

REGENERATION OF "SPENT" $ZnCl_2$ PRODUCT CATALYST
FROM HYDROCRACKING SUBBITUMINOUS COAL

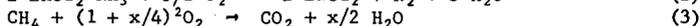
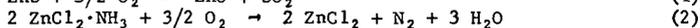
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INTRODUCTION

It has been demonstrated in batch and continuous bench-scale units that molten zinc chloride is a superior catalyst for liquefaction of coal, coal extract or other heavy hydrocarbons. High quality gasoline of 90-92 Research Octane Number is produced in high yield in a single hydrocracking step (1,2,3,4,5). Large amounts of zinc chloride are used as the catalyst for high activity, i.e., usually 1 gm of $ZnCl_2$ per gm of coal or extract feed. From 1 to 2 parts by weight of product catalyst is generated during the hydrocracking process depending on the $ZnCl_2$ /feed ratio. This product catalyst is contaminated with zinc sulfide, ammonia or ammonium chloride complexed with zinc chloride (formed by the catalyst partially reacting with the sulfur and nitrogen in the feed during the hydrocracking step), carbonaceous residue that cannot be distilled out of the melt, and coal ash, when coal is the feed to the hydrocracking process. To keep the catalyst active, these impurities must be removed in a regeneration process in which the catalyst is converted back to essentially pure zinc chloride. The impurities do not settle out of the molten product catalyst; hence, the whole product catalyst must be subjected to the regeneration process. Thus, regeneration is a key step in the $ZnCl_2$ coal liquefaction process in development at Conoco Coal Development Company.

The regeneration is accomplished by burning out the impurities in a combustor containing a fluidized bed of "inert" silica sand:



Hydrogen chloride gas is added to the feed air to convert ZnO to $ZnCl_2$ and to prevent formation of ZnO by hydrolysis of zinc chloride in the combustor:



A previous paper described regeneration of essentially coal-ash-free spent melt produced by hydrocracking coal extract (6,7). However, there appear to be economic advantages to a process employing direct coal hydrocracking over a two-step process consisting of coal extraction followed by hydrocracking of the SRC therefrom. Therefore, demonstration of regeneration with low zinc losses of the ash-contaminated spent melt produced by direct hydrocracking of coal is of high importance in the process development. The first work in this regard was done using synthetic spent melt which simulated that produced by hydrocracking subbituminous coal. This work has been published previously (5). Simulated spent melt was used because natural spent melt was not available. Subsequent to that work, successful direct hydrocracking with $ZnCl_2$ catalyst of Colstrip subbituminous coal in a continuous bench-scale hydrocracker furnished feedstock for further development of the regeneration process. Continuous regeneration of this coal-ash-contaminated spent melt from direct hydrocracking of coal and efficient zinc recovery therefrom has now been demonstrated for the first time. In this work zinc recovery was enhanced by introducing a secondary zinc recovery step in which zinc, retained in the coal ash rejected in the primary regeneration step, is largely recovered. This paper presents some of the results of this regeneration work with natural spent melt from direct coal hydrocracking.

EXPERIMENTAL

Feedstocks

Spent Melt

The two feedstocks for the primary regeneration work were low-carbon spent melts produced by direct hydrocracking of Colstrip coal in a 3 lb/h continuous bench-scale hydrocracking unit. Hydrocracking conditions were: 413°C, 24.13 MPa (3500 psig), ZnCl₂/MF solvent-free Colstrip coal ratio of 1.5 and residence times ranging from 74 to 95 min. Normally a ZnCl₂/coal ratio of 1.0 is used; the higher ratio of 1.5 was used to speed up production of spent melt. It gave a yield of about 1.75 gm of spent melt per gm of MF coal feed vs. about 1.25 which is produced at a ZnCl₂/coal ratio of 1.0. The carbon content of the two spent melt feedstocks used were 6.65 and 6.31%, slightly more than required to furnish the heat when burned for carrying out the regeneration adiabatically. The total ash content of the feed melt is based on the sum of the eight most prevalent coal ash elements (Na, K, Ca, Mg, Fe, Ti, Si, Al) expressed as oxides, since the coal ash is mixed with non-combustible materials and, therefore, cannot be determined directly. The total ash determined in this manner is lower than the ash determined in coals or chars in the conventional manner, where sulfates and carbonates may be present, that are not taken into account here. Also, traces of minor elements are not considered here. Analyses of the spent melt are given in Table I.

