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ZINC HALIDE HYDROCRACKING PROCESS FOR DISTILLATE FUELS FROM COAL

Quarterly Technical Progress Report
for the Period:
May 1 to July 31, 1976

CONOCO COAL DEVELOPMENT COMPANY
Research Division
Library, Pennsylvania 15129

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PREPARED FOR THE UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

Under Contract No. E(49-18)-1743

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ABSTRACT

The bench-scale, continuous, zinc chloride hydrocracker operated through May and completed production of 300 pounds of spent catalyst for regeneration studies. The Colstrip subbituminous coal used in this work gave a distillate oil yield of over 50 wt. % of the MAF coal.

The bench-scale, continuous regenerator operated throughout the quarter, exploring the operating limits as affected by temperature and percentage of HCl in the feed air. Good burn-out of carbon and sulfur in natural spent catalyst was demonstrated. From 0.5 to 1.5% of the zinc fed remains with the coal ash collected via cyclone. Batch studies have shown that up to 94% of this zinc can be recovered by simple secondary treatment of these solids.

Approval was received from ERDA to proceed with construction and operation of the 100 pound per hour Process Development Unit. Placing of orders is underway.

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Tables

I. Objective and Statement of Work

A. Objective

1. The objective of this contract is the production of clean liquid and gaseous fuels of which approximately 50 percent will be distillate, equivalent to four barrels per ton of coal on a moisture, ash-free (MAF) basis.

2. The work to be performed under this contract will be directed toward conducting a systematic experimental study, entailing both continuous bench-scale and process development unit work on the above process, involving investigation of zinc halide as a Lewis acid "catalyst" for the hydrogenation and hydrocracking of coal extract and of subbituminous coals and development of an economical regeneration process for the efficient recovery of zinc halide from the spent melt.

B. Statement of Work (Abbreviated)

The following experimental work will be performed to demonstrate the viability and economic potential of the zinc halide hydrocracking process for production of distillate fuels from coal with economic regeneration and recycle of the zinc halide.

Task 1 Refurbish Existing Continuous Unit

The existing continuous bench-scale zinc halide hydrocracking unit (2 lb/hr capacity) and the continuous fluidized-bed combustion unit for regeneration of spent zinc halide melt (5 lb/hr capacity) will be refurbished. This will include modification of the hydrocracking feed system to permit feeding of coals.

Task 2 Continuous Bench-Scale Hydrocracking

An experimental program will be conducted to demonstrate the utility of the continuous bench-scale hydrocracking unit for direct hydrogenation and hydrocracking of subbituminous coal using zinc halide as the catalyst or regenerable intermediate. This will be divided into the following activities:

a. Prepare Feedstocks for the Continuous Hydrocracker

This includes drying and grinding a subbituminous coal, followed by hydroextraction of some of same to prepare coal extract for start-up operations of the continuous unit.

b. Break-in Operation of Continuous Bench-Scale Hydrocracker

Initial break-in operations will be done with coal extract to facilitate shake-down of equipment and provide comparison with previous work.

c. Hydrocracking of Coal and Preparation of Spent Melt for Regeneration Tests

The first operating period for the hydrocracker will confirm operability with coal, focusing on relatively severe conditions to produce a low-carbon spent melt. A batch of 300 pounds of spent melt will be produced for the first series of regeneration runs. This study will be limited in scope to permit early operation of the regeneration unit and expedite a decision to proceed with construction of the PDU.

d. Evaluation of the Low-Conversion Hydrocracking

After the first series of regeneration runs, hydrocracking variables will again be explored, focusing on milder conditions to produce a spent melt suitable for production of fuel gas.

e. Evaluate Another Coal

If time permits, one additional coal may be evaluated following the second series of regeneration tests.

Task 3 Continuous Bench-Scale Regeneration

a. Regeneration of "Low-Carbon" Spent Melt

The bench-scale, fluidized-bed combustor will be operated on low-carbon spent melt, emphasizing confirmation of previous work with synthetic spent melts and recovery of zinc halide. Successful completion of Task 3a will be one milestone pertinent to construction of the PDU.

b. Regeneration of "High-Carbon" Spent Melt

The second series of tests will operate on high-carbon melt to seek conditions for effective melt regeneration simultaneously with production of a low-Btu fuel gas or synthesis gas.

Task 4 Design of a Process Development Unit (PDU)

PDUs for zinc halide hydrocracking and regeneration will be designed based on feeding 100 lb/hr of coal or extract. This unit is to provide information on the commercial potential for the process, effect of equipment size on reaction rate, performance of mechanical components, suitability of materials of construction, and overall reliability.

Task 5 Construction of PDU

After ERDA's authorization to proceed, construction is to be undertaken by the contractor and is expected to require about 18 months.

Task 6 Operation of PDU

A program for testing in the PDUs will be prepared to emphasize:

a. Hydrocracking to produce light distillates from both coal and coal extract as feedstocks.

b. Integrated operation of hydrocracking and regeneration following initial separate operation.

c. Operation under 3 different modes:

   (1) High severity hydrocracking to maximize light distillates.

   (2) Low pressure hydrocracking with a high-temperature final stage to increase the gas/distillate ratio.

   (3) Mild hydrocracking conditions, producing a high-carbon spent melt which in regeneration will produce a synthesis gas useful for hydrogen production.

Task 7 Supporting Laboratory Studies

Laboratory studies will be carried out simultaneously with operation of the continuous bench-scale units and PDUs. The objectives will be to:

a. Provide a more fundamental understanding of the basic physical parameters and mechanism of the zinc halide hydrocracking process as an aid to process improvements and scaleup.

b. Provide supporting tests for operation of the continuous units.

Task 8 Process and Economic Studies

Process and economic studies of commercial plant scale will be conducted in two periods:

a. Near the beginning of the contract it is desirable to define the incentive for development. This will be done first by comparing the cost of gasoline made by alternate routes of zinc halide hydrocracking and ebullated-bed hydrocracking using a coal extract derived via hydroextraction of subbituminous coal. A second study will compare direct hydrocracking of subbituminous coal with hydroextraction plus extract hydrocracking, both with molten zinc chloride catalyst.

b. After operation of the PDUs economic studies will be made to evaluate the commercial potential of the process.

Task 9 Preparation of a Final Report

The final report will summarize all the work done with appropriate data, calculations and conclusions. An economic appraisal will be part of this report.

