REGENERATION OF ZINC HALIDE CATALYSTS USED IN HYDROCRACKING OF COAL EXTRACT

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INTRODUCTION

The application of molten zinc chloride catalysis to the hydrocracking of polynuclear hydrocarbons, coal extract and coal was discussed in two previous papers.[8a,b] The zinc chloride, however, is not a catalyst in the chemical sense since it is partially destroyed by reaction with the N and S impurities in the hydrocracker feed. When coal itself is used further complications arise due to reactions with some of the inorganic components in the coal ash.

A commercial process utilizing molten zinc chloride catalysis must provide a viable scheme for regeneration of the catalyst.

Two schemes for using the catalyst were discussed in a previous paper, i.e., with and without the concomitant addition of zinc oxide acceptor.

The following reactions occur when no acceptor is added:

$$ZnCl_2 + H_2S = ZnS + 2\ HCl \qquad (1)$$

$$ZnCl_2 + NH_3 = ZnCl_2 \cdot NH_3 \qquad (2)$$

$$ZnCl_2 \cdot NH_3 + HCl = ZnCl_2 \cdot NH_4Cl \qquad (3)$$

The addition of zinc oxide acceptor eliminates reaction (3) and introduces a new reaction

$$ZnO + 2\ HCl = ZnCl_2 + H_2O \qquad (4)$$

The present paper will discuss only the regeneration of the catalyst for the non-acceptor case. The acceptor case will be discussed in a separate paper.

The melt leaving the hydrocracker thus, in general, will contain in addition to $ZnCl_2$ the following compounds: ZnS, $ZnCl_2 \cdot NH_3$ and $ZnCl_2 \cdot NH_4Cl$. The addition compounds between zinc chloride and NH_3 and NH_4Cl are written as the 1/1 adducts not because they necessarily exist as such in the melt but for convenience of discussion. The ratio of the NH_4Cl to the NH_3 adducts is dependent on the ratio of N to S in the feed. Where the moles of sulfur in the hydrocracker feed is equal to or greater than one-half the moles of nitrogen, substantially all of the NH_3 will be present as the NH_4Cl double salt.

Regeneration of the melt comprises removal of the bulk of the sulfur and nitrogen and return of the melt as relatively pure zinc chloride.

From the economic point of view it would be desirable to recover the sulfur in the form of elemental sulfur and the nitrogen as ammonia such that credits for these materials would partially defray the regeneration cost.

In addition to the inorganic impurities in the spent melt, the melt contains organic impurities which cannot be distilled out of the melt. The organic residue itself can be

divided into two parts, one soluble in MEK and the other insoluble. The first part is largely convertible to distillate oil on recycle while the latter is mostly unconvertible and can be regarded as semi-coke. The regeneration process thus must in addition remove the organic residue from the melt before it can be recycled, coked or otherwise processed.

The reactions which are involved for specific components of the spent melt are listed below. Most of these reactions involve simple reversal of the reactions by which they were formed, i.e., reactions (1), (2) and (3) above. Where this is the case the number of the reaction is primed.

Regeneration of Zinc Sulfide

$$ZnS + 2\ HCl = ZnCl_2 + H_2S \qquad (1')$$

Regeneration of Ammonium Chloride-Double Salt

$$ZnCl_2 \cdot NH_4Cl = ZnCl_2 \cdot NH_3 + HCl \qquad (3')$$

Regeneration of $ZnCl_2 \cdot NH_3$

$$ZnCl_2 \cdot NH_3 = ZnCl_2 + NH_3 \qquad (2')$$

$$ZnCl_2 \cdot NH_3 = ZnCl_2 + 1/2\ N_2 + 3/2\ H_2 \qquad (5)$$

It is the purpose of this paper to present thermodynamic and other data bearing on the feasibility of the particular regeneration scheme shown. The data on the individual process steps involved are presented. The integration of the individual process steps into the overall scheme is also given.

EXPERIMENTAL

Equipment and procedures for hydrocracking of coal extract with zinc chloride catalyst have been given previously.[8]

Figure 1 shows the apparatus used to determine the equilibria in the decomposition of the zinc chloride-ammonium chloride double salt. A flow system was used with nitrogen passing slowly through a molten bed of $ZnCl_2 + NH_4Cl$ and the exit gas being analyzed for HCl. A number of points taken over a period resulted in curves of HCl partial pressure versus the extent of NH_4Cl decomposition.

The zinc chloride and ammonium chloride used were Fisher Scientific Co. Certified Reagents. The zinc chloride was 98 percent pure, the impurities being water and zinc oxide. This material was purified at the start of each run by heating to 425°C in a flow of purified nitrogen to remove water, and then passing anhydrous HCl through it for two hours to convert ZnO to $ZnCl_2$. This was followed by a nitrogen purge of 12 to 36 hours to remove excess HCl from the melt. The nitrogen used was purified by passage through hot copper, Ascarite, and magnesium perchlorate to remove traces of oxygen, carbon dioxide and water.

After purifying the zinc chloride, the reactor temperature was lowered to 343°C to minimize the possible loss of HCl when adding NH_4Cl through a long stem funnel inserted in the stirrer annulus (3 seconds required). The reactor was then brought to the desired temperature with a low flow of nitrogen (1 ml/min). The desired temperature was controlled to ± 2°C and the nitrogen rate raised to the operating flow of 4.7 ± 0.2 cc/min (STP). The nitrogen gas reaches equilibrium HCl content in passing through the molten bed as shown by identical results at flows between 4.7 and 12 cc/min and stirring rates from the 3100 rpm used down to as low as 1500 rpm. The gas from the reactor passes through a caustic trap and is collected in a bottle by water displacement. Two recovery trains used alternately allow continuous collection.

The 0.1 or 1.0 N caustic used in the traps is titrated after use with 0.1 or 1.0 N HCl using methyl red indicator. Caustic traps are used even during lineout periods so the amount of NH_4Cl remaining in the melt can be accurately calculated.

