCO-73 | 491 | Standard - Solvent Cut | 18 |
| | | 458 | | 12 |
| | UNDHRCO-72 | 464 | Topped - Hydrogenated Heavy Ends Cut | 14 |
| Chilled Creosote Oil | UNDCCO-73 | 462 | Topped - Heavy Ends Cut | 14 |
| | | 475 | Standard Solvent Cut | 16 |
| | | 474 | Hydrogenated - Standard Cut | 16 |
| Raw Anthracene Oil | UNDRAO-73 | 511 | Topped - Heavy Ends Cut | 22 |
| | UNDRAO-73 | 455 | Standard Solvent Cut | 11 |
| | UNDHRAO-73 | 468 | Hydrogenated Standard Solvent Cut | 15 |
| Chilled Anthracene Oil | UNDCAO-73 | 510 | Topped - Heavy Ends Cut | 22 |
| | UNDCAO-73 | 465 | Standard Solvent Cut | 15 |
| | UNDCAO-73 | 483 | Standard Solvent Cut | 17 |
| | UNDCAO-73 | 484 | Standard Solvent Cut | 17 |
| | UNDHCAO-73 | 471 | Hydrogenated - Standard Solvent Cut | 15 |
| | UNDHCAO-73 | 480 | Hydrogenated - Standard Solvent Cut | 16 |
| Light Creosote Oil | USSLTCO-73 | 503 | As Received | 20 |
| Middle-Heavy Creosote Oil | USSMHCO-73 | 507 | As Received | 21 |
| | USSMHCO-73 | 508 | As Received | 21 |

[a] Project Lignite Monthly Progress Report No.

Table B-3 (Contd)

| PETROLEUM DERIVED | SOLVENT DESIGNATION | RUN NO. | DESCRIPTION | REFERENCE (PROGRESS REPORT NO.)[a] |
|---|---|---|---|---|
| Heavy Aromatic Naphtha | | 460 | As Received | 13 |
| | EXXON HAN-73 | 519 | As Received | 23 |
| NO. 6 Fuel Oil | UNDF06-73 | 473 | Standard Solvent Cut | 16 |
| | UNDF06-73 | 478 | Standard Solvent Cut | 16 |
| NO. 5 Fuel Oil | UNDF05-73 | 513 | As Received | 22 |
| | UNDF05-73 | 486 | Standard Solvent Cut | 17 |
| Aromatic Tar | EXXON AT52-73 | 496 | As Received | 19 |
| | EXXON AT52-73 | 509 | As Received | 21 |
| | EXXON AT52-73 | 495 | Standard Solvent Cut | 20 |
| Aromatic Concentrate | EXXON AC-73 | 500 | As Received | 20 |
| | EXXON AC-73 | 506 | As Received | 21 |
| | EXXON AC-73 | 494 | Standard Solvent Cut | 19 |
| | EXXON AC-73 | 501 | Standard Solvent Cut | 20 |
| Carbon Black Feedstock | GulfFS120-73 | 514 | As Received | 22 |
| | GulfFS120-73 | 485 | Standard Solvent Cut | 17 |
| | GulfFS120-73 | 497 | Standard Solvent Cut | 19 |
| LSX-745 | | 609 | As Received (Nelville Chemical Co.) | 42 |
| PAMCO | | 611 | Recycle Process Solvent From Tacoma | 43 |
| | | 612 | Recycle Process Solvent From Tacoma | 43 |
| FS-120 | | Avg. of 19 Runs | Carbon Black Feedstock (Gulf) | 42 |

[a] Project Lignite Monthly Progress Report No.

naphtha, the carbon-black feedstock, and the aromatic concentrate. Yield of standard cut solvent obtained from the as-received solvents ranged from 42.2 to 55.4 wt% except for the carbon-black feedstock (FS-120) in which case the yield was 65.9 wt%. Ease of handling of the petroleum derived solvent from best to worse was estimated by the Project Lignite personnel as:

(1) Carbon-black feedstock and heavy aromatic naphtha

(2) Aromatic concentrate and the fuel oils

(3) Aromatic tar

Filtration separation of the unconverted material and the SRL was superior with the carbon-black feed stock, (FS-120), aromatic tar and aromatic concentrate as solvents to that obtained using heavy aromatic naphtha and the fuel oils as solvents.