II. SUMMARY

The bench-scale hydrocracker operated successfully during April and May, and was shut down after having produced over 300 pounds of spent catalyst for regeneration studies. A number of material balances were made under various conditions. The use of benzene, thickened with about 8% polystyrene, as the coal vehicle proved useful as a means for obtaining yields from coal alone and to prepare distillates largely uncontaminated by start-up solvent. The yields from subbituminous coal (Table III) show 54.9% of the MAF coal converted to distillate oils in this operation.

The bench-scale regenerator operated throughout the period exploring the operating limits in the fluidized bed as affected by temperature and percentage of HCl in the feed air. Several successful runs were made with the natural spent zinc chloride catalyst from hydrocracking of subbituminous coal. Run 16 gave an excellent zinc balance and other balances are being obtained. It was shown that the unit is operable at higher operating temperatures when the HCl content of the feed gas is increased. Work is continuing to define these limits.

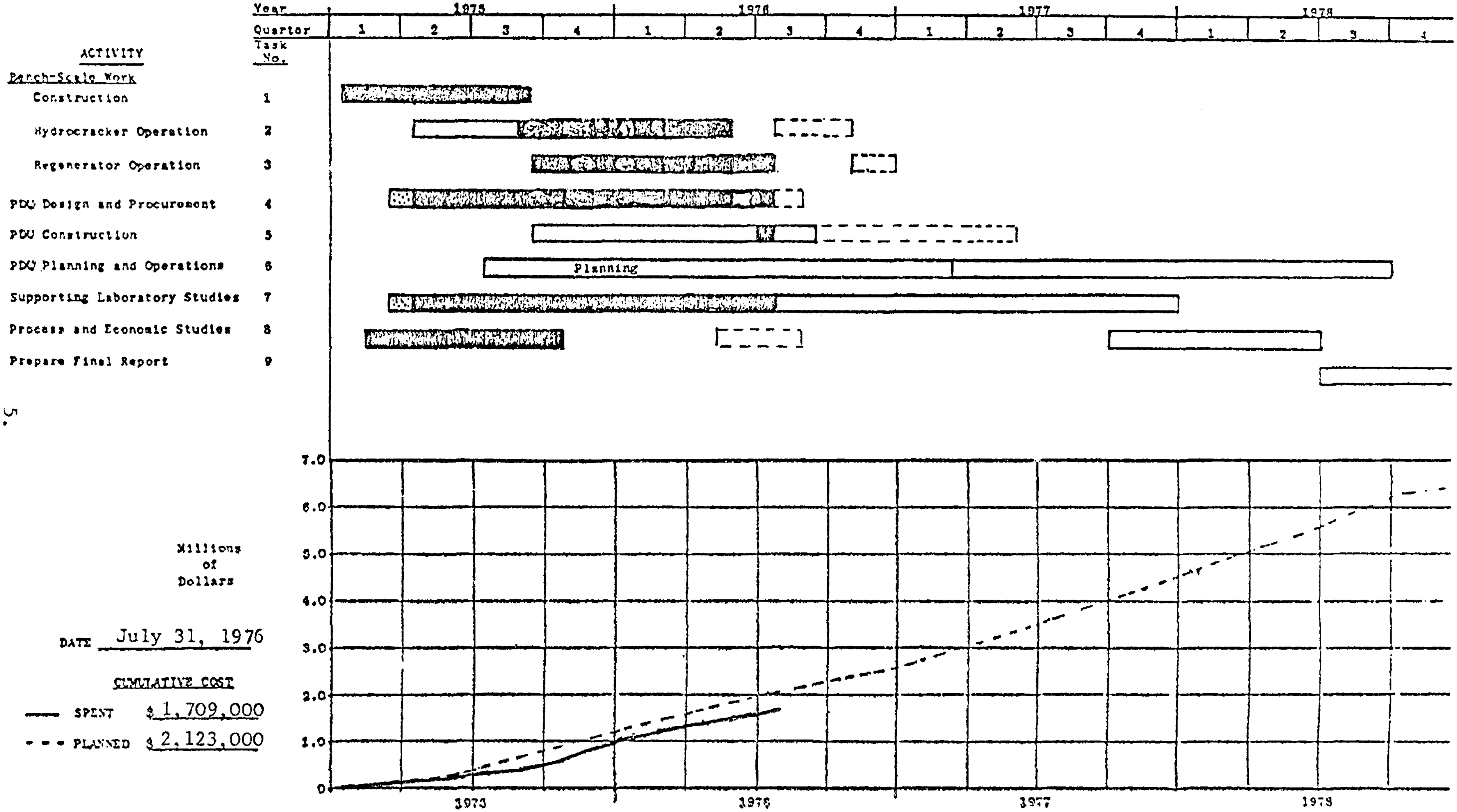
Supporting laboratory studies have shown that the coal ash recovered from the regenerator cyclone can be treated in a secondary vessel at cyclone temperature to recover additional zinc chloride. These solids normally contain from 0.5 to 1.5% of the zinc fed to regeneration, and secondary recovery can strip out up to 94% of that amount, raising overall recovery to 99.9%. These studies continue to explore appropriate variables to define the recovery limits, effect on other ash constituents and to develop design information for a continuous demonstration.

Approval was received from ERDA about July 1 to proceed with construction and operation of the 100 pound per hour Process Development Unit (PDU). The design is essentially frozen, and revised piping and instrumentation drawings have been isssued. Approval of specifications, evaluation of bids and placing of orders is underway, aiming at completion of the unit by the end of 1977. The hydrocracking section should be available for break-in by August, 1977.

The status of work by Tasks is shown on the Plan of Progress on the next page.

PROJECT PLAN AND PROGRESS REPORT

Under ERDA Contract No. E(49-18)-1743



DATE July 31, 1976

CUMULATIVE COST

—— SPENT $ 1,709,000

- - - PLANNED $ 2,123,000

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Task 1 Reactivation of the Continuous Bench-Scale Units - Complete

Task 2a Prepare Feedstocks - Complete

Task 2b Bench-Scale Hydrocracking of Coal Extract - Complete

Task 2c Bench-Scale Hydrocracking of Coal

Work on the direct hydrocracking of Colstrip coal at relatively severe conditions of temperature and pressure continued in three areas:

1. The production goal of 300 pounds of low-carbon (7 wt. % C or less) spent melt was achieved during this quarter. This natural spent melt is being used in regeneration studies of spent zinc chloride catalyst.
2. Several material balances were made at different hydrocracking conditions while operating with polystyrene-thickened benzene as vehicle in order to firm up earlier tentative conclusions obtained with Neville solvent slurry.
3. Coal hydrocracking yields were defined in the first benzene slurry run with a good material balance.