Colstrip Coal

Minus 100 mesh Colstrip subbituminous coal (Rosebud Seam, Montana) was used as the feedstock for testing, in a 3 lb/h continuous hydrocracker. The activity of regenerated spent melt was compared with virgin zinc chloride. Analyses of this coal are given in Table I.

Cyclone Underflow Ash

This material, which is generated in the primary regeneration step, contains the coal ash and generally less than 2% of the zinc in the spent melt feed to the primary regeneration. It is fed to a secondary zinc recovery step wherein the majority of this "lost" zinc is recovered. Analyses of this material are given under the heading "Composite" in Table VI.

Equipment and Procedure

Primary Regeneration

Figure 1 is a diagram of the continuous 2-7/8" I.D. fluidized bed combustion unit in the configuration used for primary regeneration. The molten "spent" catalyst is fed via a Fluid Metering, Inc. Lab Pump and is dropped from a remote drip tip into a batch bed of fluidized silica sand. The feed gas consists of a mixture of air and anhydrous hydrogen chloride which enters at the apex of the reactor cone. In the fluidized bed, the zinc chloride is vaporized, the carbon, nitrogen and sulfur impurities are burned out and any zinc oxide is largely converted to zinc chloride by the HCl in the feed gas. The gas and zinc chloride vapor entrain the coal ash, leave the reactor and pass through the cyclone where the solids are collected. The cyclone underflow solids derive solely from the melt since the sizing of the silica sand bed solids is such that there is essentially no elutriation of this material. The solids collected at the cyclone then consist largely of coal ash contaminated by small amounts of zinc in the form of zinc chloride and zinc oxide or other compounds, and any unburned carbon or zinc sulfide. The gas then passes to the condenser where zinc chloride is condensed, then to the electrostatic precipitator to remove zinc chloride fog, and then to sampling and metering. The analytical methods and calculational procedures are substantially the same as those previously described (7).

Hydrocracking

The hydrocracker and its operating procedure have been described previously (9).

Secondary Regeneration

The apparatus used to conduct the secondary recovery studies was the same unit used for the primary regeneration studies with some modifications made to accommodate the use of a solid feed. The modifications consisted of replacing the melt feed system with a metering powder feeder for feeding the cyclone underflow solids to the unit. The drip tip was plugged off since it was not used.

The cyclone underflow ash is fed at a metered rate into the air feed gas line that transports the ash into the bottom of the batch fluidized bed of silica sand. Anhydrous HCl is injected into the air stream just upstream from the reactor. Some of the ash is temporarily trapped in the fluidized bed of silica sand, building up to a steady-state concentration. The remainder of the ash is carried out of the bed by the gas stream. At steady state, the amount of ash fed per minute equals the amount of ash per minute that is transported by the gas stream out of the bed. The average ash residence time in the reactor in minutes is then "grams of ash inventory in the bed divided by the ash feed rate in grams per minute."

The gas, $ZnCl_2$ vapors, and entrained ash leave the reactor and follow the same course described above for primary regeneration.

The feed gas is electrically preheated to $316^\circ C$ ($600^\circ F$) before it enters the reactor. The remaining heat required is put in through the reactor walls by electrical heaters.

The run was started when the cyclone underflow ash feed to the reactor started. The product cyclone underflow was collected in 5 to 10 min, increments as a function of running time. The run was ended when the ash feed stopped.

The ash inventory in the bed was measured to enable precise calculation of the average residence time in the bed.

Run duration was about 40 minutes, which required about 200 grams of ash per run. This was low enough that the relatively limited ash supply was sufficient to conduct a reasonably complete program. Thus, in runs of 10-12 minutes residence time, the longest times investigated, there were at least three changes of ash inventory.

The reaction was followed by analyzing the product ash increments for total and water-soluble zinc, chlorine and iron. Steady state was indicated by constant concentrations of zinc in the increments.

In general, complete material and elemental balances were not made because the small amount of material collected in the labyrinthine collection equipment downstream from the cyclone made accurate collection of small amounts of product very difficult. Instead the yield of effluent ash was determined by a silica balance around the ash in and the ash out. This, together with metals analyses of the feed and product ash, provided the data for calculation of metals removal.

