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SUBJECT: Zinc Chloride Catalyst Recovery for a Coal Hydrogenation Process

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ABSTRACT

Recovery of a zinc chloride catalyst was investigated for the University of Utah's coal liquefaction process which occurs at 950°F and 2000 psig in a coiled tubular reactor (31). The catalyst is recovered from the liquid oil product by water washing and from the coal char by ashing followed by acid leaching. Preliminary design of the catalyst recovery section for a 25,000 ton/day coal liquefaction plant with 99% recovery was completed. The total recovery cost was \$12.07 and \$8.97 per ton of coal for recovery processes with cross flow and countercurrent flow oil washing respectively.

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1. SUMMARY

A method was devised to recover zinc chloride catalyst from the products of a 25,000 ton/day coal hydrogenation process in which coal reacts with hydrogen at 950°F and 2000 psig in a coiled tube reactor producing a mixture of product oil with water and char. Nearly equal amounts of the catalyst are retained in the two product phases. The liquid layer is decanted and then water washed twice to extract the catalyst dissolved in the product oil. The char is water-washed before being charged to a Texaco gasifier in which the zinc catalyst is converted to zinc oxide. The ash from the gasifier is leached with acid and aqueous zinc chloride is recovered by selectively precipitating unwanted metal ions followed by evaporation of hydrochloric acid. The process recovers 99% of the catalyst in the form of 70% aqueous zinc chloride solutions.

Preliminary designs were made for major equipment, and capital and operating costs were estimated. Cross- and countercurrent-flow schemes for oil washing were considered. Total costs for catalyst recovery were estimated to be \$12.07 and \$8.97 per ton of coal for cross- and countercurrent-flow oil washing, respectively. For the cross-flow oil wash process, utilities, raw materials, and labor costs were 50, 32, and 13%, respectively, of total recovery costs. For countercurrent flow these values were 33, 43, and 17%, respectively. From this preliminary analysis it was concluded that catalyst recovery is not economically feasible at this time.

To determine the most economical recovery process, a more detailed design was recommended. More experimental work is needed to determine data for optimum design of oil and char washes. The potential value of aluminum hydroxide and calcium sulfate byproducts must be thoroughly investigated to determine the maximum credit for these streams.

2. INTRODUCTION

The University of Utah, in conjunction with Fossil Energy Program of the Energy Research and Development Administration, is studying a liquefaction and hydrogenation process for low sulfur western coals (29). In the current process, dry coal, pulverized to -40 to +100 mesh, is soaked in an aqueous zinc chloride solution until the coal absorbs 5.5 wt % zinc chloride. The coal is then dried and reacted with hydrogen at 2000 psig and 950°F in a coiled tube reactor producing methane, ethane, and low molecular weight hydrocarbons. The reactor effluent is a mixture of gases, liquids, and unreacted coal char. The gases are separated from the other products and recycled to the hydrogen supply for the reactor. The solid and liquid products, each of which contains about half of the zinc chloride catalyst, are separated by filtration.

The liquefaction process will only be economically viable if a high percentage of the zinc chloride catalyst can be recovered. The 5.5% zinc chloride catalyst priced at \$0.40/lb would cost \$44.00/ton of coal or about twice the price of coal (31). If a 99% recovery of catalyst could be achieved, the direct catalyst cost would be \$0.44/ton of coal processed or about \$0.17/barrel of oil produced. This cost does not include the expense involved in recovering the catalyst.

The goal of this project was to design and evaluate the economics of a process to recover the catalyst in a 25,000 ton of coal/day liquefaction plant. The method of attack was:

1. Contact researchers at the University of Utah to identify recent advances, if any, in catalyst recovery from the char and liquid products.

2. Perform a literature search and consult by telephone to determine possible means of catalyst recovery and develop a recovery process.