Production of 300 Pounds of Low-Carbon Spent Melt

The spent melt production goal was surpassed when four hydrocracking runs in this quarter yielded an additional 125 pounds for a total of 322 pounds of low-carbon spent melt, thereby completing a milestone of the contract. The operating crew for the hydrocracker was transferred to another project at the end of May, and the unit was placed on standby. The unit was cooled to ambient temperature, washed free of $ZnCl_2$ and organics with water and MEK, then dried to prevent corrosion.

Operations during the last week of May proved to be the most successful so far with three runs and two balances for a total of 78 hours onstream. The longest run lasted for 53 hours with only two 1-1/2 hour interruptions required to change worn check valve seats in the slurry feed pump.

Two types of operating problems still remained in the hydrocracker unit:

1. The stainless steel check valve seats in the coal slurry feed pump wore out quickly to the point where pump performance was affected. Harder materials have been difficult to obtain quickly, but will be tested in future runs.
2. The gas let-down lines from the spent melt receivers became restricted during long runs. Apparently some $ZnCl_2$ fog was generated when spent melt was degassed upon pressure letdown. The fog was then carried into cold sections of the offgas lines where it formed plugs. A simple trap and demister in the low-pressure lines should take care of the problem.

No valve changes were required during that last successful week.

The exemplary operations can probably be traced to the extensive turnaround caused by an earlier mishap which forshortened the first run of the quarter (Run 10). In that run a rupture disk on the reactor broke for no apparent reason, and the resultant pressure release forced 10% caustic solution from the distillate receiver, containing 0.5 to 1.0% chloride into an upstream section of the unit. All the affected 316 ss fittings and valves were replaced and the lines and vessels washed out. Previous experience has shown that 316 ss lines and fittings located in the distillate recovery section are susceptible to severe stress corrosion, presumably due to exposure to the caustic from the distillate receivers. Several of the removed fittings exhibited stress corrosion cracks. To avoid fatigue or corrosion failure in the future, the rupture disks will be replaced on a schedule.

Extension of Variable Study in Coal Hydrocracking

Several hydrocracking runs were made in conjunction with the production campaign which support the data base obtained in the process quarter. The nominal conditions are given in the following table:

Run No.	12	10	13	14	15
Temperature, °F	775(1) →	→	→	→	→
Total Pressure, psig	3500 →	→	→	→	→
$ZnCl_2$/Vehicle-Free Coal, Wt. Ratio	(2)	1.5 →	→	→	1.0
H_2 Rate, SCF/lb Total Organic Feed	30 →	→	→	→	→
Coal Slurry Composition, Wt. %					
-100 Mesh Colstrip Coal	0	30 →	→	→	→
Vehicle, 8 Wt. % Polystyrene in Benzene	100	70 →	→	→	→
Bed Inventory, lb	3.01	2.26	2.26(3)	2.26(3)	2.33
Melt Production Rate, lb/hr	1.20	1.34	1.68	1.34	0.94
Melt Residence Time, hr	2.5	1.7	1.35	1.7	2.5
Total Run Time, hr	12.7	20.4	11.8	50.5	12.9
Material Balance Time, hr	4.5	6.0	4.8	None	5.2

(1) Temperature in Run 12 was somewhat low.
(2) Blank run without coal feed.
(3) Not measured, assumed same as Run 10.

As indicated above, three material balance runs were made with coal slurry and one blank run with the slurrying vehicle only, i.e., polystyrene-thickened benzene. The first coal run (Run 10) was a duplicate of previous runs. In Run 13, the coal slurry feed rate was increased, and in the last run of the quarter (Run 15) the $ZnCl_2$/MF coal weight ratio was decreased to 1.0. The latter run again demonstrated operability at this low catalyst-to-coal ratio, as had been shown earlier with a Neville solvent-coal slurry.

Actual Product Yields from Coal

The first good material balance run with benzene-polystyrene as the coal slurry vehicle (Run 8C) was worked up completely. The product contribution assignable to the solvent was determined separately in blank Run 12, where the organic feed contained solvent only. The operating conditions and results from these two runs are given in Tables I through V. The net product yields from coal, Table III, compare quite favorably with previous batch work in that the light hydrocarbon yields are significantly reduced and the heavy distillate yields improved. The lower gas yield will translate into a lower overall hydrogen consumption. Also, since a heavy distillate is normally preferred, but not essential as the recycle vehicle for slurrying feed coal, the 17% yield of +200°C distillate observed in this run should assure sufficient heavy recycle oil. Additional tests will measure the degree of stability of this fraction toward further hydrocracking when recycled.

The product distributions in Tables II and III were obtained by forcing the elemental balances. Zinc was forced by adjusting the spent melt recovery and carbon by adjusting the organic distillate recovery. On occasion, hangup of spent melt in the unit has been observed, and weights of melt recovered are considered less accurate than weights of molten $ZnCl_2$ salt fed from a weigh tank. Also, the organic distillate is collected over caustic solution which absorbs HCl from the overheads. This two-phase system does not separate readily because of a tendency toward emulsion formation. As a result, the weight of organic slurry fed from a weigh tank is taken to be accurate.

Work planned for the next quarter includes:

1. Complete distillation of product from the production campaign in order to recover the +150°C distillate fraction. This fraction will be tested for reactivity on recycle as a coal slurry vehicle.

2. Conduct a variable study in direct hydrocracking of Colstrip coal for use in the development of a kinetic correlation, as had been done earlier for extract hydrocracking. This information will guide PDU planning and interpretation, and also determine conditions for high-carbon spent melt production.

3. Hydrocrack coal with regenerated $ZnCl_2$ catalyst.

4. Calculate the results of all of the material balance runs made in the hydrocracker since the start of operations.

Task 3 Operation of the Continuous Bench-Scale Regenerator

Operations

Work was started in the last quarter on operation of the regenerator using low-carbon natural spent melt feedstock operating in the excess air mode. The feedstock was produced in the continuous bench-scale hydrocracker at a $ZnCl_2$/MF, solvent-free Colstrip coal ratio of 1.5, 3500 psig total pressure, and 775°F using polystyrene-thickened benzene or toluene as the vehicle in the coal feed slurry. In those regeneration runs, sintering of the coal ash occurred in the fluidized bed at 1800°F with either 8.5 or 5.5 mol % HCl in the feed air; but a successful four-hour run (Run 16) was made at 1700°F with 5.5 mol % HCl. Tables VI through XI show detailed results of Run 16 with a material balance (100 out/in) of 101.4% and a zinc balance of 99.99%. The results show essentially complete removals from the melt of carbon and nitrogen and over 90% sulfur removal. Some of the ash elemental balances of Table XI are poor. The analyses in these cases appear to be in error and are being checked.