Collection of the effluent nitrogen in bottles allowed accurate measurement of flow rates using weight of water remaining after adjustment of the gas to atmospheric pressure.

When most of the NH_4Cl had decomposed, pressure of NH_3 over the bed became appreciable, combining with HCl on cooling to form solid NH_4Cl in the glass wool trap. Analyses of these solids confirmed that they were mostly NH_4Cl. At 427°C, a small amount of $ZnCl_2$ was also found in the glass wool trap. The partial pressures of HCl calculated by caustic titration were corrected by adding the additional HCl tied up as solid NH_4Cl in the solids trap.

Equilibrium data for zinc sulfide regeneration (Reaction (1′), Table III) were determined in a static glass system. After adding ZnS, the vessel was evacuated and brought to temperature under vacuum. The vacuum was then shut off and aqueous HCl added in increments. After each increment, the slurry was stirred and allowed to reach steady state before the pressure was measured. For purposes of the rough figures reported in Table III, the H_2S pressure was taken as the total pressure minus the vapor pressure of water at the temperature used. The normality of the acid was determined by titration after completion of the run.

The phase separation studies reported in Table II were conducted in the same type of rocking autoclave used for hydrocracking tests.[8a] The synthetic spent melt, whose composition is given in Table IIA, was charged to the autoclave along with the desired amount of water or in the final test, with water plus dimethylnaphthalene (Table IIB). After flushing the air with nitrogen, the unit was heated to temperature and rocked for an additional 30 minutes. The autoclave was then tilted vertically and allowed to stand for one hour before bleeding off the contents through the bottom. The products were collected in about 8 increments which were then usually combined as "organic" and "aqueous" phases. The aqueous phase was washed with benzene to remove organics before distilling off the water. The organic phase was likewise distilled to +400°C end point to remove any light material before analysis. Methods of analysis for the zinc salts, NH_3 and NH_4Cl were given previously.[8a]

RESULTS AND DISCUSSION

1. Separation of Organic Residue from Spent Melt

No substantial separation of phases was ever observed for mixtures of zinc chloride melt with high boiling organic materials such as extract, pyrene or hydrocracking residues. A number of different conditions were tried using separation times of up to one hour, with negative results.

The results of one such experiment are summarized in Table I. In this experiment extract was hydrocracked with zinc chloride melt at 750°F and 3000 psig. When the run was completed the autoclave was placed in a horizontal and then a vertical position for 15 minutes each while maintaining temperature and pressure. A number of samples were successively withdrawn over an additional 15 minute period and analyzed as shown.

It is seen that the amount of $ZnCl_2$ and organic residue remained reasonably constant over the first six samples indicating no phase separation. The hydrocarbon distillate showed considerable fluctuation from sample to sample but no definite trend is discernable. The bulk of the distillate was withdrawn with the bulk of the gas in the last sample. It is likely that most of the distillate was actually in the vapor phase as the temperature used was above the critical temperature of most gasoline components.

It therefore does not appear possible to effect a phase separation between the high-boiling organics and the catalyst melt and this must be taken account of in any regeneration scheme. The high-boiling residue still contains substantial quantities of N, O and S which hetero atoms may complex with the zinc chloride catalyst to form a true solution. On the other hand, polynuclear hydrocarbons such as pyrene which do not contain hetero atoms also do not separate.[8a] It thus is not ruled out that one is dealing with a relatively stable emulsion.

It is noted likewise that no concentration of ZnS by settling is apparent from Table I. Separate experiments were conducted in which $ZnCl_2$ melts were mixed with powdered ZnS and allowed to stand. Again, no phase separation was observed. Since the solubility of ZnS in molten $ZnCl_2$ is known to be small,[3] this is clearly a case of a stable dispersion rather than solution.

Recovery of the organic residue therefore requires addition of another component which will cause phase separation to take place. If solution of unconverted extract is due to complex formation with zinc chloride, it would be logical to assume that phase separation could be effected by addition of agents which themselves complex with zinc chloride such as H_2O, CH_3OH, NH_3 and NH_4Cl. All of these materials have been found in preliminary experiments to be capable of effecting the desired phase separation. At the time of this writing, water addition has been most thoroughly investigated and only some of these data at 200 and 250°C are presented. Composition of the separated phases after water addition are given in Table IIA.

The feed melt composition used in this study was a simulated spent melt and had the composition given in the bottom of Table IIA. Extract was used in place of hydro residue due to shortage of the latter material. Since separation of extract from spent melt is, if anything, more difficult, the results are adequately conservative.

Adequate separation of the extract from the zinc chloride phase takes place at water/melt ratios of 0.3 or greater. The sharpness of separation of the zinc chloride from the organic phase leaves something to be desired, however, especially at low water/melt ratios. The difficulty is due to physical occlusion of aqueous zinc chloride in organic phase. The organic phase is a highly viscous mass that does not flow readily, thus making a sharp separation difficult. The high viscosity is due in part to the inherent high viscosity of the extract and secondly due to dispersion of the zinc sulfide in the organic phase. The zinc sulfide was surprisingly in all cases nearly quantitatively transferred to the organic phase.

The addition of aromatic solvents was investigated in order to improve the sharpness of separation. One such experiment is shown in Table IIB. The added solvent made it possible to withdraw the organic phase as a fluid liquid due to the effect of the solvent in cutting the viscosity. The organic phase was relatively free of inorganic components. In contrast to the previous case most of the ZnS was found in the aqueous phase. This points to physical trapping by the viscous extract as the principle reason for transferral of the ZnS to the organic phase in the previous instance.