3. Evaluate the economics of the design and determine the overall catalyst cost.

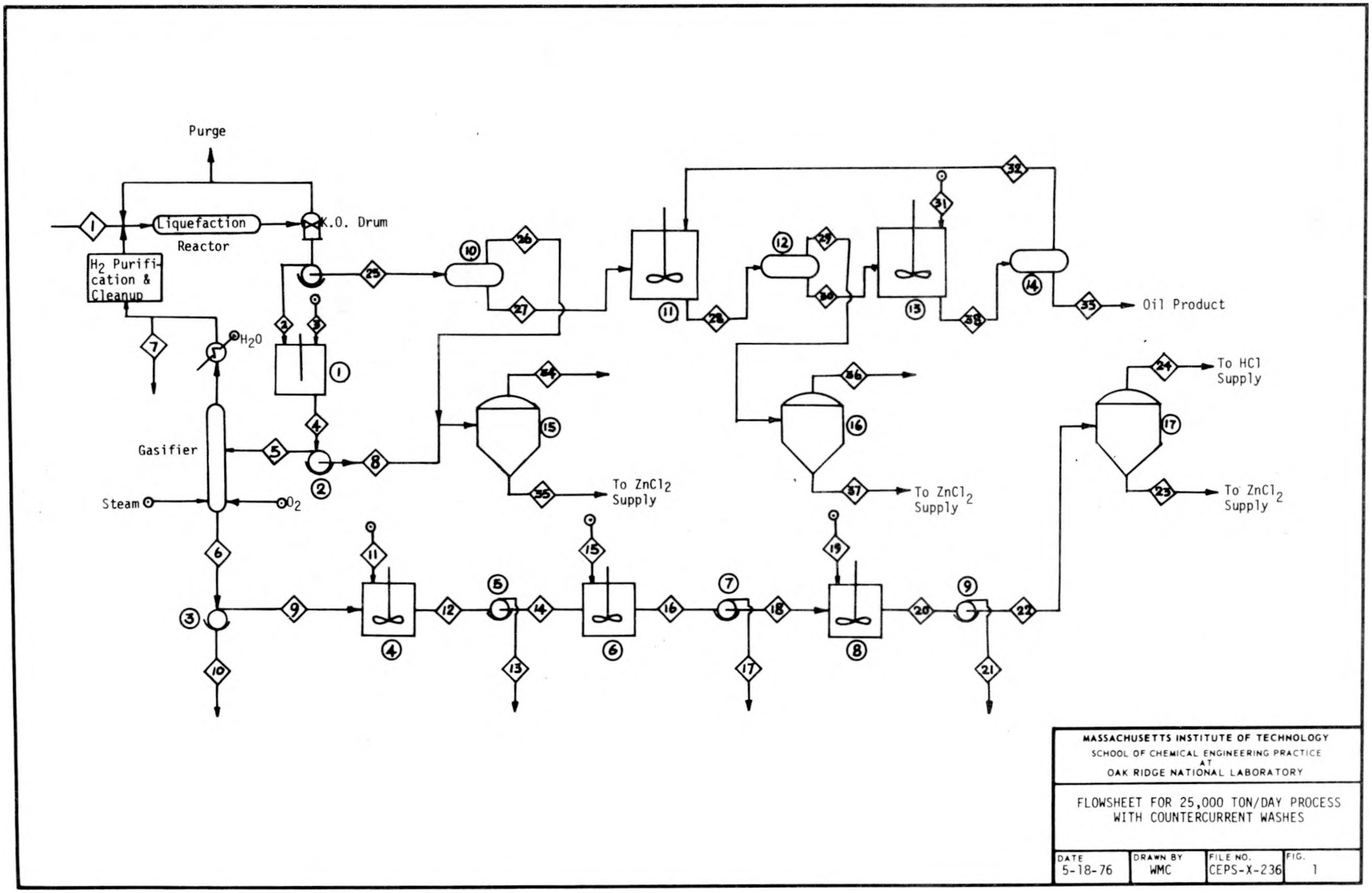
3. CATALYST RECOVERY PLANT DESIGN

The conceptual flow sheet for the catalyst recovery plant is presented in Fig. 1. The material balance for this design is given in Table 1. This preliminary design presents the selection of both the equipment required and the processing conditions. It should be recognized that this preliminary design precedes the availability of experimental results for many of the process steps.

Processing the catalyst for recovery begins after the oil and char streams from the reactor have been separated by filtration. The zinc chloride catalyst originally fed to the coal liquefaction process is nearly evenly distributed between the liquid and solid products (31). Information regarding the exact form(s) of the catalyst after reaction is incomplete (31). The zinc is thought to be in either the metallic form or associated with sulfur or organic complexes. Some of the chlorine is thought to be present as ammonium chloride.

The liquid product stream from the filter is fed to a decanter in which the water formed during the liquefaction reaction is removed. About 34% of the zinc chloride fed to the reactor is recovered in this water stream, which leaves approximately 16% of the original zinc chloride in the oil stream. The oil stream is then washed with water to recover the catalyst. Water extraction was chosen since the zinc chloride is easily recovered with water (31), and the catalyst is recovered in a form suitable for application to the coal.

Two flow schemes for the water extraction were considered, countercurrent- and cross-flow. The countercurrent-flow scheme, as presented in Fig. 1, would be the most economical, but the data necessary to design a countercurrent system, specifically the distribution coefficient of the zinc chloride between



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FLOWSHEET FOR 25,000 TON/DAY PROCESS WITH COUNTERCURRENT WASHES

DATE	DRAWN BY	FILE NO.	FIG.
5-18-76	WMC	CEPS-X-236	1

Table 1. **Material Balance for Fig. 1**
(All numbers in tons/day)

Component	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38
$AlCl_3$												937		937																								
$Al(OH)_3$																549	549																					
Al_2O_3						358			358																													
$CaCl_2$												137		137		1419		1419																				
CaO															648																							
$CaSO_4 \cdot 2H_2O$																				2201	2201																	
Char		10,000		10,000	10,000																																	
Cl		373		373	190																				22		22	22					29					
Coal	25,000																																					
$FeCl_3$												112		122																								
$Fe(OH)_3$																74	74																					
Fe_2O_3						55			55																													
HCl							177				1160									966		966	54	912														
H_2O			10,000	10,000		1841	2100	10,000		1841	2252	2538		2538		2330		2330		1817		1817	101	1716	1986	1986		3800	3800		3800	3800		11,625	361	3266	104	3800
H_3PO_4						18				18																												
H_2SO_4																			1294																			
KOH						21				21																												
$MgCl_2$												40		40		40		40																				
MgO						17			17																													
$MgSO_4 \cdot 7H_2O$																				102	102																	
NaOH						17				17																												
Oil																									10,864		10,864	10,864		10,864			10,864					10,864
SiO_2						1047			1047			1047	1047																									
TiO_2						22			22			22	22																									
Zn		343		373	174																												7					
$ZnCl_2$	1455							352				362		362		362		362		362		362	362		748	490	258	311	243	67		53			842		243	68
ZnO						217			217																													
$Ca(OH)_2$						74			74																													

the oil and water phase, is non-existent. Experimental data exist for cross flow water washes (given in Appendix 8.1). To design the countercurrent washes, the data for the cross flow washes were used, and a number of simplifying assumptions were made.