During this quarter, unit operations in the excess-air mode were continued using the low-carbon spent melt feedstock. Table VI gives the analyses of this feedstock. The conditions and some selected results of the new runs made during this quarter (Runs 17, 18, 19, 20, 21) and the runs made in the previous quarter (Runs 14, 15, 16) are given in Table XII.

Some of the results of Table XII give a measure of the operability of the runs with respect to sintering or agglomeration of ash in the fluidized bed. These are:

1. The relative proportions of cyclone underflow solids and ash retained in the bed solids expressed as percent of the feed ash. When this number is low for the cyclone solids and high for the bed solids, sintering and/or agglomeration of the ash in the bed occurs. When the reverse is the case, where the ash elutriates from the bed freely the run is highly operable and there is little or no sintering of the ash in the bed. Typically, of the order of 55% or more of the feed ash is found in the cyclone solids in a run of "good" operability. This value varies somewhat with the duration of the run since some time is required to build up a "steady-state" ash concentration in the bed in an operable run.

2. Size growth of coal ash in the bed as indicated by the screen analysis.

Some comments on the purpose and results of the new runs listed in Table XII are given below.

Runs 17 and 18 were made to help define the range of conditions which give satisfactory operability without sintering or agglomeration of the ash in the fluid bed of the reactor. The operating regimes and comments on these two runs follow:

Run 17 Ran three hours at 1700°F, then raised temperature to 1750°F and held for 1.4 hours (5.5 mol % HCl in feed air). Total run time was 4.67 hours. Rate of ash collection at cyclone dropped by more than a factor of two when temperature was raised indicating sintering at the higher temperature. Soft agglomerates present in bed.

Run 18 Ran 2.23 hours at 1700°F, then raised temperature to 1750°F and held for 1.16 hours; then raised temperature to 1800°F for 1.0 hour (8.5 mol % HCl in inlet air). Total operating time was 4.85 hours. The rate of cyclone solids collection at 1750 and 1800°F was about 65-70% of that at 1700°F. No clinkers or agglomerates were found in the bed.

Run 19 was a "long" run of 22.13 hours duration with 11.5 mol % HCl in the inlet air. It was made to demonstrate long-term operability and to help define zinc and chlorine losses as set forth in the work statement. The run gave excellent operability and shutdown was voluntary. Noteworthy is the relatively low zinc content of the cyclone solids and the fact that 69% of this zinc exists as $ZnCl_2$ as indicated by the water-soluble zinc analysis.

Run 20 was made to test operability at 1800°F with 11.5 mol % in the inlet air. The run was operable but the cyclone underflow ash tended to stick in the cyclone solids hopper. The run was shut down after 2.63 hours because of a burned-out winding.

Run 21 was made at 1700°F with 5.5% HCl in the feed air. It was intended to be a 24-hour run similar to Run 19 but to demonstrate operability and define zinc and chlorine losses with a lower feed HCl concentration. (It is desirable to keep the feed HCl concentration as low as possible in the primary regeneration step if secondary recovery of zinc from the cyclone solids is going to be employed.) The run operated well for 2.10 hours but then the spent melt feed rate increased inadvertently so that operation changed to 100% of stoichiometric air instead of 115% as in the initial stage of the run. At this time, sintering of the coal ash occurred in the bed and the run was shut down to give a total run time of 3.43 hours. A second attempt at this run was made. Operation was good for 1.4 hours when shutdown was forced by a faulty solenoid valve that caused freezing of the melt in the $ZnCl_2$ condenser. Another attempt will be made.

The following conclusions regarding operability are tentatively drawn based on the above qualitative observations and the results of Table XII:

1. With 5.5% HCl in the inlet air:

   a. 1700°F is an operable condition for at least a short period.
   b. 1750°F is a marginally operable condition because of some sintering.
   c. 1800°F is an inoperable condition because of severe sintering leading to clinker formation.

2. With 8.5% HCl in the inlet air:

   a. 1700°F is an operable condition.
   b. 1750°F is an operable condition.
   c. 1800°F probably is an operable condition but some minor size growth in the ash grain size may be expected. This may be desirable from the standpoint of preventing ash buildup in the regenerated melt.

Operability here is based on whether or not the ash leaves the bed by elutriation. However, in a unit such as the PDU or a commercial unit where the ash could be removed from a slipstream of the bed solids taken from the reactor, the condition of ash retention in the bed due to sintering of ash is not an inoperable condition unless there is clinker formation or the bed defluidizes due to stickiness. Some slight sintering may be desirable to prevent ash buildup in melt.

Table XII shows the cumulative effects on the bed solids of repeated reuse. The bed solids were reused in all runs subsequent to Run 14 in which fresh 28 x 48 mesh silica sand bed solids were charged. A property of the clinker formation and/or agglomeration and/or sintering is that there appears to be substantially no adhesion of the ash to the bed sand. This is indicated by visual observation; it is also shown by the screen analyses and zinc and chlorine analyses of the screen fractions given in Table XII. For example, the 28 x 48 mesh fraction of the effluent bed solids is generally close to 100% of the feed solids that were sized at 28 x 48 mesh. Furthermore, the zinc content of the +28 and -48 mesh fractions of the bed are relatively high whereas that of the 28 x 48 mesh fraction is low. Over the entire series of runs given in Table XII there is no trend of increasing zinc or chlorine in the bed solids, i.e., the 28 x 48 mesh fraction. Noteworthy is the fact that the zinc and chlorine contents of the 28 x 48 mesh solids after Run 19 are only 0.05% zinc and 0.00% chlorine. These data indicate that there are substantially no zinc or chlorine losses to the bed solids.

Handleability of Spent Melt

Some time was spend to evacuate natural spent melt to remove volatile matter and test its handleability thereafter. This was done to test whether sub-atmospheric flash distillation of the spent melt in the PDU would be acceptable treatment regarding subsequent melt handleability. It was determined that such flash distillation would be all right if not done at too high a temperature: natural low-carbon spent melt was molten, not excessively gassy and pumpable at 500°F after evacuation at 100 torr for 30 minutes at 550°F followed by similar treatment at 600°F. Two attempts were made to evacuate the melt at 650°F but the melt frothed so badly that the vacuum lines immediately plugged. About 1.3 wt. % of volatile matter, which was mostly water and light hydrocarbons, was removed from the melt during evacuation. It was demonstrated that the melt could be pumped via the regenerator melt pump after the above treatment.