2. Regeneration of Zinc Sulfide via Reversal of Reaction (1)

The equilibrium in reaction (1) has been measured by Britzke and Kapustinsky[2] down to the melting point of $ZnCl_2$. Their data were then extrapolated below the melting point using the heat of reaction

$$ZnCl_{2(s)} + H_2S = ZnS + 2\ HCl \qquad (1)$$

$$\Delta H = +16{,}700 \text{ cal/mole}$$

as determined from the thermochemical data given in Bichowsky and Rossini.[1] The result is

$$\log K_p = \frac{-3360}{T} + 7.62 \qquad (6)$$

The equilibrium becomes less favorable with decreasing temperature such that reversal of the reaction becomes feasible at temperatures of the order of 200°C or less, i.e., $K_p = 1.0$ at 207°C. For example, at 100°C

$$K_p = P_{HCl}^2/P_{H_2S} = 6.46 \times 10^{-3}$$

Thus, if reversal of the reaction is effected with 0.1 atmosphere of HCl, the ratio $P_{H_2S}/P_{HCl} = 15.5$ at 100°C.

In actual practice, reversal of reaction (1) can only be effected after addition of sufficient water to maintain a liquid phase. The equilibrium for reversal will now even be more favorable since there is a negative free energy change for the reaction

$$ZnCl_{2(s)} + H_2O_{(l)} = ZnCl_{2(aq)} \qquad (7)$$

The effect of using aqueous solutions in facilitating the reversal of reaction (1) is illustrated by some equilibrium data measured by us in dilute aqueous solutions as shown in Table III. The equilibrium is now much more favorable and reversal of reaction (1) with aqueous solution of zinc chloride is to be regarded as a feasible process. Experiments were conducted wherein actual spent melts from hydrocracking of extract were treated with aqueous hydrochloric acid. Rapid evolution of H_2S was noted.

3. Decomposition of Zinc Chloride-Ammonium Chloride Double Salt

The reaction in question is the reversal of reaction (3) which not only supplies the HCl required for regeneration of zinc chloride from zinc sulfide, but eliminates HCl from the melt prior to recovery of the NH_3. Equilibrium measurements were accordingly made over the range 340-450°C and for initial concentrations of NH_4Cl in the range of 10 to 20 mole percent. The partial pressure of HCl in equilibrium with the melt as a function of percent NH_4Cl decomposed is shown in the semi-log plot of Figure 2.

The smoothed data from Figure 2 are replotted to define a "pseudo" equilibrium constant K.

$$P_{HCl} = K\frac{(1-\alpha)}{\alpha} \qquad (8)$$

where α is the fraction of NH_4Cl decomposed. Adequate straight lines are obtained (Fig. 3) although slight tailing off is noted in some cases at high conversion levels. This may be due to experimental error as a result of slight losses of NH_3 from the melt. The NH_3 was collected and analyzed as NH_4Cl and corrections made for its loss. However, if the measurements of volatilized NH_3 were slightly low, it would produce the tailing off observed. The values of K are considerably greater for the 10 mole percent NH_4Cl series than for the 20 mole percent NH_4Cl series. No adequate explanation for this phenomenon can be advanced at this time.

A semi-log plot of the HCl pressure versus the reciprocal of the absolute temperature at constant percent NH_4Cl decomposition is given in Figure 4. The slopes of the lines correspond to the heat of decomposition,

$$\Delta H = 21{,}000 \pm 600 \text{ cals/mole}$$

It is now possible to express values of K as a function of the temperature in degrees Kelvin by the expressions

$$\log K = \frac{-4590}{T} + B \qquad (9)$$

where B = 6.32 and 6.14 when the initial NH_4Cl concentrations are 10 and 20 mole percent, respectively, and the HCl partial pressure in the expression for K is given in atmospheres.

In practice, HCl would be removed from the melt by stripping with hot gas in a countercurrent tower. The HCl concentration in the gas as a function of that in the melt at any point in such a tower is given by the simple material balance relationship

$$P_{HCl} = \frac{(\Delta - \Delta_f)}{(\Delta - \Delta_f + r)} \cdot \pi \qquad (10)$$

The equilibrium pressure of HCl over the melt is likewise given by

$$P_{HCl}^{eq.} = K\left(\frac{\Delta}{1 - \Delta}\right) \qquad (11)$$

where Δ = Mole fraction of total NH_3 in melt combined with HCl.

Δ_f = Value of Δ in melt leaving tower.

π = Total pressure in atmospheres.

r = Moles of stripping gas/mole of $NH_3 + NH_4Cl$ in melt.

It is clear that in order to have a net driving force for HCl evolution $P_{HCl}^{eq.} > P_{HCl}$ everywhere in the tower. Consider the case, for simplicity, where the melt is nearly quantitatively stripped of HCl, i.e., $\Delta_f \cong 0$. The above condition is satisfied if

$$\left(\frac{dP_{HCl}}{d\Delta}\right)_{\Delta = 0} \leqq \left(\frac{dP_{HCl}^{eq.}}{d\Delta}\right)_{\Delta = 0} \qquad (12)$$

Differentiating equations (10) and (11), the inequality may be written,

$$\pi/r \leqq K \qquad (13)$$

For example, if the temperature at the melt outlet is 460°C, and the mole fraction of $NH_3 + NH_4Cl$ in the melt is 0.20, then $\pi/r \cong .73$.

A net driving force for HCl evolution can still be maintained in such a tower, even if, as will normally be the case, the temperature decreases from bottom to top. The more general inequality can be obtained if the differentiation of equations (10) and (11) above is performed with the equilibrium constant K as function of Δ and therefore also of temperature (i.e., Δ is considered to be a function of temperature). The result is, again for case where $\Delta_f \cong 0$,

$$\frac{K_o}{(1 + \Delta/r)^2} \leqq \left(\frac{\Delta}{1 - \Delta}\right)\frac{dK}{d\Delta} + K\left(\frac{1}{1 - \Delta}\right)^2 \qquad (14)$$

where K_o is the value of K at melt outlet, i.e., where $\Delta = 0$. Equation (14) in combination with equation (9) thus can be employed to define the maximum allowable rate of decrease in temperature with respect to Δ in the tower and thus is useful for design purposes.