RESULTS AND DISCUSSION

Primary Regeneration

The variables and the levels at which they were investigated are:

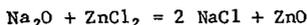
Temperature, $^\circ C$	871, 927, 954, 982
Pressure, kPa (psig)	119 (3)
% of Stoichiometric Air (nominal)	115
Mol % of Anhydrous HCl in Feed Air	5.5, 8.5, 11.5
Fluidized Bed Solids	297 x 595 μm Silica Sand
Fluidized Bed Depth, meters	0.305
Superficial Linear Velocity, meters/sec	0.305

Operability

The criterion for operability is that the coal ash leaves the bed by elutriation and that it is not retained in the bed due to size growth by sintering or clinker formation. Based on this criterion operability was as follows:

1. With 5.5% HCl in the inlet air:
 - a. 927°C (1700°F) is an operable condition, at least for short period.
 - b. 954°C (1750°F) is a marginally operable condition because of some sintering of ash in the bed.
 - c. 982°C (1800°F) is an inoperable condition because of severe ash sintering in the bed leading to clinker formation.
2. With 8.5 or 11.5% HCl in the inlet air:
 - a. 927°C is an operable condition.
 - b. 954°C is an operable condition.
 - c. 982°C probably is a marginally operable condition with some minor size growth in the ash grain size to be expected. This may be desirable from the standpoint of preventing ash buildup in the regenerated melt.

Some slight sintering may be desirable to give more efficient cyclonic removal of the ash from the gas stream. The sintering that restricts operability is likely promoted by the fluxing action of ash metal chlorides (NaCl, KCl, CaCl₂, MgCl₂) that can be formed in the hydrocracker by reactions such as



In general, 927°C was found to be the preferred temperature in that the temperature was low enough for good operability but high enough for good reaction kinetics, yielding efficient burnout of the impurities.

Results

The results presented will be confined to work done at 927°C and the effect of HCl concentration in the air on these results. Table II shows conditions and material balances for runs at 927°C with 5.5, 8.5 and 11.5 mol % HCl in the feed gas. Table II shows that good material balances were obtained. Products derived from four sources: the product melt, cyclone underflow solids, bed solids, and gas which includes water. The bed solids yield per unit of feed decreases as run duration, and hence the total amount of melt fed, increases, since a batch bed of silica was used.

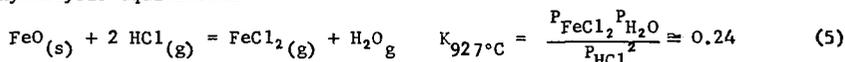
Table III shows the efficiency of regeneration for the three runs whose material balances have been given. Zinc recovery with 5.5% HCl in the feed air was 97.9% and it increased to 99.1% with 11.5% HCl in the feed air. Higher recovery is achieved with higher HCl concentration because the ZnCl₂ hydrolysis equilibrium is shifted farther to the ZnCl₂ side.

Recoveries of chlorine (Table III) greater than 100% of the chlorine in the feed melt reflect conversion of ZnO and ZnS in the feed to ZnCl₂ by interaction with the HCl in the gas.

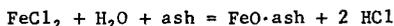
The small amounts of nitrogen, carbon and sulfur in the product melts (Table III) reflect the high efficiency of burnout of the NH₃, ZnS and carbonaceous residue, since essentially all of the remaining carbon, nitrogen and sulfur are in the unit offgases as combustion products: SO₂, CO, CO₂, N₂ and H₂O. Nitrogen and sulfur burnout were generally greater than 97% and carbon burnout was greater than 99%.

The low percentage of the feed ash in the product melt (Table III) shows that ash rejection at the cyclone was very efficient. Rejection of the individual metals of which the ash is comprised, was also efficient except for sodium and potassium, most of which appear in the melt. This is undoubtedly due to the formation of the highly-stable NaCl and KCl which are slightly volatile at regeneration

conditions (~ 3 and 5 torr vapor pressure at 927°C, respectively). A substantial fraction of the iron, most likely as FeCl₂ also appears in the melt. Over many cycles of hydrocracking and regeneration, vapor-liquid equilibria with respect to NaCl and KCl at a regeneration temperature of 927°C will limit the buildup of the sum of their concentrations in the ZnCl₂ catalyst to about 1.0 to 1.5 mol % when the regeneration is conducted at 3 atm pressure or even less at higher pressures. The hydrolysis equilibrium



or reactions such as



will restrict the FeCl₂ concentration in the regenerated ZnCl₂ catalyst to less than 10 mol %. A run in which the melt to regeneration was spiked with FeCl₂ tends to confirm this. Batch hydrocracking data indicate that, at these levels, these ash metal chlorides present essentially no problem regarding catalyst activity.