Equipment

It was found that a Hastelloy C cooling coil in the $ZnCl_2$ condenser is superior to one of Inconel 600. The latter failed after about 30 hours of run service, whereas the Hastelloy coil was intact but corroded upon removal after about 60 hours.

Blending of Natural Spent Melt

The last half of the natural low-carbon spent melt produced in the continuous hydrocracker (171 pounds) was blended in the molten state to give one large uniform batch of feedstock for regeneration operations. The carbon content of the blended melt is 6.26 wt. %.

Work Planned for the Next Quarter

1. Make a long run at 1700°F in the excess air mode with 5.5% or 8.5% HCl in the feed air.

2. Possibly, make a second long run at another set of conditions that will be chosen later.

3. Investigate operability using a large amount of excess air, i.e., about 150% of stoichiometric.

4. Investigate operability in the air deficient mode, i.e., 45% of stoichiometric since Run 21 indicated operation with deficient air may give operability difficulties.

All of the above runs will be made with low-carbon spent melt.

Task 4 Design of the Process Development Unit (PDU)

A. Flow Sheet and P&I Reviews

A safety and startup and shutdown review resulted in the following changes:

1. A lockhopper was added to the zinc chloride melt to eliminate possible exposure of personnel to fumes.
2. The hydro reactor vent system was revised to permit voluntary emptying of the high-pressure vessels. This would bypass the usual exit gas system and allow the vessel contents to be dumped quickly in case of emergency. As this is an overhead system; most of the melt would remain in the vessels.
3. The vent system for the oxygen-bearing gases in regeneration was revised to a separate system with its own knock-out pot and flame arrestor.
4. Monel was specified for HCl service at low temperature and pressure since it is superior to Inconel in this service. Consequently, the overhead vacuum lines together with F409 and F208 will be Monel.
5. Underground storage was specified for C_5 x 200 and C_5 x 150 light ends, and surge tank F504 and pump J506 were eliminated. Heavier materials will be disposed of by mixing them with the fuel oil supply to our boilers.
6. In regeneration, the sand withdrawal system was simplified, and a permanent char feeder was made available to the sand feed system.
7. Provision was made to permit bypass of the regenerated melt storage tank during integrated operation.
8. Numerous alarms and sensors were added as needed to improve safety and operability.

In addition, detailed line and instrument numbers were added.

B. Selection of Valves

The decision on the material of construction for low-pressure valves for zinc chloride service remains open. A Hastelloy valve would cost about \$400 versus about \$50 for one of carbon steel. A carbon steel valve was taken off the bench-scale unit, sectioned and examined. The stainless steel seats were cracked. However, the carbon steel body was essentially intact although corroded. The design philosophy of the PDU is to be conservative with materials of construction so that the process can be tested with a high degree of reliability without worry of construction materials failing. Consequently, if a high metallurgy valve can be obtained at a reasonable price it will be used, otherwise we will go with carbon steel.

Alternative valves for use in the high-pressure section have been narrowed down to two which will be tested in the bench-scale hydro unit before choosing which will go into the PDU.

C. Heat and Material Balances for Low-Conversion Option

The data available for use in making a heat and material balance for 2000 psig low-conversion operation were reviewed. As the major product in this mode is a fuel oil, it was decided not to evaluate the use of extract. Extract is already intended to be a boiler fuel or fuel oil substitute, and it is unlikely that one would want to go through the entire zinc chloride process to convert a fuel oil substitute to fuel oil. For the coal case, there was insufficient data to warrant choosing between liquid-liquid extraction and high-temperature hydrogen stripping as a means of removing the +475°C oils from the melt. It was decided to defer the heat and material balance for the hydro section until more data are in hand. However, it is presumed that no matter how the melt is treated to separate the +475°C oils, a fairly high level of carbon will remain and a substoichiometric regeneration step will be required. Efforts were, therefore, concentrated on this regeneration step.

Preliminary calculations confirm the conclusions inferred from Figure V-31 of Book 2(1) that a carbon content of 10% or less, and a rather low air rate of the order of 40% of stoichiometric would be required to be in heat balance at 980°C (1796°F). When construction of the PDU was approved, these calculations were temporarily set aside in favor of the increased review workload occasioned by preparing solicitations to vendors and carrying out program planning activities. The substoichiometric heat and material balances will be continued as time allows.

D. Cooling of Effluent Melt

The alternatives for converting melt to an easily handled and stored form have been narrowed down to either a flaker or a prilling tower. A test made by a flaker vendor on natural spent melt showed that a thin section could be solidified to a brittle state within 20 seconds from 650°F (343°C). A thin section of pure $ZnCl_2$ was solidified from 700°F (371°C) within 15 seconds. There was no difficulty in removing the melt from the stainless steel plate; in fact, the solidified salt tended to curl up away from the belt. There should be no problem in applying the flaker to our purpose.

E. Corrosion

Reports on corroded samples sent to Conoco's Ponca City research facility have been received. Failure of the zinc chloride condenser thermowell was due to severe sulfur corrosion of the Inconel 600. The metal had melted through, apparently, due to the formation of a low-melting, nickel-sulfur eutectic. Possibly, the liquid zinc chloride, which acts as a metal flux and solvent, also contributed to the failure. A material more resistant to sulfur, such as Incoloy 825 or Inconel 718, was recommended.

A report on the air fluidizing line for the regenerator itself indicated that severe corrosion occurred due to the high-temperature oxidizing environment. Possibly, temperatures considerably higher than the nominal bed temperature are experienced at the point where the air first contacts the bed contents.

A Hastelloy C coil in the bench-scale zinc chloride condenser was removed and sent to Ponca City for a detailed metallurgical examination. The previously used Inconel 600 coils failed after about 30 hours. The Hastelloy coil had not failed after 60 hours, but it was removed as a precautionary measure prior to a planned long run.

A number of corrosion coupons are now in place in the condenser. These will be removed when the large batch of natural spent melt being tested is used up. Examination of the coupons will permit specification of the material of construction for the PDU condenser. The present tentative specification is Hastelloy C. As noted earlier, the use of a more constant cooling regime plus the recycle of cool melt should give longer life to the PDU zinc chloride condenser.

Tungsten carbide coupons were prepared for installation in the bench-scale hydrocracker.

F. General Task Work and Scheduling

Layouts and mechanical design are ongoing items which will take some time to complete.