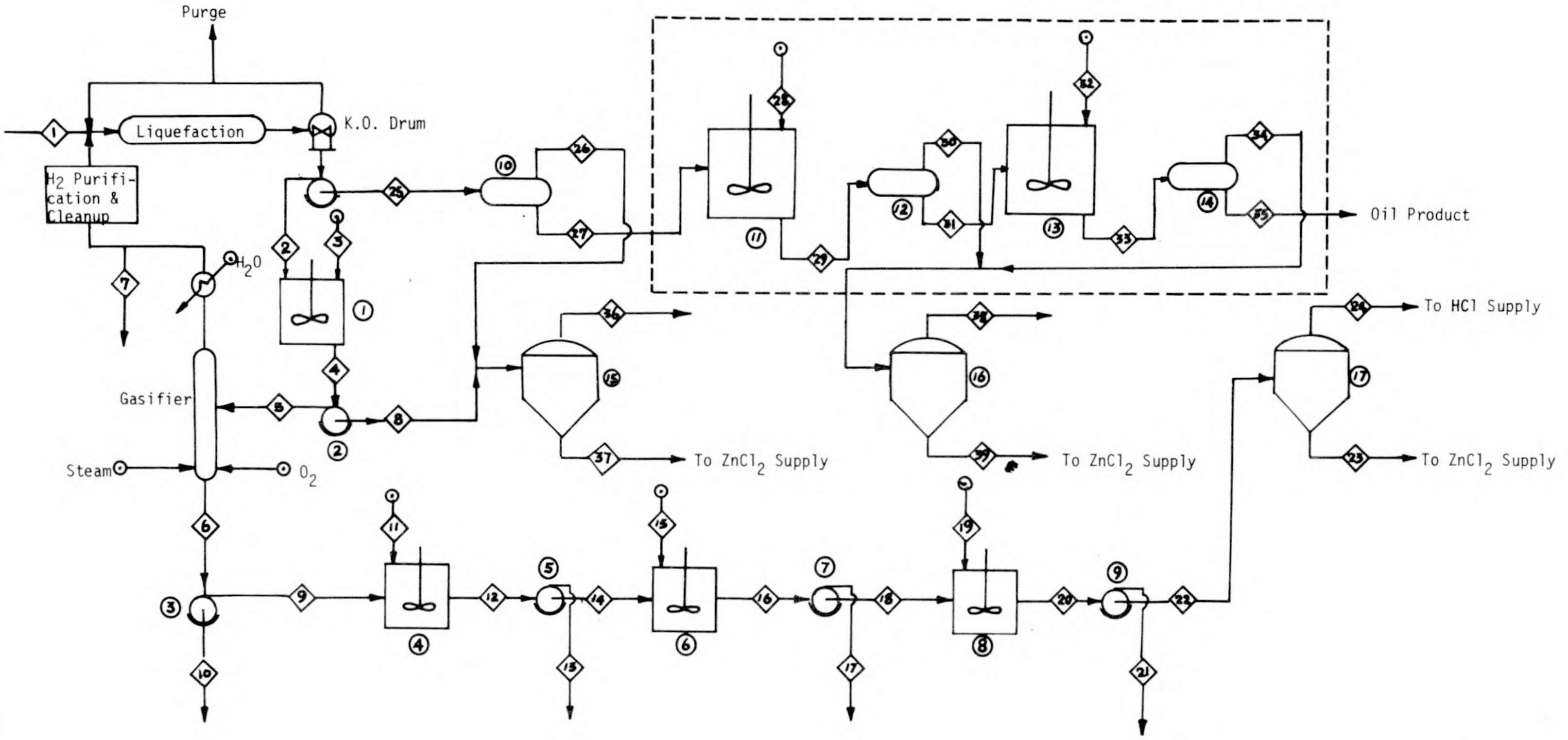
First, equilibrium was assumed to exist between the zinc chloride in the aqueous and organic phases formed in the reactor. This should be a good assumption since these streams were formed at a high temperature and pressure and then cooled gradually and separated. A distribution coefficient for zinc chloride between the aqueous and organic layers was calculated based on the zinc chloride concentrations of the streams leaving the decanter. Due to the lack of experimental data, this distribution coefficient was assumed to be concentration independent. Also, each mixer-settler combination was assumed to be an ideal stage. The water-zinc chloride stream from the countercurrent wash is sent to an evaporator where it is concentrated to a 70 wt % zinc chloride solution which is then used to load the coal feed with the catalyst. Detailed calculations and remarks concerning these assumptions are in Appendix 8.3.

The oil leaving the countercurrent water wash contains seven tons of zinc and 29 tons of chlorine. The chlorine is thought to be primarily in the form of ammonium chloride (30). The zinc in this stream is the only zinc lost in the recovery process.

The plant flowsheet for the cross flow water wash scheme is presented in Fig. 2. The only differences in this flowsheet from Fig. 1 is the piping arrangements between the vessels inside the dotted lines. The material balance for this flowsheet is presented in Table 2. Only four tons of zinc are lost in this process, but a much larger quantity of water, which eventually has to be evaporated, is used.

The water wash system and the reactor effluent decanter recover about half of the catalyst fed to the process. The other half of the catalyst is in the char formed in the reactor.

The char which is filtered from the reactor effluent is first washed with water which removes about half of the zinc chloride in the char. At this point the char has approximately the same heating value as the coal fed to the process, as shown in Table 3 and about twice as much sulfur. In a 25,000 ton/day plant, either additional coal, or the char, could be used to generate process steam for the liquefaction plant or to produce hydrogen for the reactor. Unlike burning the high sulfur char to generate steam, burning the low sulfur coal would require no pollution control equipment for sulfur oxides. If the char was gasified to produce hydrogen, the sulfur could easily be scrubbed from the gasifier off-gas stream as hydrogen sulfide. Thus, gasification of the char was chosen. A Texaco gasifier was selected for this process since it can handle the -40 to 100 mesh solids employed in the coal liquefaction process (18, 27).



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FLOWSHEET FOR 25,000 TON/DAY PROCESS
WITH CROSS FLOW WATER WASHES

DATE	DRAWN BY	FILE NO.	FIG.
5-18-76	JPD	CEPS-X-236	2

Table 2. Material Balance for Fig. 2
(All numbers in tons/day)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39
$AlCl_3$												937		937																									
$Al(OH)_3$																549	549																						
Al_2O_3						358			358																														
$CaCl_2$												137		137		1419		1419																					
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Char		10,000		10,000	10,000																																		
Cl		373		373	190																				22		22		22		22		22		27				
Coal	25,000																																						
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Fe_2O_3						55			55																														
HCl							177				1160									966		966	54	912															
H_2O			10,000	10,000		1841	2100	10,000		1841	2252	2538		2538		2330		2330		1817		1817	101	1716	1986	1986		10,864	10,864	10,864		10,864	10,864	10,864		11,625	361	21,621	107
H_3PO_4						18				18																													
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KOH						21				21																													
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MgO						17			17																														
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NaOH						17				17																													
Oil																									10,864		10,864		10,864		10,864		10,864		10,864				
SiO_2						1047			1047			1047	1047																										
TiO_2						22			22			22	22																										
Zn		343		343	174																														4				
$ZnCl_2$	1455							352				363		362		362		362		362		362	362		748	490	258		258	138	120		120	111			842		249
ZnO						217			217																														
$Ca(OH)_2$						74			74																														

Table 3. Proximate and Ultimate Analyses of Starting Coal and Some Selected Chars (31)

Sample	Proximate Analysis (as is basis)					
	% Moisture	% Ash	Volatile Matter	Fixed Carbon	% Sulfur	Btu/lb
Coal (Hiawatha, Utah)	2.43	6.70	44.24	46.63	0.88	11,450
Char 1271 61.4% Conversion	0.48	17.63	29.90	51.99	1.42	12,050
Char 1272 59.6% Conversion	0.24	17.54	29.95	52.27	1.31	12,200

The chloride in the char fed to the gasifier is thought to form hydrogen chloride under the gasifier reaction conditions. This hydrogen chloride will be condensed from the product gases along with the excess steam from the gasifier when the off-gases are passed through a heat exchanger to produce steam and preheat boiler feed water for the plant process steam boilers. The coal ash, which now contains the zinc as zinc oxide (29), leaves the bottom of the gasifier as a water slurry and is filtered.