Table IV shows analyses of the product regenerated melts. The melts obviously are close to pure ZnCl₂ since the Zn:Cl atomic ratios are 1.95, 1.97 and 2.02.

After separating out the trapped ash and sampling, the used 28 x 48 mesh silica sand bed solids were employed in consecutive runs. The silica bed is almost inert to interaction with zinc and chlorine as shown by their extremely small contents in the silica sand bed after 54 hours of use in spent melt regeneration (Table V). There is some reaction of calcium and magnesium with the silica sand bed as indicated by an increase with time up to the concentrations of 1.49 and 0.44% of CaO and MgO after 54 hours.

Table VI gives analyses of the coal ash rejected by the cyclone during primary regeneration. The yields of these ashes were about 5.8% per 100 grams of feed melt exclusive of the steady-state concentration of ash trapped in the bed when the run was terminated. These ashes contain essentially all of the feed zinc not found in the product melt. The zinc retained in the ashes represent 1 to 2% of the feed zinc to regeneration, the retained zinc being lower when the HCl concentration in the air increases. It is in two forms: 1) zinc in the form of zinc chloride (water-soluble zinc) which is adsorbed on, entrained by, or diffuses to the cyclone underflow ash during the regeneration process, and 2) zinc in the form of ZnO, ZnO·SiO₂ and ZnO·Al₂O₃ (water-insoluble zinc) which is not completely converted to the ZnCl₂ because of equilibrium restrictions in reaction (4) and reactions of the type



Accordingly, the concentration of the water-insoluble zinc decreases as the HCl concentration in the feed air increases, whereas the water-soluble ash concentration remains more or less constant.

Since 1% zinc "loss" represents about 4¢ per gallon gasoline, recovery of the zinc in the ash is worthwhile from the economic aspect as well as from the environmental and conservation aspects. Therefore, investigations of "Secondary Zinc Recovery," that is, recovery of the zinc retained in the cyclone ash were made.

Secondary Zinc Recovery

Secondary recovery consisted of treatment of the cyclone underflow ash from the primary regeneration with ZnCl₂-free air plus HCl. The principle of this treatment is to reverse equilibria such as in reactions (4), (6) and (7) so that the water-insoluble zinc values are converted to ZnCl₂ which is evaporated from the ash substrate and recovered.

The cyclone ash used as feed in this work was a composite from a number of primary regeneration runs. Analysis of this feedstock is given in Table VI.

The levels of the variables studied in secondary zinc recovery are tabulated below:

Temperature, °C	816, 927, 1038
°F	1500, 1700, 1900
Pressure, kPa	119, 195, 271
psig	3, 14, 25
Mol % Anhydrous HCl in Feed Air	0 to 60
Feed Ash Residence Time, min	1.5 to 12.7
Fluidized Bed Solids	297 x 595 μ m Silica Sand
Fluidized Bed Depth, meters	0.013, 0.062, 0.124
Superficial Linear Velocity, meters/sec	0.18, 0.24, 0.30

Operability

Runs at all conditions tested gave excellent operability. No sintering of ash was found in any of the runs, even those at 1038°C.

Results

Figures 2, 3 and 4 summarize the results.

Figure 2 shows the breakdown of the recovery of water-soluble and water-insoluble zinc as functions of time and temperature, with a feed gas consisting of 20 mol % HCl in air. Essentially 100% of the water-soluble zinc in the cyclone ash was recovered in as little as one minute residence time at all the conditions tested. This is not surprising since no reaction is required, only volatilization of the ZnCl₂ that the water-soluble zinc represents. It has been shown that HCl is not required for this H₂O-soluble zinc recovery, that essentially 100% recovery can be obtained using HCl-free air or nitrogen. Figure 2 shows that the extent of secondary recovery of zinc is limited by the rate of reaction of the water-insoluble zinc to form volatile zinc chloride. The rate of recovery of the water-insoluble zinc is very fast initially but slows down markedly after the first minute of reaction time. Recovery is better the higher the temperature in the range of 816 to 1038°C.