During the liquefaction process, sulfur content of the solvent fraction was reduced in all cases. All solvents used on the as-received basis showed a net increase in the amount of standard cut solvent after one pass through the liquefaction step. Recovery of solvent was sufficiently high for the standard cut solvents to indicate that the process might be self sustaining except for the aromatic tar and aromatic concentrate.

The following is a description of results of tests made with solvents as noted below:

Light creosote oil - a low fraction of suitable solvent cut in the as-received solvent.

Middle-heavy creosote oil - solvent gave operating difficulties as it was difficult to handle and gave poor filtration characteristics. The SRL had a high sulfur content and a reduced H:C ratio.

Heavy aromatic naphtha - a high fraction of light oil in as-received solvent and poor filtration characteristics of product slurry.

Fuel Oils - poor filtration characteristics for both, and excessive yield of gas with #5 oil.

Aromatic tar - reduced solvent recovery and a relatively high gas yield for the standard cut fraction. Initial solvent was difficult to process.

PAMCO process solvent - gave reduced SRL recovery and showed evidence of cracking when used for liquefaction of lignite.

FS-120 solvent - carbon-black feedstock from Gulf: Solvent gave good SRL recovery, low light oil yields, good handling and filtration characteristics.

LSX-745 solvent - a petroleum derived solvent from Neville Chemical Co. gave results comparable to FS-120.

Several general conclusions regarding the various solvents are:

(1) On the as-received basis, the fraction of standard cut solvent present were higher for the coal-derived than the petroleum-derived solvents.

(2) Hydrogenation of coal-derived solvents prior to use significantly changed properties of creosote oils but did not for anthracene oils.

(3) During processing, coal-derived solvents were more highly hydrogenated than the petroleum-derived solvents as indicated by infrared analyses.

(4) Some hydrodesulfurization of all solvents except the aromatic tar was evident during processing.

(5) A net increase in standard cut solvent was noted when processing as-received or heavy ends input solvents indicating that some heavy ends distillable from the SRL should be included as recycle solvent.

(6) Gas yields, water consumption, and the fraction of unconverted material were nearly the same for most solvents although standard solvent cuts from coal-derived solvents gave higher light oil yields than did the petroleum-derived solvents.

(7) The SRL had a higher sulfur content when obtained using petroleum-derived solvents than with coal-derived solvents. The higher sulfur content of the petroleum-type solvents apparently retards desulfurization of the SRL.

The results of the solvent evaluation study, as reported by Project Lignite personnel, indicated that of all the solvents tested, based on availability and cost, carbon black feedstock (FS-120), anthracene oil, and creosote oil appear to be the most promising liquefaction. Based on availability and cost, FS-120, the carbon black feedstock, is the best selection for PDU startup solvent with LSX-745 as a possible satisfactory substitute.

### C. Effect of Lignite Storage

Based on tests conducted over a total of 70 weeks, we performed data analysis which indicated that there appeared to be no significant change in liquefaction properties of lignite stored under water or in nitrogen (air-free) environments. Air storage of lignite showed a light decrease in lignite reactivity. More details of these test results are presented in Section 4 of this report.

### D. Solvent Recycle Series

For this test series, we performed an analysis of the data and generated correlations. These are discussed in more detail in Section 4 of this report. In general, the results of recycle solvent tests showed no evidence of solvent degradation and strong indications that the PDU would be able to attain steady state operation on FS-120 after initial startup. The data correlations indicated a trend of solvent hydrogenation and desulfurization with number of recycle passes.