The zinc is recovered from the ash with a process similar to that employed in the manufacturing of zinc chloride (11). First, the ash is reacted with hydrochloric acid to convert the zinc, aluminum, calcium, iron (III), and magnesium from oxides to chloride salts. The stoichiometry of the reactions occurring in this ash treatment process are listed in Appendix 8.2. The titanium dioxide and silica do not react with the acid and are filtered from the liquid which contains the soluble chloride salts.

Next, the iron (III) and aluminum are removed from the solution by selective precipitation. Calcium oxide is added to the liquid stream in sufficient quantities to precipitate the aluminum as aluminum hydroxide and the iron (III) as ferric hydroxide. Precipitation is made possible by the differences in the solubilities of the hydroxides of zinc, aluminum, and iron (III). The solubility constants for these compounds are given in Table 4. As can be seen, the solubility constants of aluminum hydroxide

Table 4. Solubility Product Constants of Hydroxides (7)

Compound	Solubility Constant
$Al(OH)_3$	1.3×10^{-33}
$Fe(OH)_3$	4.0×10^{-38}
$Zn(OH)_2$	1.2×10^{-17}

and ferric hydroxide are significantly different so that these two compounds can be removed separately with two mixer-filter systems if it is desirable to enhance the value of these byproducts (see Appendix 8.9). The aluminum and iron (III) hydroxides are filtered out before the liquid stream is sent to the next reactor.

In the final reactor, the addition of sulfuric acid removes calcium and magnesium through precipitation of their hydrated sulfates, along with the generation of hydrochloric acid. The hydrated calcium and magnesium sulfates are filtered out, and the liquid stream is sent to an evaporator to be concentrated. The product from the bottom of the evaporator is a 70 wt % zinc chloride solution. The hydrochloric acid is recovered from the evaporator overhead for reuse.

Significant waste streams are produced in this process. They are listed in Table 5. Detailed studies of waste stream disposal have not been performed, but the problem has been investigated. The 8% hydrochloric acid stream could be sold to an acid manufacturer for reconcentration (1). The titanium oxide and silica could be used for landfill. The aluminum hydroxide stream could be sold to an alum manufacturer (21), but the presence of iron (III) hydroxide poses some problems. As stated before, the aluminum and iron (III) hydroxide could be separated by selective precipitation.

Table 5. Waste Streams

Stream Number*	Component	Tons/Day
7	8 wt % hydrochloric acid	2272
13	SiO_2, TiO_2	1069
17	$Al(OH)_3$, $Fe(OH)_3$	623
21	$CaSO_4 \cdot 2H_2O$, $MgSO_4 \cdot 7H_2O$	2303

*See Figs. 1 and 2.

Calcium and magnesium sulfates are used in cements, gypsum board, and plaster of Paris. The sulfate waste stream from this process could be sold to cement manufacturers (10, 17), but the price is highly location-dependent due to freight costs.

4. ECONOMIC EVALUATION

Preliminary engineering design and cost analyses were performed for the zinc chloride catalyst regeneration process shown in Figs. 1 and 2. The characteristic size and type, total installed capital cost, and annual utilities cost for major equipment are given in Tables 6 and 7. The design and cost estimation techniques are explained for each major piece of equipment in Appendices 8.4 through 8.8. Although there is little difference between total installed costs for the cross flow and countercurrent extraction sections for removing zinc chloride from the product oil, it can be seen from Table 7 that the countercurrent process requires an annual process steam cost of $5,753,000 for evaporation while the cross flow process requires $33,800,000. Although the catalyst recovery plant might have access to low pressure waste steam from the coal hydrogenation plant, it was assumed that the recovery section would be charged for steam at a typical value of $2/1000 lb (28). Calculations based on data for liquid treatment of the hydrogenation products from Wood and Wiser (31) gave distribution coefficients of 10.4, 1.2, and 12.3. Although these values are not equal, it was assumed that the value 10.4 for the first separation was most accurate if it is assumed that the products of liquefaction are closest to equilibrium as they first leave the reactor. Thus, the value 10.4 was taken for design of the countercurrent extraction system, while the cross flow system was designed directly from the data of Wood and Wiser (31).

With countercurrent oil washing, the largest annual utility cost, $18 million from Table 6, is for steam in evaporator 15 to concentrate the zinc chloride solution produced by washing the product char prior to gasification. The char wash was necessary to reduce the cost of raw materials and equipment needed to convert the zinc oxide in the gasifier ash into the chloride form. However, the large utility cost might be unrealistically high since it is the result of equipment design based on the only data available (31). The largest overall equipment costs are for filtration equipment to separate the huge quantity of solids from the liquid phases. This equipment is difficult to design, because the filtration rate is unknown and will be different for each multicomponent stream.

The data basis for filter sizing was recommendations made by filter manufacturers who indicated that the cost could vary from $\$0.5 \times 10^6$ to $\$1.0 \times 10^6$ for each filter (25) depending on filtration characteristics of each stream. A value of $\$0.75 \times 10^6$ was used for each filter. All process vessels were sized for a 10-min residence time while decanters were based on a residence time of 0.5 hr (9). Pumps were sized based on capacity and a total discharge head of 20 psig. The cost for process vessels, decanters, pumps, and agitators was based on correlations by Guthrie (12, 13, 14, 15).