4. Decomposition of Zinc Chloride-Ammonia Adduct

The final regeneration of the spent melt requires that a major fraction of the ammonia be removed. This can be done in principle by thermal decomposition of the adduct which amounts to a reversal of reaction (2). This would be attractive since recovery of NH_3 would bring substantial by-product credits.

The design of such an NH_3 adduct decomposition tower requires equilibrium data which give the partial pressure of ammonia over the melt as a function of its ammonia content and temperature. Equilibrium measurements in this system have been made by Kurilov,[6] Koeneman[4] and Krasnov.[5] The above authors in the order named measured the ammonia pressures at successively increasing temperatures and decreasing ammonia content.

The data of these authors are summarized in graphical form in Figure 5. A log-log plot is used to permit some extrapolation outside the range of the data. No experimental points are available below 3.4 wt. percent of NH_3.

The ammonia content of the melt sent to the ammonia decomposer in practice will vary between 1.5 and 5.0 wt. % depending upon the melt circulation rate used. It is clear, however, from the data of Figure 5 that it will be very difficult to achieve very low NH_3 concentrations, i.e., below 1% in the regenerated melt unless temperatures well above those investigated are used.

It is not necessary, however, to reduce the NH_3 content of the regenerated melt to zero. It has been found, for example, that the reaction

$$ZnO + 2(ZnCl_2 \cdot NH_4Cl) \rightarrow 2\ ZnCl_2 \cdot NH_3 + ZnCl_2 + H_2O \qquad (15)$$

goes quantitatively to the right at temperatures in the neighborhood of 400°C. The melt leaving the NH_4Cl decomposer will therefore be free of zinc oxide. This is in contrast to the feed melt to the hydrocracking runs described in a previous paper[8b] which contained 2.8 mole % of ZnO. Equivalent hydrocracking results will therefore be obtained with a regenerated melt containing .056 moles NH_3/mole $ZnCl_2$ (0.7 wt. % NH_3) to those reported experimentally which contained .056 moles NH_4Cl/mole $ZnCl_2$. The above result follows since reaction (15) proceeds in the melt used in the experimental work to produce an identical melt composition in both cases. The activity of the melt in this case [cf. Figure 6 of previous paper[8b]] is only negligibly less than that of a melt containing no NH_4Cl.

The ammonia decomposition equilibrium at lower NH_3 concentrations and higher temperatures is presently being investigated in the Consolidation Coal Co. laboratories but no data are available as yet.

One interesting observation has been made, however, that the reaction

$$ZnCl_2 \cdot NH_3 = ZnCl_2 + 1/2\ N_2 + 3/2\ H_2 \qquad (5)$$

is readily catalyzed by oxidized metal surfaces. Thus, it appears to be possible, if desired, to eliminate the last traces of ammonia from the melt by catalytic decomposition at temperatures of the order of 550-600°C.

5. Removal of Ash

Coal extract feed will contain anywhere from 0.1 to 0.4 wt. % ash depending on its method of preparation. Ash must be periodically removed from the melt during its regeneration to prevent its build up. Several methods are available such as filtration after dilution with water and removal of zinc sulfide. It also may be removed by distillation of zinc chloride vapor from a side stream to leave an ash residue.

6. Overall Regeneration Scheme

The integration of the various process steps discussed above into a single regeneration scheme is illustrated in Figure 6. Appropriate operating ranges for each process step are likewise given.

A material balance around the operation is given in Table IV. The spent melt entering regeneration is assumed to be the same composition as that from the 5 stage coal extract hydrocracking run reported in a previous paper[8b] {cf. Table IV}. The regenerated melt composition is adjusted such that the composition of the spent melt after hydro is consistent with elimination of 98.0% of the sulfur and 87.5% of the nitrogen from the feed extract, i.e., in accord with experimentally observed results in the 5 stage run.

The performance of the NH_3 decomposition tower was calculated from the data of Figure 5 assuming isothermal operation at 530°C, 4 theoretical stages and a total pressure of 1.5 atms.

In practice, one would have a temperature increase in the NH_3 decomposition tower since heat would be supplied by condensing zinc chloride vapor from the boiler. Thus, fewer stages would be required.

Recovery of NH_3 from the gases leaving the ammonia decomposer can be effected according to the data of Kurilov (cf. Figure 5) by scrubbing with a $ZnCl_2$ melt relatively concentrated in NH_3 at lower temperatures as shown in Figure 6.

The melt is readily decomposed to yield pure NH_3 gas at temperatures of the order of 400°C. Of course, other more conventional methods of ammonia recovery could also be used.

The above scheme is likewise adaptable to spent melts used in hydrocracking of coal itself. In this case the melt will contain a larger percentage of ash and accordingly more ash will have to be rejected in the vaporization step. In practice, a higher proportion of the melt will have to be vaporized, and this would be one of the disadvantages of using coal as compared with extract.

ACKNOWLEDGMENT

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(b) "Molten Zinc Halide Catalysts for the Hydrocracking of Coal Extract and Coal."

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TABLE I

Phase Separation of Organic Residue from Zinc Chloride Melt

Hydro Condition: $ZnCl_2$/Extract, Wt. Ratio = 1
Total Hot Pressure = 3000 psig
Temperature = 750°F

Sample No.	1	2	3	4	5	6	7	8
Cum. Wt. % of Total Liquid Withdrawn	7.8	17.6	25.4	35.3	45.7	58.0	64.7	100
Cum. Wt. % of Total Gas Withdrawn	1.9	3.2	4.2	5.6	7.0	8.1	10.2	100
Type of Sample	Melt →							Lt.Oil + Gas
Analysis, Wt. % of Sample								
Hydrocarbon Distillate -400°C	5.5	10.5	7.8	16.2	9.4	9.8	21.9	100
Organic Residue +400°C	18.0	20.3	21.6	15.4	18.2	17.3	29.5	--
$ZnCl_2$	62.7	54.4	58.2	56.9	61.8	61.9	40.4	--
$ZnCl_2 \cdot NH_3$ + $ZnCl_2 \cdot NH_4Cl$	9.3	10.8	8.5	11.5	6.5	6.8	4.0	--
ZnS	4.5	4.0	3.9		4.1	4.2	4.2	--