### E. Effects of Reducing Conditions

Prior to the start of PDU operations, a series of batch autoclave runs were made by Project Lignite Personnel to evaluate the effect of reducing conditions on liquefaction of lignite. The purpose of this work was to determine the effects of reducing gas composition with and without solvent on lignite conversion and product yields. The tests were conducted using North American 74-1 (E) lignite. Reducing gases used were hydrogen, carbon monoxide, and a 50/50 mixture of $H_2/CO$ (syngas). For these tests, pyridine extraction was used to determine conversion. The data collected from this test series were tabulated in Project Lignite Progress Reports as reference in Table B-4. The following is a summary of results from recent tests conducted:

| Reducing Agent | Run No. | Wt% Conv.* | Liq. Yield, Wt%* |
|---|---|---|---|
| None | 599 | 30 | 4 |
| $H_2$ | 601 | 69 | 38 |
| $H_2/CO$ | 598 | 83 | 54 |
| CO | 591 | 94 | 63 |
| Solvent | 600 | 48 | 19 |
| Solvent, $H_2$ | 603 | 78 | 50 |
| Solvent, $H_2/CO$ | 607 | 96 | 64 |
| Solvent, CO | 602 | 96 | 81 |

*Based on MAF Lignite.

Table B-4 - Data Source Index
Effects of Reducing Conditions

| RUN NO. | REFERENCE (PROGRESS REPORT NO.)[a] |
|---|---|
| 591 | 39 |
| 597 | 39 |
| 598 | 40 |
| 599 | 40 |
| 600 | 40 |
| 601 | 40 |
| 602 | 40 |
| 603 | 40 |
| 606 | 41 |
| 607 | 41 |
| 608 | 41 |

[a] Project Lignite Monthly Progress Report No.

As shown in the above table, CO plus solvent gave the highest net yield of SRL and highest conversion. Conversion and liquid production was still high with only CO and no solvent. The syngas run with solvent represents the most attractive reducing conditions for PDU operation since use of pure CO would probably be impractical.

## F. Effect of Dehydration on Liquefaction

From a process standpoint, lignite dehydration would limit the water-gas shift reaction when using syngas as the hydrogenation agent and thereby, reduce the concentration $CO_2$ in the product gas. This would reduce the size of the acid gas removal facilities required for the recycle gas in a commercial facility with a corresponding impact of about 2 to 3% reduction in plant major equipment costs. Another point worth mentioning is that dehydration of the lignite could reduce stress - corrosion cracking experienced in the PDU since moisture in the presence of chloride ions accelerates the stress corrosion process.

For the above reasons, a series of batch autoclave tests were conducted to determine the impact of dehydration on lignite liquefaction. The first series of tests compared baseline yields with dehydrated lignite using $CO/H_2$ (syngas). One run was made using pure $H_2$. Solvents used were chilled Anthracene oil and carbon-black feedstock (FS-120).

The test results are summarized in the following table:

| Run No. | 484 | 530 | 532 | 497 | 531 |
|---|---|---|---|---|---|
| Dehydration | no | yes | yes | no | yes |
| Reaction Gas | $CO+H_2$ | $CO+H_2$ | $H_2$ | $CO+H_2$ | $CO+H_2$ |
| Solvent | -Chilled Anthracene Oil- | | | Carbon Black Feedstock | |
| Yields, Wt% MAF Lignite | | | | | |
| Gas | 43.9 | 12.5 | 13.1 | 38.2 | 20.5 |
| Liquid | 61.0 | 46.1 | 54.2 | 63.4 | 36.0 |
| Unconverted | 8.0 | 35.3 | 23.9 | 9.8 | 41.6 |
| Water | -12.9 | 6.1 | 8.8 | -11.4 | 1.9 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| Light Oil | 15.1 | 14.6 | 11.5 | 10.6 | 9.7 |
| Net SRL | 45.9 | 31.5 | 42.7 | 52.8 | 26.3 |
| $CO_2$, Mol% | 32.0 | 12.3 | 0.1 | 35.1 | 12.3 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| Filtration Index, Ml./Min. | 27 | 1 | 19 | 75 | 69 |
| Progress Report No. | 17 | 25 | 26 | 29 | 26 |

Conversion of lignite during liquefaction was reduced significantly by the drying process as compared with baseline tests using nearly full moisture content lignite. Both liquid and gas yields were also lower although liquid yields with hydrogen were higher than with synthesis gas. Operational problems were increased because of reduction in filtration rates using the dehydrated lignite. However, carbon dioxide content in the product gas was reduced.