Table 8 shows the total direct costs for procurement and installation on-site of major equipment, and the additional indirect costs associated with major construction: freight and taxes, construction overhead, and engineering. These costs are based on percentages of total capital and installation costs from Guthrie (15). The cost for piping, land, and buildings to house the equipment is not included with this analysis. A 15%

Table 6. Installed Capital Cost and Annual Utilities Cost for Major Equipment[1]

	Capital Cost ($1975)	Annual Steam Cost[2] ($1976)	Annual Electricity Cost[3] ($1976)
CSTR 1	38,550		40,297
CSTR 4	44,550		5,091
CSTR 6	64,000		5,091
CSTR 8	64,000		5,091
Filter 2	7,850,000		64,483
Filter 3	1,308,350		107,446
Filter 5	1,308,350		107,446
Filter 7	1,308,350		107,446
Filter 9	1,308,350		107,446
Evaporator 15	722,000	18,091,572	
Evaporator 17	5,700,000	3,542,492	
Decanter 10	6,100		
Pumps	221,700		66,094
Total Cost	19,944,300	21,634,064	615,931

[1] Total process less oil wash.

[2] Based on $2/1000 lb process steam (28).

[3] Based on $0.01989/kwhr (25)

Table 7. Installed Capital Cost and Annual Utilities Cost for Major Equipment

	Capital Cost ($1975)	Annual Steam Cost[1] ($1976)	Annual Electricity Cost[2] ($1976)
A. Countercurrent Oil Washing			
CSTR 11	16,000		62,347
CSTR 13	16,000		62,347
Decanter 12	7,900		
Decanter 14	7,900		
Evap. 16	361,000	5,752,978	
Pumps	86,200		124,786
Net Cost	495,000	5,752,978	249,480
B. Cross Flow Oil Washing			
CSTR 11	16,000		45,747
CSTR 13	16,000		45,747
Decanter 12	7,900		
Decanter 14	7,900		
Evap. 16	1,100,050	33,800,000	
Pumps	82,050		44,235
Net Cost	1,229,900	33,800,000	135,729

[1] Based on $2/1000 lb process steam (28).

[2] Based on $0.01989/kWhr (25).

Table 8. Direct and Indirect Costs of Catalyst Recovery Process

	Cross Flow Oil Wash ($1975)	Countercurrent Oil Wash ($1975)
F.O.B. Equipment	11,627,500	11,286,750
Direct Materials	3,202,600	2,993,500
Direct Field Labor	6,347,900	6,159,150
Total Direct Cost	21,178,000	20,439,400
Freight and Taxes	1,186,400	1,142,400
Construction Overhead	4,297,500	4,147,600
Engineering	2,017,000	1,942,200
Total Indirect Cost	7,500,900	7,232,200
Total Direct and Indirect Costs	28,678,900	27,671,600
Contingency	4,301,900	4,150,800
Total Installed Capital Cost	32,980,800	31,822,400

contingency is added to total direct and indirect costs, resulting in total design costs of approximately $33 and $32 million, respectively, for construction of the cross flow and countercurrent catalyst recovery plants.

Table 9 shows the annual costs for raw materials required in the catalyst recovery process. Except for makeup zinc chloride, these chemicals are needed to convert the zinc oxide which is formed in the gasifier, into zinc chloride and to recover the catalyst by selectively precipitating undesirable components. The process recovers all the zinc chloride entering the reactor with coal except 0.8% retained in the oil after two water washings, which is worth $4.09 million/yr. Assuming that the 8% hydrochloric acid recovered from the gasifier offgas can be separated and returned to the supplier for credit at half the price of 34% hydrochloric acid on a hydrogen chloride basis, $4.80 million/yr must be spent for acid leaching. Costs for lime (CaO) and sulfuric acid are based on the amounts which are consumed in the process. The credit for removal of the relatively pure aluminum hydroxide, which is a valuable raw material for manufacturing alum is not accounted for. Calcium sulfate, which might be valuable to gypsum board and concrete manufacturers, is not credited in this evaluation. It was assumed that stream 10 in Figs. 1 and 2, containing less than 3% H_3PO_4, KOH, and NaOH in aqueous solution, and the silica in stream 13, could be discarded at no added cost. For a 25,000 ton coal/day plant the total raw materials cost for catalyst recovery amounts to $35.11 million each year of plant operation, equivalent to about $4/ton of coal. The largest material cost is for sulfuric acid to precipitate aluminum and calcium as sulfates in the second step of selective precipitation to purify the product. It is important to point out from an economic perspective that both lime and sulfuric acid are totally consumed in this process. The possibility of converting calcium sulfate to sulfuric acid by heating and water scrubbing was eliminated since this process is probably not economically feasible (8).

Table 9. Cost of Raw Materials (4)

Material	TPD	$/ton	10^6 $/yr
$ZnCl_2$	14	800	4.09
HCl (34%)*	487	27	4.80
CaO	648	25	5.91
H_2SO_4 (100%)	1294	43	20.31
Total			35.11

*Credit taken for the 8 wt % waste stream at half the price of 34 wt % acid on a per ton HCl basis.

The annual operating costs for the catalyst recovery plant are shown in Table 10. Raw materials costs are taken directly from Table 9. Maintenance costs are 4% of the installed plant cost, the minimum amount suggested by Perry (24). Taxes and insurance costs are estimated to be 2% of installed plant cost, the same figure used by the Refinery Economics Dept. of AMOCO, Chicago, Ill. (9). Capital recovery is based on an extended plant payment period of 20 yr for which the annual cost charged to plant operation is 10.185% of installed cost, based on 8% compound interest (22). The labor costs for zinc chloride manufacturing could not be found in the literature. Using data which shows labor costs as a fraction of plant output for existing chemical plants (5), an estimate of 4.5 manhours/ton $ZnCl_2$, the approximate cost of KCl and ZnO labor costs, was made.

Table 10. Annual Operating Costs of Catalyst Recovery Process

	Cross Flow Extraction		Countercurrent Flow Extraction	
	($1975)	(%)	($1975)	(%)
Utilities	55,434,100	50.3	27,387,100	33.4
Raw Materials	35,110,000	31.9	35,110,000	42.9
Labor (@$6/hr)	14,235,000	12.9	14,235,000	17.4
Capital Recovery	3,359,100	3.1	3,241,200	4.0
Maintenance	1,319,300	1.2	1,272,900	1.6
Tax and Insurance	659,700	0.6	636,500	0.8
Total Annual Cost	110,117,200		81,882,700	
Annual Cost ($/ton coal)	12.07		8.97	

Total annual catalyst recovery costs are estimated to be approximately $110 million and $82 million, respectively, for cross flow and countercurrent oil washing; the difference is due mainly to the added cost of about $30 million for steam to evaporate the additional water from the cross flow oil washing. The annual costs to recover the catalyst are estimated to be $12.07 and $8.97 per ton of coal. Since this economic analysis does not include tax expenses, annual tax credit in the form of plant depreciation is not included in these results.