Figure 3 is a plot similar to Figure 2 but it shows the total combined recovery of water-soluble and water-insoluble zinc. It is apparent from this plot that as high as 70% of the total zinc in the cyclone solids was recovered in as little as one minute residence time.

Greater than 73% of the chlorine in the cyclone underflow ash was volatilized and removed from the feed ash at all conditions tested.

Figure 4 shows that the water-insoluble zinc recovery increases moderately with increasing HCl partial pressure. The increase is unaffected by the HCl/air ratio. Hence, at a given HCl concentration in the feed air, the zinc recovery can be enhanced by increasing the total pressure and thereby the HCl partial pressure. Therefore, at the projected commercial operating pressure of 5 atm, 4 mol % HCl in the feed air should give results equivalent to the use of 20% HCl at 1 atm.

Thus, it has been shown that 70% or more of the zinc in the ash retained in the cyclone solids can be recovered in a relatively simple step added to the primary regeneration system. With secondary recovery of 70%, overall zinc recovery of 99.6 to 99.7% has been demonstrated. The secondary zinc recovery gives a savings in zinc makeup costs of about 3.5¢ per gallon of gasoline produced from coal via the ZnCl₂ process (8).

Hydrocracking Activity of Regenerated Melt

A run was made in the continuous bench-scale 3 lb/h hydrocracker in which the product ZnCl₂ catalyst from regeneration Run 19 was tested in hydrocracking Colstrip coal. As shown in Table VII, the regenerated catalyst was somewhat more reactive

than virgin zinc chloride. This is likely due to the fact that the regenerated catalyst contained less ZnO, which depresses ZnCl₂ activity, than the virgin zinc chloride.

References

1. Consolidation Coal Co., R&D Report No. 39, Office of Coal Research, U. S. Dept. of the Interior. Interim Report No. 2, "Research on Zinc Chloride Catalyst for Converting Coal to Gasoline--Phase I--Hydrocracking of Coal and Extract with Zinc Chloride," Vol. III, Book 1, March, 1968.
2. Zielke, C.W., Struck, R.T., Evans, J.M., Costanza, C.P., Gorin, E., "Process Design Develop.," Ind. Eng. Chem. (1966) 5, 151.
3. Ibid., 158.
4. Struck, R.T., Clark, W.E., Dudd, P.J., Rosenhoover, W.A., Zielke, C.W., Gorin, E., Ind. Eng. Chem. (1969) 8, 546.
5. Zielke, C.W., Rosenhoover, W.A., Gorin, E. -- Shale Oil, Tar Sands, and Related Fuel Sources (T. F. Yen, ed.) Advances in Chemistry Series No. 151, 153 (1976).
6. Zielke, C.W., Struck, R.T., Gorin, E., Ind. Eng. Chem. (1969) 8, 552.
7. Consolidation Coal Co., R&D Report No. 39, Office of Coal Research, U. S. Dept. of the Interior. Interim Report No. 2, "Pre-Pilot Plant Research on the CSF Process--Phase I--Regeneration of Zinc Chloride Catalyst," Vol. III, Book 2, March 1968.
8. Parker, W.A., et al., Conoco Coal Development Co. Report No. FE-1743-45 to DOE, Nov. 20, 1977.
9. Zielke, C.W., Klunder, E.B., Maskew, J.T. and Struck, R.T., "Continuous Hydroliquefaction of Subbituminous Coal in Molten Zinc Chloride," presented at the 85th National Meeting, A.I.Ch.E., Philadelphia, Pa., June 1978. Submitted for publication in I&EC, Proc. Des. Dev.