Generally, because of the adverse effect on liquefaction characteristics by dehydration, drying prior to liquefaction does not appear to be advantageous. A similar conclusion was previously reached when air dried lignite was processed under otherwise normal liquefaction conditions.

A second series of dehydration tests were conducted to determine if there would be any generation of liquids suitable as vehicles for drying purposes. Also of value would be any sulfur reduction during the severe drying. If the method proved feasible, an oil based drying system could be devised which would dehydrate and treat the lignite in one operation so as to improve handling and shipping characteristics.

The dehydration conditions were reported in Project Lignite Progress Report No. 32. Briefly, the lignite was mixed with solvent in the autoclave, the mixture purged with $N_2$ at atmospheric pressure while heating to 400°F over about 1 1/2 hours.

A summary of pertinent data from the two drying tests on a 100 percent recovery, MAF basis, is as follows:

| Run No. | 569 | 570 |
|---|---|---|
| Drying Agent | Chilled Anthracene Oil | #2 Fuel Oil |
| Yield, Wt% MAF Lignite |  |  |
| Gas | 0.5 | 2.9 |
| Liquid | -7.5 | -13.3 |
| Unconverted | 101.0 | 106.5 |
| Water | 6.0 | 3.9 |
|  | 100.0 | 100.0 |
| Percent of Total Filtrate in Residue | 13.7 | 6.5 |

The negative liquid yields indicate both solvents have either polymerized or reacted with components of the lignite. The percentages of unconverted material greater than 100 indicate that the organic content of the coal increased because of some reaction with the solvent. In addition, the positive yields of water may be due to the thermal removal of chemically-bound water or hydroxyl groups from the coal. It seems that No. 2 fuel oil is more reactive in this regard than chilled anthracene oil. Sulfur removal from the coal was negligible for both solvents.

It appears that at 400°F drying temperature, the No. 2 fuel oil shows less physical retention on the surface of the coal particles than chilled anthracene oil; however, it has a greater tendency to polymerize or react with the coal components and remain in a solid, or at least an insoluble, form.

As there was appreciable loss of drying medium with the solid material, it appears that there was no net generation of liquids so the process is not self sustaining. The extent of solvent loss resulted in high makeup requirements that would make the process unattractive, since no improvement other than moisture reduction was apparent.

A third series of dehydration experiments were conducted to further evaluate the effect of a pure hydrogen atmosphere on lignite liquefaction. The following results were obtained:

| Run No. | Average | 604 | 605 |
|---|---|---|---|
| Atmosphere | $H_2/CO$ | $H_2$ | $H_2$ |
| Moisture | Yes | No | No |
| Yield, % MAF Lignite | | | |
| Gas | 34.0 | 13.3 | 11.5 |
| Liquid | 64.6 | 59.5 | 52.3 |
| Unconverted | 11.4 | 16.0 | 23.7 |
| $H_2O$ + Ash | -10.0 | 11.2 | 12.5 |
| Total | 100.0 | 100.0 | 100.0 |
| Light Oil | 6.6 | 11.0 | 10.6 |
| Net SRL | 58.0 | 48.5 | 41.6 |
| Progress Report No. | | 40 | 41 |

Unconverted lignite was higher in the hydrogen atmosphere tests using dried lignite than when moist lignite and a syngas atmosphere was used. Yields of SRL were lower and light oil higher. More gas was produced in the syngas atmosphere because of carbon dioxide produced by reaction with the moisture. Although conversion of lignite was reduced in the hydrogen atmosphere with dried lignite, conversion is thought to be sufficient for operation of the PDU, especially since light oil production increased.