TABLE II

A. Phase Separation Studies with Water Addition

60 Minute Phase Separation Time Used

Wt. Ratio H_2O/Feed		0.3		0.5		1.0		0.5		1.0	
Temperature, °C		200		200		200		250		250	
Effluent Composition Wt. % of Feed	Feed Melt	Aqueous Phase	Organic Phase	Aqueous Phase	Organic Phase	Aqueous Phase	Organic Phase	Aqueous Phase	Organic Phase	Aqueous Phase	Organic Phase
$ZnCl_2$	81.9	57.6	20.3	71.1	9.1	75.0	3.6	75.8	5.2	79.0	2.3
ZnS	4.8	0.0	4.4	0.0	4.0	0.0	5.5	0.0	3.8	0.0	4.3
NH_3	1.2	1.0	0.3	1.0	0.2	1.0	0.0	1.3	0.1	1.1	0.0
Extract	12.1	0.4	16.0	0.5	9.2	0.6	13.2	0.9	9.2	0.7	10.3
Total	100.0	59.0	41.0	72.6	22.5	76.6	22.3	78.0	18.3	80.8	16.9

B. Phase Separation with Water and Dimethylnaphthalene (DMN) Solvent Addition

Wt. Ratio H_2O/Feed 0.56

Wt. Ratio, Dimethylnaphthalene/Feed 0.22

Temperature, °C 250

Effluent Composition Wt. % of Feed	Aqueous Phase	Organic Phase
$ZnCl_2$	44.4	--
NH_4Cl	2.8	--
ZnS	2.3	0.5
Extract	1.4	48.6
Total	50.9	50.1

Feed Melt Composition, Wt. %	
$ZnCl_2$	44.4
NH_4Cl	2.8
ZnS	2.8
Extract	50.0

TABLE III

Equilibrium Data Compared for Reactions

$$ZnS + 2\ HCl = ZnCl_{2(s)} + H_2S \qquad (1')$$

$$ZnS + 2\ HCl = ZnCl_{2(aq)} + H_2S \qquad (1'')$$

Temperature, °C	50	66
Normality of Equil. Mixture		
HCl	2.6	0.68
$ZnCl_2$	0.4	0.32
P_{H_2S} (atm)	1.52	0.10
P_{HCl} (atm) (1)	7.9×10^{-5}	1.3×10^{-5}
P_{H_2S}/P_{HCl}^2 obs. for reaction (1″)	2.4×10^{8}	5.9×10^{8}
P_{H_2S}/P_{HCl}^2 Calc. for reaction (1′)	4.9×10^{3}	1.5×10^{3}

(1) From literature data at the measured acid concentration of International Critical Tables Vol. III, pg 301.

TABLE IV

Material Balance in Regeneration of Zinc Chloride Melt from 5 Stage Extract Hydro Run at 750°F - 3000 psig

Process Step	From Extract Hydro	From ZnS Decomposer	Melt from Decanter	From NH_4Cl Decomposer	From Condenser	From Primary NH_3 Decomposer
Temperature, °C	393	~ 100	200	427	400	530
No. of Stages	5	1	1	NC	1	4
Moles/100 lbs Extract Fed to Hydro						
Liquid Phase						
$ZnCl_{2(l)}$ (2)	0.197	0.252	0.252	0.252	0.0024	0.343
$ZnCl_2 \cdot NH_{3(l)}$ (2)	0.018	0.018	0.018	0.129	0.0078	0.038
$ZnCl_2 \cdot NH_4Cl_{(l)}$ (2)	0.111	0.111	0.111	--	--	--
$ZnS_{(s)}$ (1)	0.055	--	--	--	--	--
+400°C Organic Residue (lbs)	17.4	17.4	--	--	--	--
Gas Phase						
Stripping Gas	--	--	--	NC	0.550	0.550
NH_3	--	--	--	--	0.091	0.0988
$ZnCl_{2(v)}$	--	--	--	--	--	0.0102
H_2S	--	0.055	--	--	--	--
HCl	--	--	--	0.111	--	--