It was decided to use metric units of temperature and weight in specifying instrumentation for the PDU. Additional use of S.I. notation was judged to be impractical due to the unavailability of commercial metric equipment.

G. Work Forecast for Next Quarter

Goals for the next quarter are:

1. Finalize the decision of which valves to use in both high and low pressure zinc chloride service.
2. Specify material of construction for the zinc chloride condenser.
3. Continue design and review of mechanical equipment items.
4. Work on heat and material balances for substoichiometric regeneration.
5. Start on piping drawings as they are needed to enable vessel installation to be carried out.

Task 5 Procurement and Construction of the PDU

All pumps except one have been selected and ordered.

Installation of furnishings and fixtures for the PDU laboratory is underway and will be completed in the next quarter.

A CPM critical path diagram has been made for the PDU construction. Equipment delivery and work progress will be evaluated each month, and new data will be inserted into the CPM diagram.

Bids have been received on the regenerator and smaller Inconel and stainless steel vessels. They are presently being evaluated. Heat exchanger design is nearly complete and we will go out for quotes early in August.

Bids were received for electric immersion heaters and orders for this equipment will be placed soon. Design was completed for electric furnace heaters and we are out for bids on this equipment.

High-pressure valves have been counted and we are now out for bids on these items. The detail design for all high-pressure Inconel vessels has been approved by CCDC. Autoclave Engineers has most material on hand for the vessels and is proceeding with construction per schedule.

Construction of the hydrogen and recycle compressor by Rix Corp. are on schedule. Compressor forgings are on hand and machine work is proceeding. We received delivery of high-pressure Hastelloy tube from Cabot Corp.

All material for the barricade has been ordered and some material is on hand. Welding work will be started soon.

Work has started on electric conduit routing. This work should be finished in August.

Task 6 PDU Program Planning and Operation

A suggested program and schedule for the PDU break-in and operation is being prepared. Upon agreement on the schedule, a detailed work plan and milestone chart will be composed.

Work planned for the next quarter includes putting together a corrosion test program and starting on an operating manual.

Task 7 Supporting Laboratory Work

A. Batch Autoclave Work

1. Kinetics Studies on Coal Liquefaction

This work was severely limited during this period in favor of studies on secondary recovery of zinc from regenerator cyclone underflow solids. Two batch autoclave runs were made on the kinetics study of direct hydrocracking of Colstrip coal with $ZnCl_2$ catalyst. They were 15 and 120 minute runs at 750°F and 2000 psig hydrogen partial pressure. The 15 minute run was a repeat of a previous run in which the material balance was poor. The results for these runs remain to be completed.

B. Investigation of Secondary Recovery of Zinc from Regenerator Cyclone Underflow Solids

Most of the supporting laboratory effort was devoted to continuing studies begun in the last quarter on secondary recovery of zinc from regenerator cyclone underflow solids.

Further studies of secondary recovery were conducted at a long residence time to determine the "maximum" extent of zinc recovery possible as a function of conditions. The apparatus and procedure used in these studies was presented in the previous quarterly report.(2) Results confirmed earlier work showing over 90% recovery of the zinc remaining in the cyclone solids and up to 99.9% recovery overall of zinc fed to regeneration.

In addition, a preliminary batch kinetics study was conducted to get a rough idea of the residence time that might be required for efficient secondary zinc recovery in a continuous unit. The apparatus was the same as that used in long residence time studies except that a thin layer of cyclone solids (1/16") in an open-ended boat was used to minimize diffusion time of gases into and out of the ash layer. The results indicate that the kinetics of the secondary zinc recovery process is fast enough for practical purposes.

Considerable time was spent developing a continuous feeder for feeding cyclone underflow solids to a continuous bench-scale secondary zinc recovery operation. Successful feeding was demonstrated at atmospheric pressure in a preliminary feeder. A feeder suitable for operation above atmospheric pressure was then designed and is being built.

C. Work Planned for the Next Quarter

1. Make a few more runs on the batch kinetics study of secondary zinc recovery using a different feed gas than those used thus far.
2. Investigate the kinetics of continuous removal and recovery of zinc from regenerator cyclone underflow solids. This will be done using the bench-scale regenerator as the secondary zinc recovery vessel with appropriate modifications for the kinetics work.
3. As time permits make batch autoclave runs on coal liquefaction. Included in this work are:
    a. Kinetics runs of zinc chloride hydrocracking of Colstrip coal at 800°F, 3000 psig hydrogen partial pressure.
    b. A run with Colstrip coal using as the catalyst regenerated spent $ZnCl_2$ melt derived from the continuous hydrocracker and continuous regenerator.
    c. Runs to test with $ZnCl_2$ catalyst the reactivity of distillate fractions produced with Colstrip coal in the continuous hydrocracker using polystyrene-thickened benzene as the vehicle in the coal feed slurry. Runs will be made with the following feeds:
        (1) 100 x 200°C distillate
        (2) 200 x 325°C distillate
        (3) 325 x 475°C distillate
        (4) +475°C distillate

Task 8 Process and Economic Studies

One study has been completed; no activity is currently scheduled.

IV. LITERATURE CITED

1. Gorin, Everett, et al., Research on Zinc Chloride Catalyst for Converting Coal to Gasoline, U.S. Dept. of the Interior R&D Report No. 39, Vol. III, Book 2, OCR Contract 14-01-0001-310 with Consolidation Coal Company, 1968.

2. Conoco Coal Development Company, ERDA Report No. FE-1743-20, Zinc Halide Hydrocracking Process for Distillate Fuels from Coal, Quarterly Technical Progress Report for the Period February 1 to April 30, 1976.

TABLE I

Continuous Bench-Scale Hydrocracking

Operating Conditions

Run Number	518.02-8C	518.02-12
Reactor Temperature, °F	775 (413°C)	775 (1) (413°C)
Reactor Pressure, psig	3500	3500
Organic Feed Rate, gm/hr	1485	1215
MF Coal Feed Rate, gm/hr	367	trace
MF Coal Feed Rate, lb/hr-ft^3	57.0	57.7
Catalyst Feed Rate, gm/hr	548	555
H_2 Feed Rate, SCFH	88.4	67.5
Reactor Inventory, gm	N.A. (2)	1367
Reactor Volume, cc	600	600
Liquid Residence Time, hr	1.2	2.5
Carbon in Residue, Wt. %	7.6	0.7
Conversion, Wt. % MAF Coal	78.0	--
Hydrogen Consumption (3)		
Wt. % MAF Organic Feed	1.80	1.40
Wt. % MAF Coal Feed (4)	7.9	--

(1) Nominal value; actual temperature about 30°F lower because of heat losses.