### G. Miscellaneous Parameters

1. Filtration Temperature. To facilitate laboratory solid-liquid separations following batch autoclave runs, a series of experiments were performed by Project Lignite personnel to determine a suitable filtration temperature. These tests were made using standard liquefaction conditions as described in the previous sections and anthracene oil as solvent. Filtration temperatures were varied from 500°F to 400°F by adjusting the temperature at which the slurry was discharged from the autoclave. The data collected for this series of test are tabulated in Project Lignite Progress Report No. 4.

The results indicated that temperatures of 450°F to 500°F caused problems with solvent volatilization and corresponding increased slurry viscosity and poor filtration rates as reported by Project Lignite personnel based on visual observations in the laboratory. Temperatures of 400°F to 425°F gave good filtration rates with no noticeable solvent volatilization.

These results indicate that 400°F is a reasonable temperature when anthracene oil is the solvent. For other solvents, the filtration temperature will be dependent on the solvent volatility as well as slurry viscosity.

2. Reaction Time. In order to evaluate the effect of reaction time on lignite liquefaction characteristics, a brief series of tests were conducted by Project Lignite personnel in which the reaction time in the autoclave was held at 30 minutes and 2 hours. The data collected for this series of tests are tabulated in Project Lignite Progress Report No. 4.

The following results were obtained:

| Run No. | 419 | 418 |
|---|---|---|
| Reaction Time | 30 min. | 2 hrs |
| Yield, wt% MAF Lignite | | |
| Net gas | 35.2 | 49.3 |
| Net liquid | 68.7 | 56.8 |

The above results indicate that reaction times greater than around 30 minutes, result in excessive decomposition of the lignite causing higher gas yields and reduced liquid yields.

This brief test indicates that the liquefaction process is quite rapid and therefore, reactor residence times for the PDU should be relatively short to avoid excessive decomposition of desirable liquid products.

3. Particle Size of Lignite. Previous lignite liquefaction information had indicated that it was necessary to pulverize the coal to -100 mesh to achieve rapid reaction rates. However, this criterion has a measurable cost impact if required for a commercial plant. Therefore, a brief study of two runs were made in the batch autoclave, using standard liquefaction conditions previously described, where coal particle size was evaluated for liquefaction characteristics.

For this study, lignite was tested at -100 mesh and -0.25 inch for a comparison of resulting product yields. The data collected for this series of tests are tabulated in Project Lignite Progress Report No. 17.

The following table illustrates the results:

| Run No. | 483 | 487 |
|---|---|---|
| Lignite size | -100 mesh | -0.25 inch |
| Yields, Wt% MAF | | |
| Net gas | 46.9 | 45.6 |
| Net Product | 56.9 | 61.0 |
| Unconverted coal | 8.9 | 4.7 |

The above data indicates that, within the size range tested, particle size is not a significant factor in lignite liquefaction.

4. Phenol Pretreatment of Lignite. When treated with phenol, coals are known to swell indicating that certain constituents in the coal have an affinity for phenol. Therefore, it was felt that phenol pretreatment of lignite might improve liquefaction characteristics.

To test this approach, a series of tests were conducted in the autoclave in which lignite was pretreated with a phenol-water mixture prior to liquefaction. The data collected for this test series is tabulated in Project Lignite Progress Report No. 37.

For these tests, undehydrated lignite was used as feed and treated with aqueous phenol ranging from 30 to 100% phenol. In one instance, phenol was added directly to the autoclave just prior liquefaction.

Generally, following the phenol treatment the lignite was washed with warm water to remove excess phenol. After the rinse step, the lignite was processed using standard liquefaction procedures.