The estimated costs for catalyst recovery, $12.07 and $8.97 per ton of coal processed are beyond the limits of feasibility based on the current value of coal, $22/ton. The cost of piping as well as buildings and land, which are needed to complete the economic evaluation, were not considered in this preliminary analysis. A good estimate of process piping can be made only after the plant layout is complete. These costs will add to the cost of recovery, but will not have an extremely large effect on overall economic viability of the process.

Approximately 50 and 33% of the annual cost for the processes with countercurrent and cross flow oil washing in the catalyst recovery process is for utilities, and 99% of this cost is for process steam. Since approximately 80% of total recovery cost is for utilities and raw materials, a recovery process can only be feasible when these costs, as well as others, are reduced substantially. The steam costs in this evaluation may be unrealistically high since a basis of $2/thousand lb of steam was used and low pressure steam from other areas of the plant was not considered. It is recommended that a detailed design of the combined liquefaction-catalyst recovery plant utilize available low pressure steam for catalyst recovery.

Since the three evaporators employed in this design are single effect, utilities costs may be reduced by using multiple effect evaporators, although material problems may arise due to the corrosive nature of vapors. Another method of reducing steam consumption is to reduce the amount of water in the char wash which must be removed from the dilute zinc chloride wash solution by evaporation. Savings will also result if a countercurrent char wash is employed. Both of these design changes will have substantial savings in utilities costs, but more data are needed to predict the extent of these savings. The reduction in cost for catalyst recovery per ton of coal processed can be seen in Table 11 when two stages are added to the countercurrent extraction system which removes the catalyst from the oil. The total cost per ton of coal can be reduced 4% by doubling the number of stages. This savings results from a 53% reduction in steam required in the evaporation step. However, data are needed for catalyst distribution in the char-water and oil-water systems before savings in utilities costs can be used in future design work for a more efficient catalyst recovery process.

Table 11. Recovery Costs for Multistage Countercurrent Extraction

Number of Extraction Stages	Steam Consumption (ton/yr)	Annual Steam Cost* ($ million)	Total Cost ($/ton coal)
2	1,437,989	5.753	8.97
4	678,141	2.551	8.66

*Calculations based on a distribution coefficient for $ZnCl_2$-H_2O-Oil system 10.4.

The annual labor cost for plant operation, $14.235 million corresponds to $1.55/ton of coal processed. This value, which was estimated based on the labor costs for potassium chloride and zinc oxide could be questionable. Since the process for catalyst recovery is continuous, this labor cost may be high. However, if it is realistic or low, labor costs alone are a major portion of recovery costs which most likely cannot be changed substantially by design improvements. Thus, more accurate knowledge of labor requirements for catalyst recovery are needed to determine the process feasibility.

The Stauffer Chemical Co. (21) indicated that aluminum hydroxide, $Al(OH)_3$, can be used as a raw material to manufacture alum, as long as the iron content is reduced to 1%. Since the dollar value of aluminum hydroxide depends on iron content and plant location, Stauffer was hesitant to quote a price for this byproduct. The Martin Marietta Corp. stated that the byproduct mixture of calcium and magnesium sulfates is a valuable raw material which can be mixed with cement clinker to function as a cement curing time extender (17). However, zinc compound impurities must be kept to a minimum, and the mixture must be in the form of pellets of a specified size. At the value of $7/ton for gypsum rock purchased in Colorado by Martin Marietta (10), the maximum value for stream 21 amounts to approximately $5.6 million annually. Thus, this stream has a maximum potential value for credit to catalyst recovery process of $5.6 million which is roughly the cost of lime shown in Table 9. When this table was computed, credit was not given for the aluminum hydroxide and the mixture of calcium sulfate and magnesium sulfate since the value of these byproducts is strongly dependent upon location as well as purity and form of these materials. Since these materials have large potential value, it is recommended that a more detailed study be performed to ascertain the true value of these byproducts.

5. CONCLUSION

Catalyst recovery and makeup costs are $12.04 and $9.10/ton of coal with cross flow and countercurrent flow oil wash processes respectively.

6. RECOMMENDATIONS

1. More experimental work is required to determine data for design of oil and char washes which may significantly affect the economic viability of the catalyst recovery process.

2. The potential value of byproduct streams should be more thoroughly investigated.

3. An ecologically-safe method of disposal for the waste streams containing a mixture of silica and titanium dioxide and the dilute aqueous solution of phosphoric acid, potassium hydroxide, and sodium hydroxide must be determined.

7. ACKNOWLEDGMENT

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8. APPENDIX

8.1 Calculation of Material Balance

The overall material balance was calculated from experimental data obtained at the University of Utah. These data are shown in Table 12. It should be noted that the numbers presented for mass of each component in the liquid treatment do not show conservation of species. Contact with workers at the University of Utah (30) revealed that they were at a loss to explain these discrepancies other than the suggestion that there may have been some error in their zinc analysis.

Table 12. Recovery of $ZnCl_2$ Catalyst from Reaction Products (31)

Coal charge		1070 g coal, 60 g ash, 70 g $ZnCl_2$
Products		
	a.	428 g char, 60 g ash, 34.4 g $ZnCl_2$
	b.	550 g coal liquids, 35.6 g $ZnCl_2$
	c.	92 g gas
		Liquid Treatment
Separation of water from oil in liquid product.		
	d.	465 g oil, 3.3 g Zn, 8.7 g Cl_2
	e.	85 g water, 23.6 g $ZnCl_2$
First water rinse of oil		
	f.	oil, 1.4 g Zn, 4.7 g Cl_2
	g.	465 g water, 5.9 g $ZnCl_2$
Second water rinse of oil		
	h.	oil, 0.19 g Zn, 1.16 g Cl_2
	i.	465 g water, 4.75 g $ZnCl_2$

The amount of oil and water produced by the liquefaction reaction was assumed to be the same percentage of the coal feed as shown in Table 12.