(1) Percent of sulfur released from extract feed as ZnS = 98.0

(2) Percent of nitrogen released from extract feed as $NH_3 + NH_4Cl$ = 87.5

Figure 1

APPARATUS FOR EQUILIBRIUM STUDIES

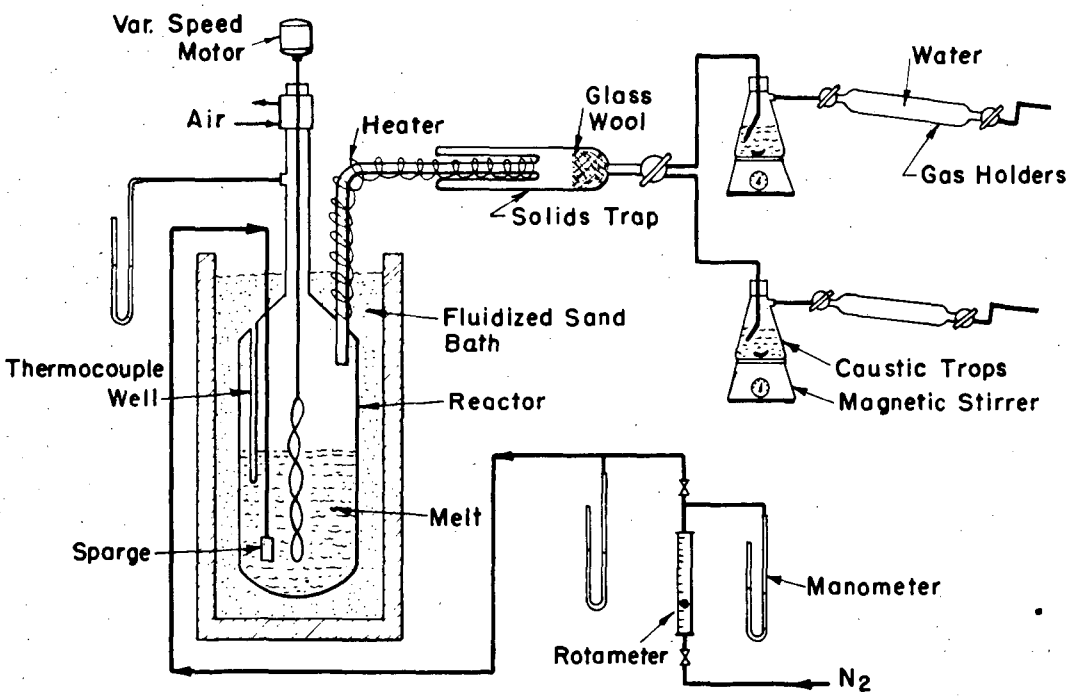


Figure 2