The following table summarizes the test results:

| Run No. | PTR-1 | PTR-2 | PTR-3 | PTR-4 | PTR-5 | PTR-6 |
|---|---|---|---|---|---|---|
| Yields, Wt% MAF Lignite | | | | | | |
| Net Gas | 47.9 | 39.4 | 40.4 | 42.1 | 56.3 | 37.0 |
| Net Liquid | 64.2 | 52.0 | 62.2 | 56.2 | 62.9 | 68.9 |
| Unconverted | 6.1 | 10.0 | 8.8 | 6.2 | 5.5 | 7.1 |
| Net $H_2O$+Ash | -18.2 | -1.5 | -11.4 | -4.5 | -24.7 | -12.7 |

Conditions

PTR-1, Base; PTR-2, 100% Phenol treat, 212°F wash, light rinse;

PTR-3, 100% phenol treat, 140°F wash, light rinse;

PTR-4, 100% phenol treat, Ambient wash, light rinse;

PTR-5, phenol treat, crystals added;

PTR-6, 100% phenol treat, light rinse.

The results of these tests indicate only relatively minor changes in product yields when compared to the baseline run PTR-1. Therefore, it was concluded by U.N.D., that phenol treatment is an unnecessary process step.

## B.2 PHASE II CARBONIZATION OF LIGNITE

The objective of this work is to conduct carbonization studies of typical lignite to determine yields of liquids, solids, and gas. Methods will be developed for upgrading each of the major products.

Bench-scale attempts were made to incorporate carbonization into the process technology. Treatment of the lignite by carbonization prior to liquefaction was considered as a means to improve liquefaction characteristics. Potentially, initial mild carbonization could drive off some of the large amounts of oxygen present in young coals such as lignite as $CO_2$, and therefore improve hydrogenation during the lignite liquefaction step.

Carbonization conditions were 700°F and 30 minutes with and without solvent. Following the carbonization, standard liquefaction procedures, as described in the preceding sections, were followed. The results of these tests as shown in the following table, indicated that prior carbonization was only partially effective in evolving $CO_2$.

Most of the $CO_2$ was still evolved after liquefaction. Also substantial amounts of $CH_4$ were evolved during both process steps.

Moles of Gas Evolved/100 Lbs Dry Lignite

| | Carbonization | | Liquefaction | | Total | | |
|---|---|---|---|---|---|---|---|
| Run | $CO_2$ | $CH_4$ | $CO_2$ | $CH_4$ | $CO_2$ | $CH_4$ | Progress Report No. |
| 451 | 0.261 | 0.025 | 0.955 | 0.064 | 1.216 | 0.089 | 10 |
| 452 | 0.216 | 0.078 | 0.882 | 0.049 | 1.098 | 0.127 | 10 |
| 457 | 0.170 | 0.022 | 1.008 | 0.092 | 1.178 | 0.114 | 12 |
| 455 (Base Line) | | ----- | 1.459 | 0.096 | 1.459 | 0.096 | 11 |

It was also observed and reported by Project Lignite that liquid yields from liquefaction were significantly reduced when the lignite was precarbonized. Any appreciable pyrolysis and even drying, appeared to significantly decrease the reactivity of the lignite toward liquefaction, and therefore, any gain in yields by carbonization were more than offset by loss in yields in attempting to convert the remaining char. No further work is planned in this area.

## B.3 PHASE III SRL UPGRADING

The objective of this work was to develop a process for upgrading the solid SRL product from the liquefaction of lignite. This would permit conversion of lignite to more desirable premium low sulfur liquid fuels. The approach for achieving this objective was to use a two step process. The first step is conventional liquefaction utilizing low or mild severity conditions in the dissolvers. The second step is catalytic hydrogenation of the SRL products from the first step. The current state-of-the-art of catalytic hydrogenation involves the use of special catalysts which are easily poisoned by certain feed components such as trace amounts of arsenic and other related heavy metals present in the coal. With a two step process the liquefaction process at the front end offers the potential of removing these undesirable catalyst poisons.