$$\text{oil produced} = \left(\frac{465 \text{ g oil}}{1070 \text{ g coal}}\right)\left(\frac{25{,}000 \text{ ton coal}}{\text{day}}\right) = 10{,}864 \text{ tons oil/day}$$

$$\text{water produced} = \frac{85\text{ g }H_2O}{1070\text{ g coal}}\left(\frac{25{,}000\text{ ton coal}}{\text{day}}\right) = 1986\text{ tons }H_2O/\text{day}$$

Now, the distribution of zinc chloride in the water from the decanter and for the cross flow water washes can be calculated from the experimental data. The zinc chloride in the water stream from the decanter is:

$$\frac{23.6\text{ g }ZnCl_2}{70\text{ g }ZnCl_2}\left(\frac{1455\text{ ton }ZnCl_2}{\text{day}}\right) = 490\text{ ton }ZnCl_2/\text{day}$$

The zinc chloride in the first water wash is:

$$\frac{5.9\text{ g }ZnCl_2}{465\text{ g }H_2O}\left(\frac{10{,}864\text{ ton }H_2O}{\text{day}}\right) = 138\text{ ton }ZnCl_2/\text{day}$$

The amount of $ZnCl_2$ in the second cross flow water wash is

$$\frac{4.75\text{ g }ZnCl_2}{465\text{ g }H_2O}\left(\frac{10{,}865\text{ ton }H_2O}{\text{day}}\right) = 111\text{ ton }ZnCl_2/\text{day}$$

To calculate the amount of zinc and chlorine lost with the oil, the analysis of the oil from the second water rinse was used. The amount of zinc lost is:

$$\frac{0.19\text{ g Zn}}{465\text{ g oil}}\left(10{,}864\ \frac{\text{tons oil}}{\text{day}}\right) = 4\text{ tons/day}$$

The amount of chlorine lost is equal to

$$\frac{1.16\text{ g }Cl_2}{465\text{ g oil}}\left(10{,}864\ \frac{\text{tons oil}}{\text{day}}\right) = 27\text{ tons }Cl_2/\text{day}$$

The amounts of zinc and chlorine in the char were calculated by taking the difference between the zinc and chlorine that leaves with the oil and water, and the zinc and chlorine fed to the process as zinc chloride.

8.2 Stoichiometry of the Catalyst Recovery Process

In reactor number 4 (Figs. 1 and 2), the following reactions occur:

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O \qquad (1)$$

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O \qquad (2)$$

$$CaO + 2HCl \rightarrow CaCl_2 + 2H_2O \qquad (3)$$

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \qquad (4)$$

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O \qquad (5)$$

In reactor number 6, the following reactions occur:

$$2AlCl_3 + 3CaO + 3H_2O \rightarrow 3CaCl_2 + 2Al(OH)_3 \qquad (6)$$

$$2FeCl_3 + 3CaO + 3H_2O \rightarrow 3CaCl_2 + 2Fe(OH)_3 \qquad (7)$$

The following reactions occur in reactor number 8:

$$CaCl_2 + H_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2HCl \qquad (8)$$

$$MgCl_2 + H_2SO_4 + 7H_2O \rightarrow MgSO_4 \cdot 7H_2O + 2HCl \qquad (9)$$

8.3 Recovery of $ZnCl_2$ in a Countercurrent Extractor

A distribution coefficient for $ZnCl_2$ in oil and water was calculated on the basis of the data in Table 12. From the material balance calculations the following information was available (Fig. 2 and Table 2):

	Decanter 10		Decanter 12		Decanter 14	
Stream Number	26	27	30	31	34	35
Oil		10,864		10,864		10,864
$ZnCl_2$	490	258	138	120	111	9
H_2O	1986		10,864		10,864	
lb $ZnCl_2$/lb solvent	0.247	0.0237	0.0127	0.011	0.0102	0.000828
distribution coefficient	10.42		1.15		12.32	

where the distribution coefficient is defined as,

$$\frac{\text{tons } ZnCl_2/\text{ton water}}{\text{tons } ZnCl_2/\text{ton oil}}$$

The distribution coefficients for decanters 10 and 14 were approximately the same. Decanter 10 was assumed to be an ideal separation stage and the distribution coefficient for the calculation was based on this separation. This assumption is valid since the oil and water from liquefaction were always in contact and should be in equilibrium. Based on this, the distribution coefficient was chosen to be 10.4.

To calculate the amount of water required to recover the zinc chloride in a countercurrent process, two quantities must be set arbitrarily. These can be the number of stages, the water flow rate, or the concentration of zinc chloride in the oil stream leaving the last stage.

For the sample calculation shown here, the recovery of zinc chloride was set at 99% of the overall zinc chloride and the number of stages to two. The amount of zinc chloride leaving the second stage is

$$(1455 \text{ tons } ZnCl_2/\text{day})0.01 = 14.5 \text{ tons/day}$$

and the concentration in the oil is,

$$\frac{14.5 \text{ tons/day } ZnCl_2}{10{,}804 \text{ tons/day oil}} = 0.00133 \text{ tons } ZnCl_2/\text{ton oil}$$

The concentration of the water stream leaving the second stage and entering the first is then,

$$0.00133(10.4) = 0.0183 \text{ tons } ZnCl_2\text{/ton water}$$

By a trial and error technique the flow rate of water required to recover the zinc chloride from the oil can be calculated. The total amount of zinc chloride in the oil is 258 tons/day. The amount to be recovered is

$$258 - 14.5 = 243.5 \text{ tons/day}$$

If a water flow rate of 3000 tons/day is assumed, the amount of zinc chloride recovered in the second stage is

$$3000 \text{ tons water/day}(0.0183 \frac{\text{ton } ZnCl_2}{\text{ton water}}) = 41.4 \text{ ton/day } ZnCl_2$$

The total amount of zinc chloride leaving the first stage and entering the second is

$$41.4 + 14.5 = 55.9 \text{ ton/day}$$

The concentration of the $ZnCl_2$ in this oil stream is

$$\frac{55.9 \text{ tons } ZnCl_2}{10{,}804 \text{ tons oil}} = 0.00517$$

The water leaving the first stage has a concentration of

$$0.0057 \frac{\text{ton } ZnCl_2}{\text{ton oil}}(10.4 \frac{\text{ton } ZnCl_2\text{/ton } H_2O}{\text{ton } ZnCl_2\text{/ton oil}}) = 0.057 \frac{\text{ton } ZnCl_2}{\text{ton water}}$$