EQUILIBRIUM PARTIAL PRESSURE OF HCl VS % NH_4Cl DECOMPOSED

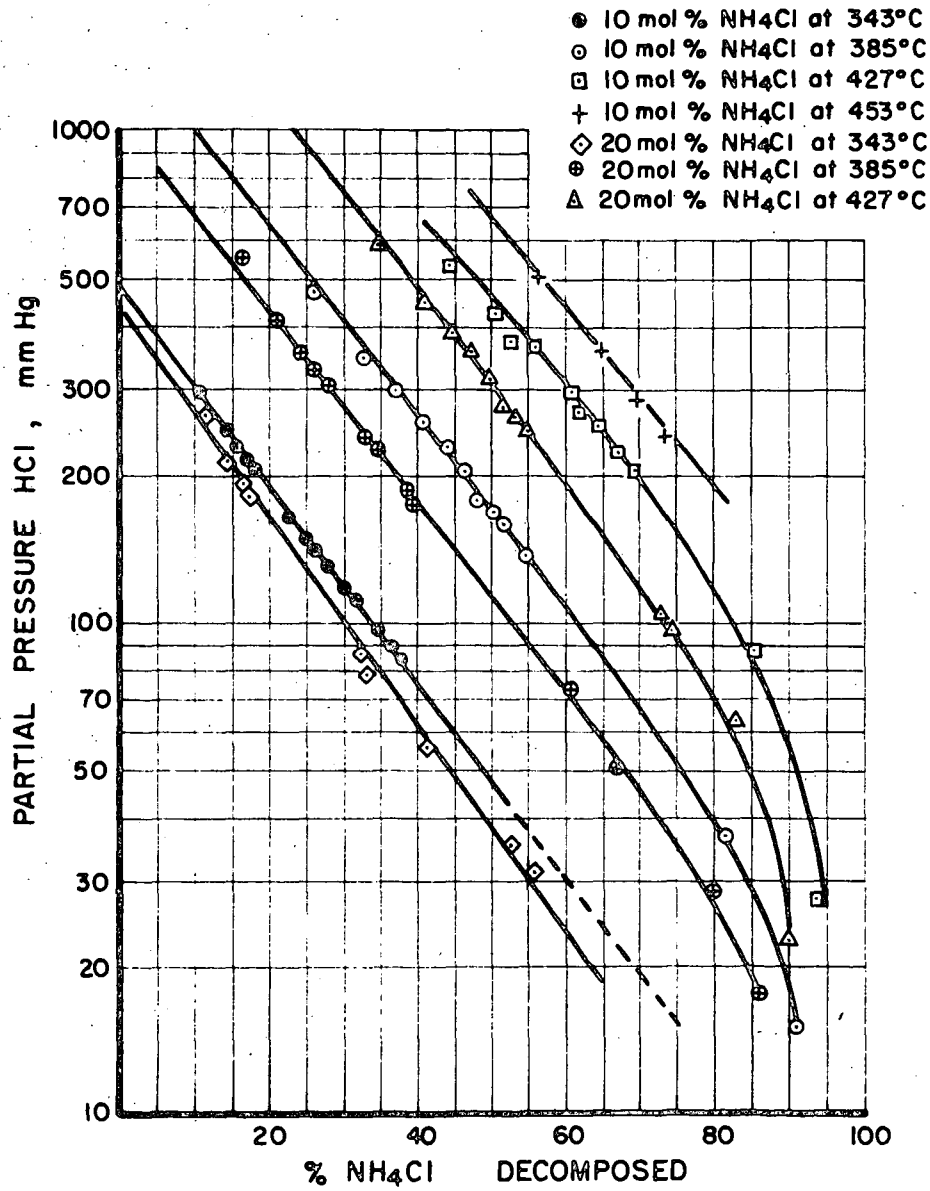


Figure 3

EQUILIBRIUM CONSTANT FOR REACTION

$ZnCl_2 \cdot NH_4Cl = ZnCl_2 \cdot NH_3 + HCl$

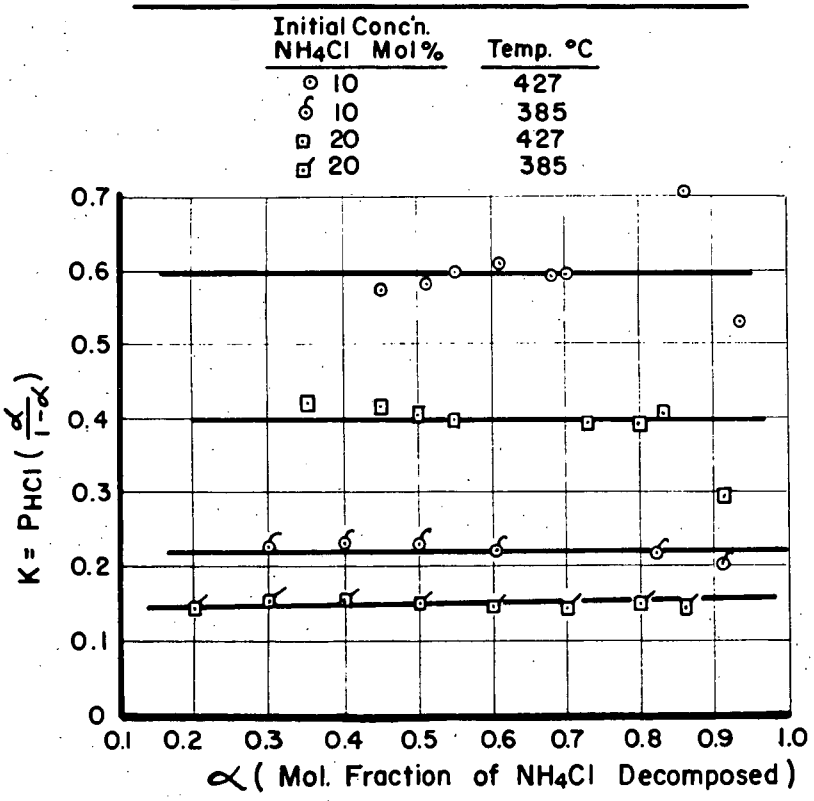


Figure 4

EFFECT OF TEMPERATURE ON HCl EQUILIBRIUM PARTIAL PRESSURE