Acknowledgment

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TABLE II

Primary Regeneration
Conditions and Material Balances

Run Number	16	22	19
Reactor Temperature, °C	115	927	119
% Stoichiometric Air		125	119
Pressure, psig		3	
Superficial Linear Velocity, m/sec		0.305	
Fluidized Bed Depth, m		0.305	
Inlet Gas Composition, Mol %			
Air	94.5	91.5	88.5
Anhydrous HCl	5.5	8.5	11.5
Melt Feed Rate, kg/h/m ²	305	299	294
Run Time, h	4.0	10.9	22.1
Feedstock Used	F-6	F-7	F-6
In, gm/100 gm Feed Melt			
Feed Melt	100.00	100.00	100.00
Air (ex argon)	126.52	129.16	131.17
Anhydrous HCl	9.39	15.25	21.78
Bed Solids	26.66	10.04	4.99
Total	262.57	254.45	257.94
Out, gm/100 gm Feed Melt			
Product Melt	83.73	85.39	85.57
Cyclone Solids	3.86	5.79	4.92
Bed Solids	28.93	10.62	5.46
HCl	8.80	17.47	22.02
H ₂ O	7.48	6.30	6.72
CO ₂	20.96	22.36	25.78
CO	1.90	1.86	1.60
SO ₂	1.01	0.81	0.40
N ₂	102.00	96.65	95.04
O ₂	6.65	7.15	6.33
Total	266.30	254.37	253.84
(out/in) (100)	101.4	100.0	98.4

TABLE I

Analysis of Feedstocks for
Primary Regeneration and
Coal Hydrocracking

	"Spent" ZnCl ₂ Melt, Feed to Primary Regeneration		-100 Mesh Colstrip Coal, Feed to Hydro- cracking
	F-6	F-7	
Volatiles Matter	4.82	5.51	41.73
Ash (SO ₃ -free)	0.77	0.69	12.53
Organic Hydrogen	6.65	6.31	4.03
Carbon	0.22	0.05	66.53
Organic Nitrogen	0.03	0.00	1.00
Oxygen (by diff.)			14.72
Organic Sulfur	0.02	0.00	0.92
Pyritic Sulfur			0.27
Sulfate Sulfur	80.28	77.36	0.05
ZnCl ₂	0.91	1.28	
ZnS	2.71	3.31	
ZnO	0.56	0.72	
NH ₃	3.03	4.72	
Unidentified			
Ash Composition, Wt. %			
Na ₂ O	1.02	0.53	0.31
K ₂ O	0.40	0.27	0.31
CaO	13.43	13.58	12.72
MgO	5.09	5.36	5.59
Fe ₂ O ₃	9.37	8.93	7.55
TiO ₂	1.90	1.48	1.07
SiO ₂	49.46	52.34	51.33
Al ₂ O ₃	19.33	17.51	21.45

TABLE III

Efficiency of Primary Regeneration

Run No.	16	22	19
Mol % HCl in Air	5.5	8.5	11.5
	% of Feed Melt Component in Regenerated Melt		
Zn	97.9	98.8	99.1
Cl	102.0	107.3	106.2
C	0.6	0.7	0.9
S	9.7	2.0	2.4
N	0.0	2.7	2.5
Total Coal Ash	6.4	3.2	4.4
Na	63	92	75
K	80	122	66
Ca	1.9	1.7	2.6
Mg	1.7	1.4	2.6
Fe	33	12	20
Si	1.6	1.2	1.7
Al	2.1	1.7	0.2

TABLE IV

Primary Regeneration
Analysis of Product Melts

Run No.	16	22	19
<u>Anal. of Melt, Wt. %</u>			
H	0.15	0.13	0.17
C	0.05	0.05	0.07
N	0.00	0.02	0.02
O (by diff.)	1.49	1.63	0.40
Organic S	0.00	0.00	0.00
Sulfide S	0.04	0.01	0.01
Sulfate S	0.00	0.00	0.00
Zn	47.61	47.40	47.32
Cl	50.30	50.59	51.83
Ash	0.36	0.17	0.18
<u>Anal. of Ash, Wt. %</u>			
Na ₂ O	10.22	19.00	24.98
K ₂ O	5.23	12.55	8.71
CaO	4.03	9.20	11.29
MgO	1.43	3.01	4.36
Fe ₂ O ₃	49.21	19.55	20.11
TiO ₂	11.06	1.73	1.46
SiO ₂	12.41	23.68	27.72
Al ₂ O ₃	6.41	11.28	1.37

TABLE V

Primary Regeneration
Analysis of Effluent
Bed Solids

Run No.	19	22
Hours Used	32	54
	Weight %	
H	0.06	0.03
C	0.34	0.06
N	0.00	0.00
S	0.01	0.02
Zn	0.05	0.15
Cl	0.00	0.00
Na ₂ O	0.02	0.01
K ₂ O	0.05	0.04
CaO	0.78	1.49
MgO	0.30	0.44
Fe ₂ O ₃	0.20	0.19
TiO ₂	0.04	0.00
SiO ₂	97.35	96.23
Al ₂ O ₃	0.79	1.30