For the reasons stated above, a study was conducted with SRL as feed to catalytic hydrogenation using a batch autoclave. The work was done by the UND Chemistry Department using a batch autoclave, under a subcontract from Project Lignite. Approximately 90 hydrogenation runs were made on both SRL and SRC to determine the effect of processing conditions on conversion to distillable liquid products. These runs examined the effects of catalyst type, pressure, temperature, and solvent. The run data are summarized in tables attached to Project Lignite R&D Report 106 Interim Report No. 3 which is expected to be published in the near future.

The SRL used in most of the hydrogenation tests were from P&M's Merriam, Kansas laboratory and was produced from North Dakota lignite. The SRC was also from P&M's laboratory from a blend of Kentucky #9 and #14 coals.

Catalysts tested, as described in Table B-5, are typical commercially available hydrogenation catalysts from Harshaw and Air Products Company. Four of the Harshaw catalysts were presulfided using hydrogen sulfide prior to testing.

The first series of runs established baseline conditions and used tetrahydrofuran (THF) as the solvent. However, further tests showed that tetralin was a better solvent than THF due to its higher critical temperature and ability to donate hydrogen. Based on these initial experiments, general conditions selected by the UND Chemistry Department personnel for catalyst testing were: initial hydrogen pressure of 2,500 psig, 700°F reaction temperature, tetralin solvent, and two hours residence time.

Utilizing the above standard test conditions, a series of batch autoclave tests were performed to evaluate the various catalysts for upgrading SRL. The effect of presulfiding was examined using Ni-W-$Al_2O_3$, CO-Mo-$Al_2O_3$, and Ni-Mo-$Al_2O_3$ catalysts.

In general, presulfiding the catalysts gave a higher yield of lower boiling fractions than the non-presulfided catalysts. Of the catalysts tested, the presulfided Ni-Mo-$Al_2O_3$ catalyst gave the highest conversion of SRL to gaseous and liquid products.

Following these catalyst screening tests, a series of experiments were conducted using presulfided Ni-Mo-$Al_2O_3$ in order to develop optimum conditions for SRL hydrogenation. These experiments examined catalysts conditioning, pressure, temperature, and solvent requirements. The results of this series of tests as reported by UND analysis of the data were as follows:

(1) Catalyst conditioning in a hydrogen atmosphere prior to use had essentially no effect on SRL conversion and therefore, this step was considered an unnecessary procedure.

(2) The effect of pressure in the range of 1,000 psig to 2,500 psig indicated that increasing pressure resulted in increased conversion up to 2,500 psig. Further pressure increases had no significant effect on conversion.

(3) The effect of temperature in the range of 700°F to 840°F showed that SRL conversion increased almost linearly with temperature. However, at temperatures greater than 840°F, excessive hydrocracking occurs. Based on these findings and product yield data, 840°F was selected to be most favorable for this test series.

Table B-5 - Catalysts Used in SRL Hydrogenation

| Catalyst | Supplier | Trade Name | Composition, Wt. pct. | Pore Vol. cc/g | Surface Area $m^2/g$ | Shape |
|---|---|---|---|---|---|---|
| $Co-Mo-Al_2O_3$ | Harshaw | Co-Mo-0401-T | 3 CoO, 9 $MoO_3$ | 0.40 | 160 | 1/8" tablets |
| $Co-Mo-Al_2O_3$ | Harshaw | Co-Mo-0402-T | 3 CoO, 15 $MoO_3$ | 0.40 | 200 | 1/8" tablets |
| $Ni-W-Al_2O_3$ | Harshaw | Ni-4303-E | 6 Ni, 19 W | 0.54 | 152 | 1/12" extrudates |
| $Ni-W-SiO_2-Al_2O_3$ | Harshaw | Ni-4301-E | 6 Ni, 19 W | 0.37 | 228 | 1/12" extrudates |
| $Al_2O_3$ | Harshaw | Al-1404-T | 97 $Al_2O_3$ | 0.42 | 180 | 1/8" tablets |
| $Ni-Mo-Al_2O_3$ | Harshaw | HT-100-E | 3.8 Ni, 16.8 Mo | 0.54 | 190 | 1/16" extrudates |
| Zeolite | Houdry | HZ-1 | 45 $Al_2O_3$, 53 $SiO_2$ | --- | 100-150 | 0.2" pellets |
| Nickel | Harshaw | Ni-1404-P | 68% Ni | --- | 115 | powder |
| $WS_2$ | Alfa Inorganics | | | | | powder |
| $SnCl_2$ | | | | | | |
| $SnCl_2-Al_2O_3$ | | | | | | |