(2) 824 grams in Run 8B.

(3) H out - H in, but excluding H_2 gas.

(4) With assumption that solvent does not take up hydrogen.

TABLE II

Product Yields - Wt. % of MAF Organic Feed

Run No.	518.02-8C	518.02-12
Gases		
CO	0.26	< 0.001
CO_2	0.39	0.0
CH_4	0.27	0.005
C_2H_6	0.28	0.03
C_3H_8	0.98	0.10
i C_4H_{10}	0.92	0.01
n C_4H_{10}	0.09	< 0.001
Distillate		
C_5 x 200°C	84.64	98.49
200 x 325°C	1.87	1.23
325 x 475°C	2.43	0.91
+475°C	1.81	0.69
H_2O	2.92	--
Residue		
100 x 200°C	0.35	0.01
200 x 325°C	0.12	0.09
325 x 475°C	0.06	0.04
+475°C MEK-Solubles	2.74	0.10
MEK-Insolubles	1.01	0.05
H_2O Soluble Hydrocarbons	0.18	0.11
O to Catalyst	0.01	--
N to Catalyst	0.18	--
S to Catalyst	0.23	--
H to Catalyst	0.05	--
	101.79	101.87

TABLE III

Net Product Yields from MAF Coal

Run No.	518.02-8C
Gases	
CO	1.12
CO_2	1.69
CH_4	1.17
C_2H_6	1.13
C_3H_8	3.94
i C_4H_{10}	3.97
n C_4H_{10}	0.39
Distillate	
C_5 x 200°C	37.71
200 x 325°C	4.01
325 x 475°C	7.59
+475°C	5.58
H_2O	12.81
Residue	
100 x 200°C	1.52
200 x 325°C	0.22
325 x 475°C	0.11
+475 MEK-Solubles	11.71
MEK-Insolubles	4.26
H_2O Soluble Hydrocarbons	0.42
O to Catalyst	0.05
N to Catalyst	0.78
S to Catalyst	0.99
H to Catalyst	0.24
	101.41

TABLE IV

Feed Compositions, Wt. %

Run No.	518.02-8C	518.02-12
Total Organic Feed		
MF Coal	24.70	trace
Moisture	1.10	--
Benzene	68.26	92.0
Polystyrene	5.94	8.0
	100.00	100.0
MAF Organic Feed		
MAF Coal	22.79	--
Benzene	71.03	92.0
Polystyrene	6.18	8.0
	100.00	100.0
Catalyst Feed		
$ZnCl_2$	97.22	97.22
ZnO	1.25	1.25
H_2O	1.53	1.53
	100.00	100.00
MF Coal		
Hydrogen	4.38	
Carbon	67.30	
Nitrogen	0.98	
Oxygen	15.08	
Sulfur Inorganic	0.32	
Sulfur Organic	0.62	
Ash	11.32	
	100.00	

TABLE V

Preliminary Forced Balances

Run No.	518.02-8C	518.02-12
Zinc	100.94	100.94
Carbon	100.09	99.98
Nitrogen	99.99	--
Oxygen	100.00	--
Sulfur	99.06	--
Chlorine	100.00	99.90

TABLE VI

Continuous Bench-Scale Regeneration

Run 518.05-16

Detailed Conditions and Material Balance

Conditions	
Melt Type	Low-Carbon Natural
Reactor Temperature, °F	1700
Cyclone Temperature, °F	1500
Nominal % of Stoichiometric Air	115
Inlet Gas Composition	94.5 mol % air-5.5 mol % HCl
Cyclone Gas Underflow Rate, SCFM	about 0.0017
Superficial Linear Velocity, fps	1.0
Fluidized Bed Depth, ft	1.0
Bed Solids	28-48 M silica sand
Avg. Melt Feed Rate, gm/min	21.3
Run Time, min	240
Inlet Gas Rate, SCFM	
Air	0.712
Anhydrous HCl	0.041
Argon Purges	0.048
Bed Solids Charge, grams	1362

Material Balance

In, gm/100 gm Feed Melt	
Feed Melt	100.00
Air (ex argon)	126.52
Anhydrous HCl	9.39
Bed Solids	26.66
Total	262.57
Out, gm/100 gm Feed Melt	
Product Melt	84.72
Cyclone Solids	3.86
Bed Solids	28.93
HCl	8.80
H_2O	7.48
CO_2	20.95
CO	1.90
SO_2	1.01
N_2	102.00
O_2	6.65
Total	266.30
(Out/In)(100)	101.4

TABLE VII

Run 518.05-16

	Feed Melt Composition, Wt %	Effluent Melt Composition, Wt %
H	0.77	0.15
C	7.04	0.05
N	0.61	0.00
O (diff.)	1.56	1.37
Organic S	0.03	--
Sulfate S	0.00	0.04
Sulfide S	0.35	0.00
Zinc	41.22	47.61
Chlorine	41.23	50.30
Ash (as oxides)	7.19(1)	0.48

	Ash Analysis, Wt %	Ash Analysis, Wt %
Na_2O	.79	7.73
K_2O	.28	3.96
CaO	9.49	3.05
MgO	4.83	1.08
Fe_2O_3	5.82	37.23
TiO_2	1.87	8.37
P_2O_5	2.59	24.34
SiO_2	51.94(2)	9.39
Al_2O_3	22.39(2)	4.85
Σ	100.00	100.00

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(1) This value is being checked; its true value likely will be about 6.0%.

(2) These values appear to be erroneously high and are being checked.

TABLE VIII

Run 518.05-16

Bed Solids Analyses, Wt %

	Feed	Product
H		0.011
C		0.215
S		0.021
Na_2O	0.00	0.039
K_2O	0.02	0.035
CaO	0.00	0.996
MgO	0.00	0.413
Fe_2O_3	0.00	0.501
TiO_2	0.00	0.069
P_2O_5	0.17	0.047
SiO_2 (diff.)	99.81	95.055
Al_2O_3	0.00	1.395
Zn	0.00	0.926
Cl	0.00	0.065
O as ZnO	0.00	0.212
Σ	100.00	100.000

TABLE IX

Run 518.05-16

Cyclone Solids Analysis, Wt %

H	0.11
C	0.35
N	--
O as SO_3	0.51
O as ZnO	2.45
Sulfide S	0.00
Sulfate S	0.34
Zn	15.81
Cl	6.27
Na_2O	.168
K_2O	.038
CaO	9.65
MgO	4.04
Fe_2O_3	3.67
TiO_2	0.67
P_2O_5	0.19
SiO_2	33.36
Al_2O_3	14.20
Unid. (diff)	8.18
Σ	100.000

TABLE X

Run 518.05-16

Effluent Gas Analysis, Mol %

H_2S	0.00
CO_2	8.78
CO	1.25
H_2	0.00
SO_2	0.29
A	6.67
N_2	67.08
O_2	3.83
HCl	4.45
H_2O	7.65
Σ	100.00
Yield, * SCF/lb Feed Melt	19.48
5 liters/100 gm Feed Melt	121.53

* 32°F, 1 atm.