TABLE VI
 Primary Regeneration
Analysis of Cyclone Underflow Solids

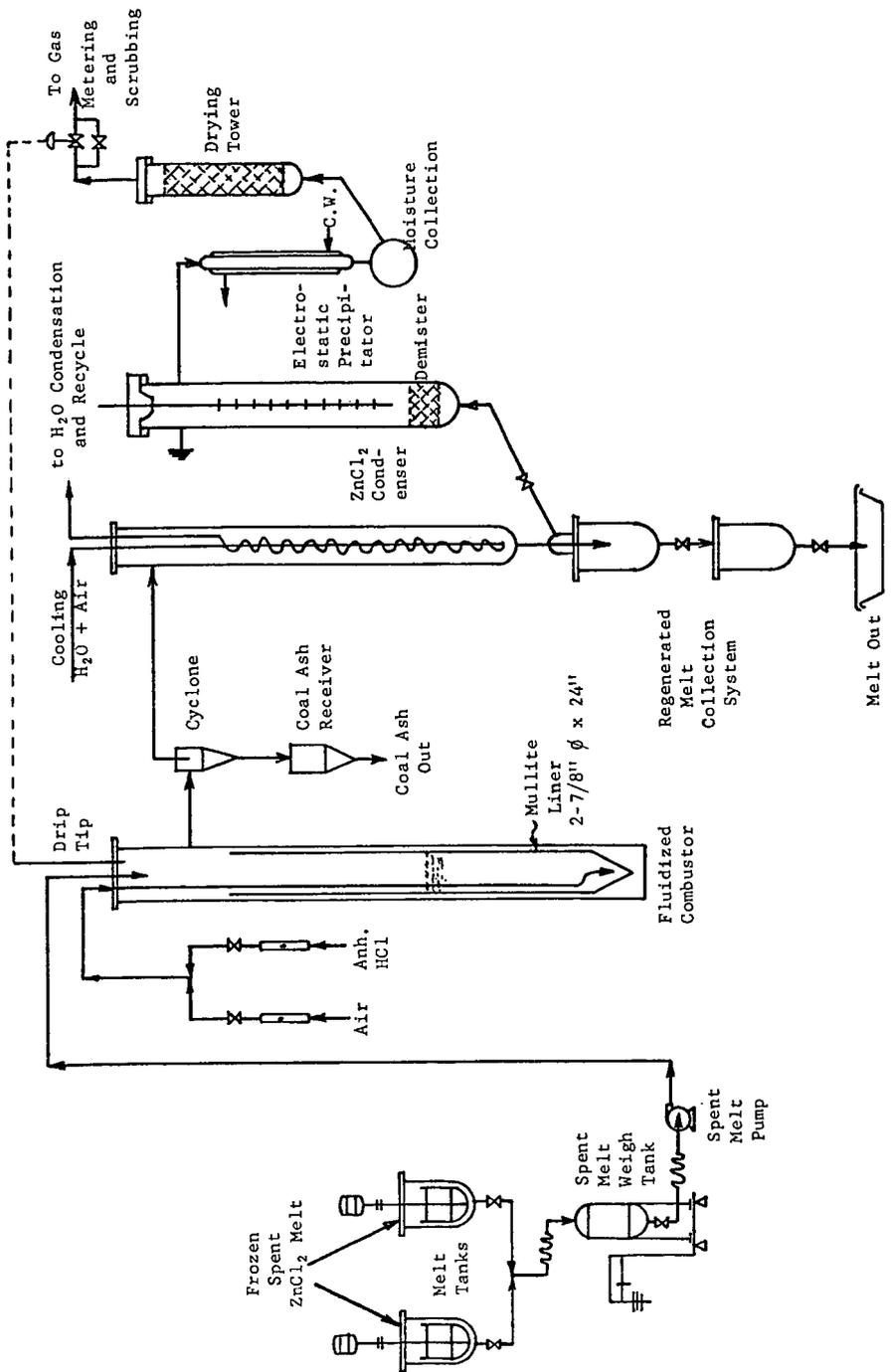
Run No.	16	22	19	<u>Composite</u>
% HCl in Feed Air	5.5	8.5	11.5	
<u>Analysis, Wt. %</u>				
Zn in ZnCl ₂ *	4.73	3.57	4.10	2.94
Zn in ZnO, ZnO·SiO ₂ , ZnO·Al ₂ O ₃ **	11.08	4.07	3.33	4.54
Cl	5.30	4.80	5.54	4.92
H	0.11	0.12	0.13	0.08
C	0.35	0.14	0.35	0.09
S (sulfate)	0.34	0.30	0.23	0.37
Na ₂ O	0.17	0.08	0.12	0.10
K ₂ O	0.04	0.02	0.02	0.03
CaO	9.65	11.87	9.48	11.40
MgO	4.04	4.41	4.14	4.45
Fe ₂ O ₃	3.67	4.06	2.98	3.90
TiO ₂	0.67	0.00	0.84	0.94
SiO ₂	33.36	44.75	43.21	42.86
Al ₂ O ₃	14.20	18.19	19.48	18.41