(4) The effect of solvent type, and solvent to SRL ratio was studied by UND as regards its effect on SRL conversion. In general, UND concluded that tetralin was best, but that a commercial grade solvent such as carbon black feedstock (FS-120) was almost as good. Solvent to SRL ratio studies indicated that a ratio of 1 to 1 was optimum.

Finally, a series of tests were conducted to determine if the catalytic conversion process is applicable to both SRC as well as SRL prepared from different sources. Samples of SRC and SRL from P&M at Kansas City, and SRC from Tacome were tested along with samples of SRL from both batch autoclave and the PDU from Project Lignite. In general, the results of these tests showed that regardless of source, SRL or SRC can be converted to distillable liquids under the reaction conditions developed for SRL upgrading.

In conclusion, the initial baseline tests established general conditions for the catalyst comparisons. These conditions consisted of an initial hydrogen pressure of 2,500 psig, 50% catalyst by weight, tetralin solvent, and 700°F reaction temperature. Under these conditions, a total of eight catalysts were tested with SRL. The best two were Ni-Mo-$Al_2O_3$ (Harshaw HT-100) and stannous chloride catalyst, which yielded high conversion of SRL to distillable liquid products. The next series of batch autoclave experiments utilized presulfided catalysts. Here, Ni-Mo-$Al_2O_3$ was more effective in removing the heteroatoms nitrogen and oxygen, and gave higher conversions. The study of reaction temperature indicated that the conversion of SRL to distillable liquid and gases increased almost linearly with reaction temperature over the range studied, with a high of 88 percent conversion at 840°F. In the solvent experiments, tetralin was shown to be the best solvent, but in the absence of solvent a relatively high conversion was still obtained. The solvent refined coals, (SRC and SRL) regardless of their sources, could be converted to gases and distillable liquids in relatively high yields under the reaction conditions developed primarily for SRL conversion. From these experiments, conditions for the most effective conversion of SRL are: initial hydrogen pressure of 2,500 psig, tetralin solvent, presulfided HT-100 catalyst, 840°F and two hours reaction time.

The results of these tests showed that catalytic hydrogenation of SRL and SRC is technically feasible. However, the final choice for use of this process step will be dependent on economic considerations in order to evaluate the impact of the higher capital and operating costs for production of a higher priced premium product.

## B.4 PHASE IV DIRECT HYDROGENATION OF LIGNITE

The objective of this phase of work is to conduct studies on continuous low-pressure hydrogenation of lignite to determine product distribution and yield under a range of operating conditions.

Direct hydrogenation of lignite involves contacting pulverized lignite with hydrogenation gas such as $CO/H_2$ in the presence of a catalyst.

Prior to initiation of continuous low pressure hydrogenation studies, Project Lignite attempted to explore direct hydrogenation of lignite using available autoclave data. These runs are discussed under Phase I laboratory studies with catalyst effects discussed under "Effect of Cations" and hydrogenation effects discussed under "Effect of Reducing Conditions." So far a catalyst system has not yet been selected based on the preliminary nature of the data. The design of a continuous unit will commence when sufficient bench-scale data permit selection of processing conditions and a catalyst system. However, due to pressing problems with the PDU and associated bench scale work on liquefaction, no further work is currently planned.

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