TABLE XI - - - - Material and Elemental Balances

Run 518.05-16

	Total Grams	H	C	N	O	S	Zn	Cl
In								
Air	6,463.72		0.93	4945.32	1517.47			
Anhydrous HCl	479.65	13.23						466.42
Bed Solids	1,362.00							
Melt	5,108.64	39.34	359.65	31.16	79.69	19.41	2105.78	2106.29
Σ	13,414.01	52.57	360.58	4976.48	1597.16	19.41	2105.78	2572.71
Out								
Melt	4,328.50	6.49	2.16	zero	59.30	1.73	2060.80	2177.23
Bed Solids	1,478.00	.16	3.18		3.13	.31	13.69	.96
Cyclone Solids	197.10	.22	.69	-	5.83	.67	31.16	12.36
Fixed Gas	6,769.30		333.68	5210.78	1199.07	25.77		
HCl	449.58	12.41						437.17
H_2O	381.91	42.81			339.10			
Σ	13,604.39	62.09	339.71	5210.78	1606.43	28.48	2105.65	2627.72
(Out/In)(100)	101.4	118.1	94.2	104.7	100.6	146.7	99.99	102.1

In	Total Grams	Na_2O	K_2O	CaO	MgO	Fe_2O_3	TiO_2	P_2O_5	SiO_2	Al_2O_3
Air	6,463.72									
Anhydrous HCl	479.65									
Bed Solids	1,362.00	.00	.00	.00	.00	.00	.00	2.31	1359.41	.00
Melt	5,108.64	2.92	1.03	34.88	17.72	21.37	6.88	9.51	190.81	82.24
Σ	13,414.01	2.92	1.03	34.88	17.72	21.37	6.88	11.82	1550.22	82.24
Out										
Melt	4,328.50	1.61	.82	.63	.22	7.74	1.74	5.06	1.95	1.01
Bed Solids	1,478.00	.58	.52	14.72	6.10	7.40	1.02	.69	1402.36	20.62
Cyclone Solids	197.10	.33	.07	19.02	7.96	7.23	1.32	.37	65.75	27.99
Fixed Gas	6,769.30									
HCl	449.58									
H_2O	381.91									
Σ	13,604.39	2.52	1.41	34.37	14.28	22.37	4.08	6.12	1470.06	49.62
(Out/In)(100)	101.4	86.3	136.9	93.5	80.6	104.7	59.3	51.8	94.8	60.34

TABLE XII

Continuous Bench-Scale Regeneration

Common Conditions

Feedstock = Natural spent melt containing ca. 6.0% ash and 7.04% carbon
Pressure = 3 psig
Superficial Linear Velocity = 1.0 ft/sec
Fluidized Bed Depth = 12 inches
Bed Solids = 28 x 48 mesh silica (fresh in Run 14, used from previous run in subsequent runs)
Nominal Amount of Air = 115% of stoichiometric
Cyclone Temperature = 1500°F

Run Number 518.05-	14	15	16	17		18			19	20	21	
Reactor Temperature, °F	1800	1800	1700	1700	1750	1700	1750	1800	1700	1800	1700	
Inlet Gas Composition, Mol %												
Air	91.5	94.5	94.5	94.5 (91.5)(1)		91.5			88.5	88.5	94.5	
Anhydrous HCl	8.5	5.5	5.5	5.5 (8.5)		8.5			11.5	11.5	5.5	
Running Time at Temperature, hours	1.4	3.0	4.0	3.0	1.67(3)	2.23	1.62(2)	1.00	22.13	2.63	2.10	1.33(5)
Results												
Cyclone Solids, Wt % Feed Ash	28.3	10.7	64.3	46.6	22.5	74.2	51.4	47.4	81.1	55.7	53.6	18.7
"Ash" in Bed Solids, Wt % Feed Ash	49.4	88.2	37.8	39.2		30.8			7.8	36.1		
Effluent Bed Solids Screen Analysis, % of Feed Bed Solids(6)												
+20		8.4	0.1	0.6		0.07			0.2	0.3		
28		0.9	0.2	1.0		0.07			0.1	0.2		
48		100.1	101.3	103.1		98.8			99.8	101.5		
-48		5.1	6.9	9.6		6.4			8.6	3.2		
Σ		114.5	108.5	114.3		105.3			108.7	105.2		
% Zn in Cyclone Solids		12.98	15.81	12.54	17.87	9.26	10.81	11.01	7.42(7)			
% Cl in Cyclone Solids		7.77	6.27	6.58	11.85	5.69	6.93	6.98	5.54			
Bed Solids Analyses												
% Zn in +28 mesh		11.99(4)	22.93	11.30(4)		--			--			
% Zn in 28 x 48 mesh		0.09	0.16	0.21		0.19			0.053			
% Zn in -48 mesh		10.82	11.95	5.76		4.77			4.43			
% Cl in +28 mesh		0.16(4)	0.91	0.39								
% Cl in 28 x 48 mesh		0.00	0.04	0.00		0.07			0.00			
% Cl in -48 mesh		0.18	0.44	0.18		0.11			1.02			
Comments:	Reactor plugged at outlet	Clinker formation	Good run	A few soft agglomerates in bed		Good ——→ fair operability No bed agglomerates			Good operability No bed agglomerates	Fair operability No agglomerates in bed		

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(1) Higher HCl rate during last 0.4 hour at 1750°F.
(2) Includes 15 min to go from 1700 → 1750°F and 13 min to go from 1750 to 1800°F.
(3) Includes 13 min to go from 1700 → 1750°F.
(4) +20 mesh fraction.
(5) At the beginning of this period the spent melt feed rate increased inadvertently so that the operation was with ca 100% of stoichiometric air instead of the 115% of stoichiometric air that was intended.
(6) Weight of feed bed solids was 1362 gm ± 1.
(7) Sixty-nine percent H_2O soluble zinc, i.e., zinc in form of $ZnCl_2$.