* Water-soluble zinc
 ** Water-insoluble zinc

TABLE VII
 Comparison of Hydrocracking
 Results With New and Regenerated
ZnCl₂ Catalyst

<u>Conditions</u>		
Feedstock	-100 Mesh Colstrip Coal	
Temperature, °C	399	
Total Pressure, psig	3500	
Melt Residence Time, h	1.29	
ZnCl ₂ /MF Coal, Wt. Ratio	1.0	
	<u>Regenerated ZnCl₂ Catalyst</u>	<u>New ZnCl₂ Catalyst</u>
<u>Yields, Wt. % MAF Coal</u>		
C ₁ -C ₃	1.2	2.1
C ₄	4.2	2.7
C ₅ x 200°C Distillate	41.5	33.5
200 x 475°C Distillate	16.2	20.9
+475°C Distillate	6.0	6.1
MEK-Soluble Residue	17.7	15.8
MEK-Insoluble Residue	2.5	4.9
H Consumed	6.4	6.8
Conversion to Distillate	79.8	79.3

FIGURE 1
SIMPLIFIED FLOW DIAGRAM OF BENCH-SCALE (4 LB/HR) REGENERATOR



SECONDARY ZINC RECOVERY GRAPHS

FIGURE 2

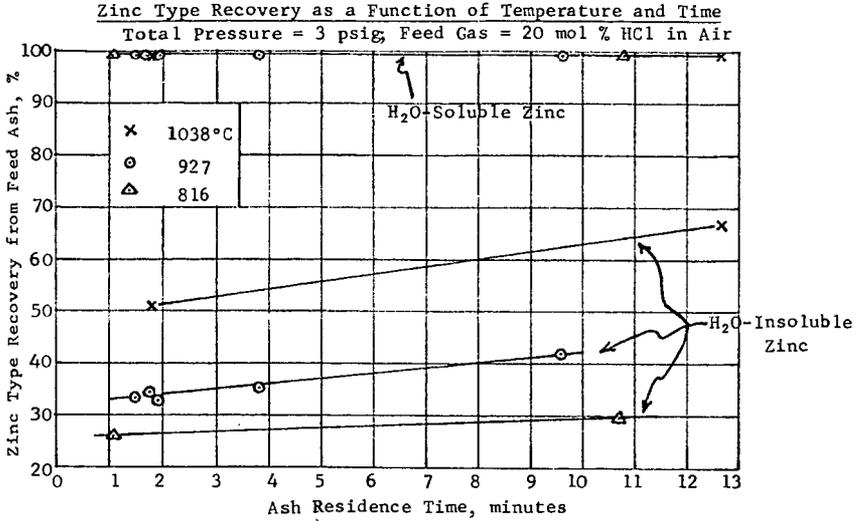


FIGURE 3

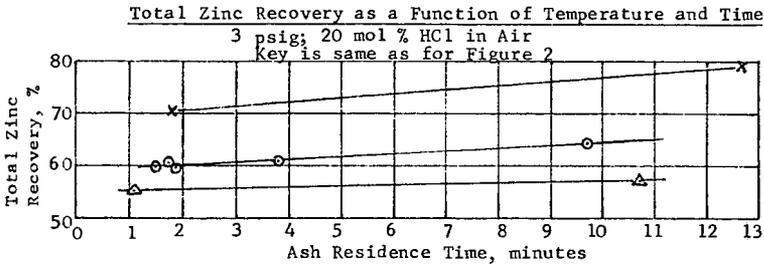


FIGURE 4