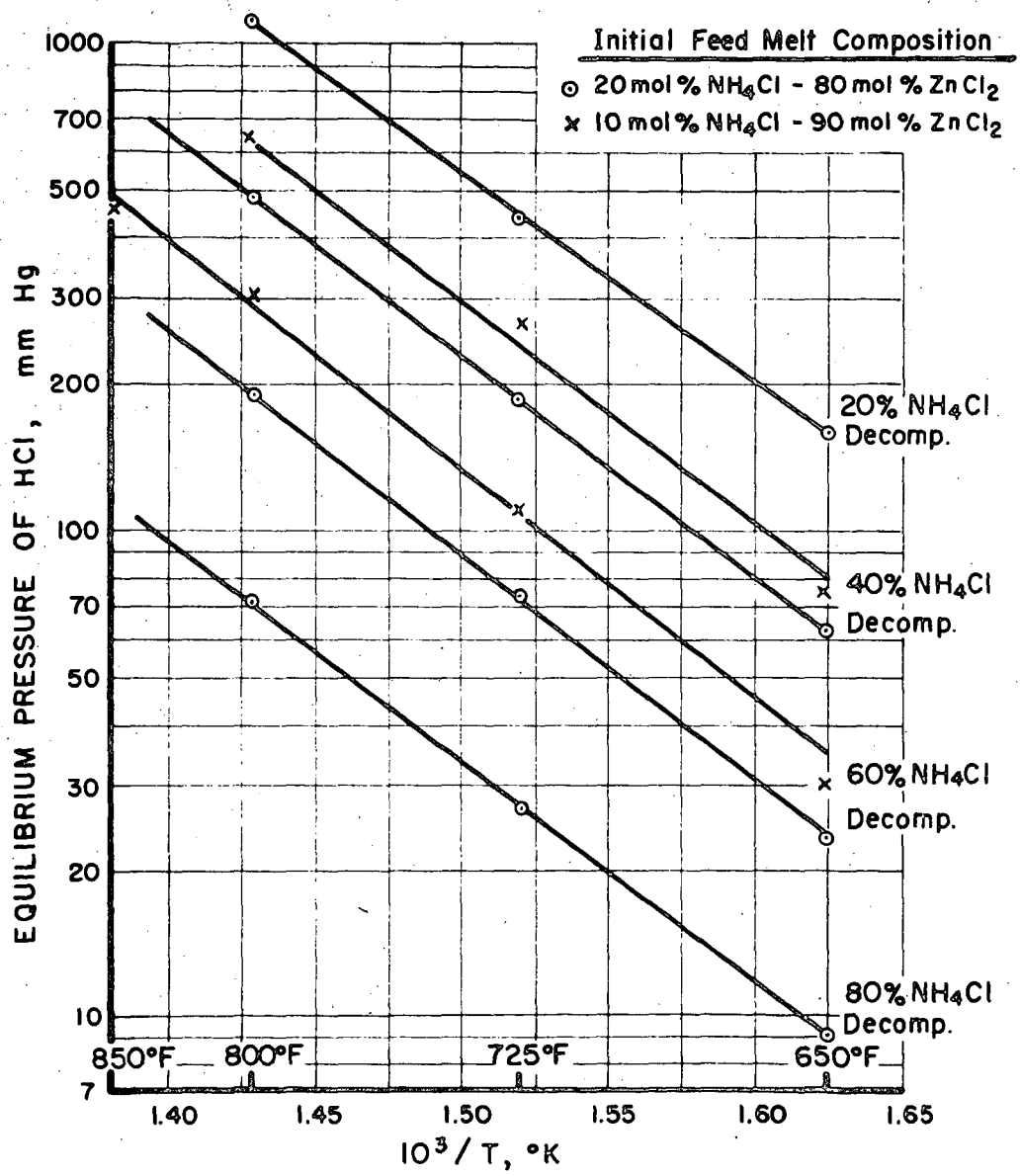


Figure 5

SUMMARIZED DATA ON DISSOCIATION PRESSURE OF NH_3 OVER $ZnCl_2$ MELTS

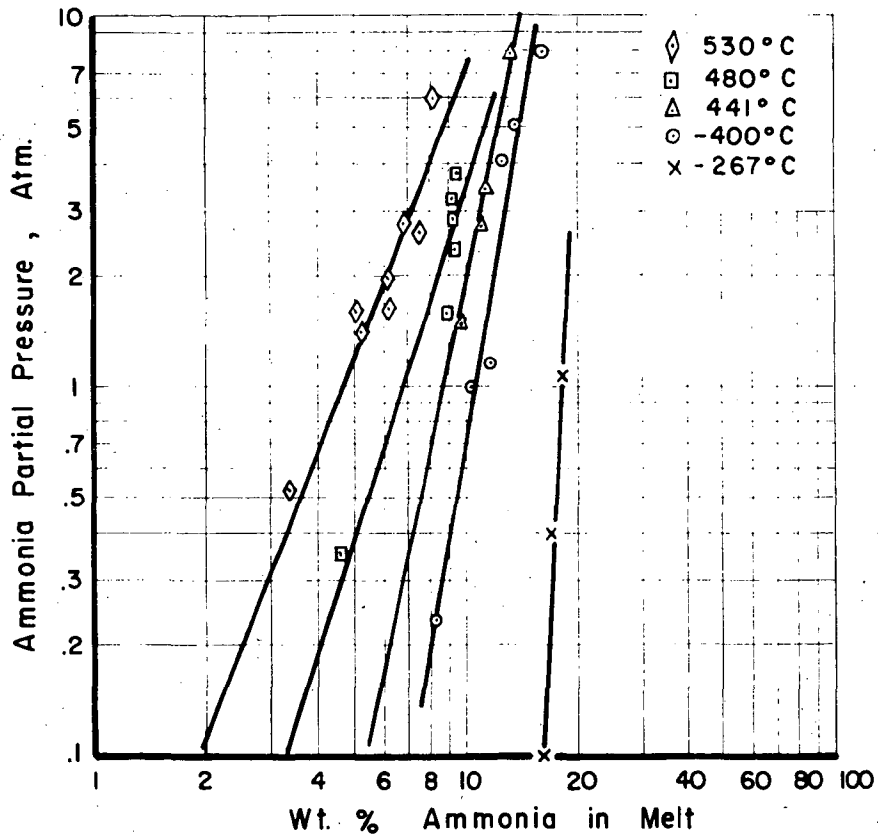
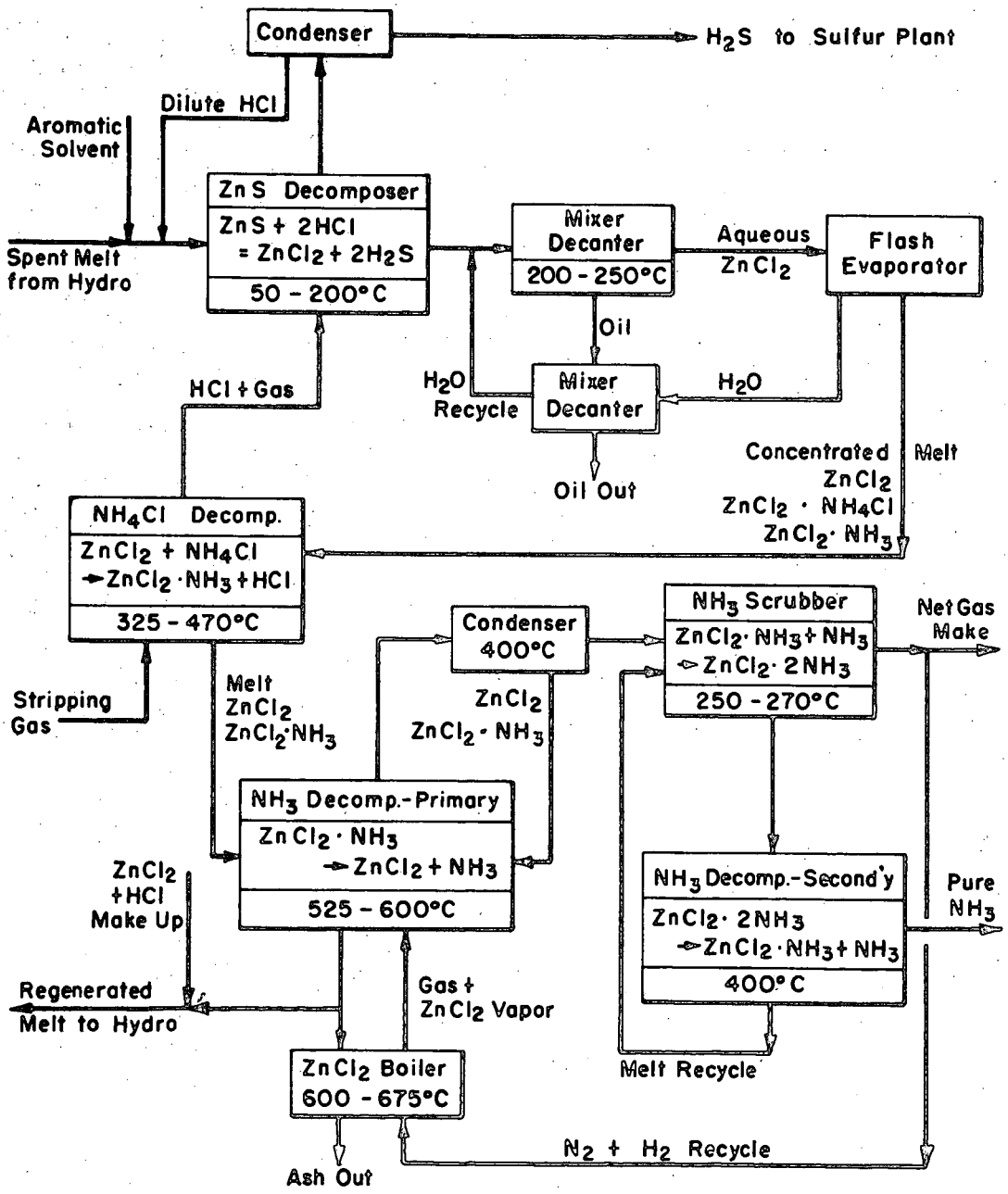


Figure 6

SCHEMATIC DIAGRAM OF REGENERATION SCHEME