With a flow rate of 3000 ton/day of water the $ZnCl_2$ recovered is

$$3000 \text{ tons/day water}(0.057 \frac{\text{ton } ZnCl_2}{\text{ton water}}) = 161.1 \text{ tons/day } ZnCl_2$$

This amount is too low compared to the 243.5 tons/day that must be recovered. Thus, the water flow rate must be increased. At a flow rate of 3800 ton/day, the amount of $ZnCl_2$ removed in the second stage is:

$$3800 \text{ tons } H_2O\text{/day}(0.0183 \frac{\text{ton } ZnCl_2}{\text{ton } H_2O}) = 52.44 \text{ tons/day}$$

The amount of $ZnCl_2$ leaving the first stage is

$$52.44 + 14.5 = 66.94 \text{ tons/day}$$

and the concentration is

$$\frac{66.94 \text{ ton } ZnCl_2}{10{,}804 \text{ ton oil}} = 0.00616 \text{ tons } ZnCl_2\text{/ton oil}$$

The concentration of the water stream leaving the first stage is then,

$$(0.00616)(10.4) = 0.0641$$

The total amount of $ZnCl_2$ recovered is then,

$$3800 \text{ ton } H_2O(0.0641 \frac{\text{ton } ZnCl_2}{\text{ton water}}) = 243.5 \text{ tons/day } ZnCl_2$$

which is the exact amount to be recovered.

8.4 Continuous Stirred Tank Reactor Design and Cost Estimation

The CSTR for recycling the zinc chloride from the ash after gasifying the char was designed on the basis of an assumed 10-min residence time. Since all the reactions are acid-base reactions, they occur almost instantaneously. Therefore, a 10-min residence time should be adequate. The volume of the reactor was calculated by:

$$V = F\theta \tag{10}$$

To convert all the oxide in the ash to chloride form in reactor No. 4, the reactor size required was

$$V = F\theta = 79 \text{ ft}^3\text{/min}(10 \text{ min}) = 790 \text{ ft}^3 \approx 800 \text{ ft}^3$$

From McCabe and Smith (20), the agitator power required for such a volume was calculated as:

$$\text{H.P. required} = (\text{volume, gal})(3\ \text{H.P.}/1000\ \text{gal})(1.2) \tag{11}$$

$$= \frac{(800\ \text{ft}^3)(7.48\ \text{gal/ft}^3)(3\ \text{HP})(1.2)}{1000\ \text{gal}}$$

$$= 21.5\ \text{H.P.}$$

If 50% motor efficiency is assumed, the brake horsepower for the CSTR is:

$$\text{brake H.P.} = \frac{\text{H.P.}}{\text{eff.}} = \frac{21.5}{0.5} = 43\ \text{H.P.} \tag{12}$$

The cost of the CSTR was calculated by assuming that the reactor was a combination of a vertical vessel plus an agitator. The costs of vertical process vessels and agitators were outlined by Guthrie (12). Cost of the process vessel was estimated by,

$$C = \$(C_B \cdot F_m \cdot F_p)(I_p) \tag{13}$$

For about 800 ft^3 vertical vessel, from Fig. 5 of Guthrie (12), the base cost of the vessel was \$7000. For a vessel made of carbon steel, $F_m = 1$, and for an operating condition less than 50 psi, $F_p = 1$. Therefore, the expected cost (Dec. 1975) was

$$\$7000(1)(1)(1.76) = \$12{,}320$$

Since the chemicals in the tank are corrosive in nature, silicate cement lining is required. The unit price for lining silicate cement is \$4/ft^2 for 1/100-in. thick (16). For lining of 1/4-in. thick, the cost of silicate cement lining is \$100/ft^2. The area of the reactor requiring lining is

$$A = \frac{\pi D^2}{4} + \pi Dh = \frac{\pi(10)^2}{4} + \pi(10)(10) = 394\ \text{ft}^2 \tag{14}$$

Therefore,

$$\text{cost of lining} = 394(\$100/\text{ft}^2) = \$39{,}400$$

The cost of the agitator was obtained from Guthrie (14). All tabulated prices were for mid 1968. To update the cost, the CE fabricated equipment cost index was used. The index in mid 1968 was 109 (2) and the index in December 1975 was 191.3 (3). The escalating price index was calculated as 191.3/109. This factor was 1.76.

The cost of the agitator (December 1975) is

$$C = C_B I_p = (\$2625)(1.76) = \$4,620$$

8.5 Decanter Design and Cost Estimation

The volume of decanters was based on a residence time of 0.5 hr for all species. The design department of AMOCO, Chicago, Ill., uses this assumption for preliminary design of decanters (9). Because of the large sizes involved, the cheapest material of construction, concrete, was chosen and the decanters were designed for installation in the ground to eliminate the cost of support systems.

To estimate the capital cost of such a decanter, the capital cost estimating technique outlined by Guthrie (15) for one-story concrete warehouses was used.

The total volume based on residence time for decanter 12 with countercurrent extraction is

$$V = F\theta = [(10,896\ \frac{\text{ton}}{\text{day}})(\frac{2000\ \text{lb/ton}}{67\ \text{lb oil/ft}^3})(\frac{1\ \text{day}}{24\ \text{hr}}) + $$

$$+ (3370\ \frac{\text{ton}}{\text{day}})(\frac{2000\ \text{lb/ton}}{62.4\ \text{lb/ft}^3})(\frac{1\ \text{day}}{24\ \text{hr}})]\ (0.5\ \text{hr}) = 9025\ \text{ft}^3$$

This volume corresponds to design dimensions of 20 x 25 x 25 ft. Table 13 shows the calculations based on Guthrie's data which shows a cost of $7830.

Table 13. Labor and Materials Costs for Decanter 12

Description	1968 Unit Cost	Quantity	Materials Cost* ($ 1975)	Ratio L/M	Labor Cost ($ 1975)
Site Preparation:					
clear	$0.15/yd^2	70 yd^2	20	0.18	10
grade	$0.44/yd^2	70 yd^2	50	0.48	30
Foundation Excavation	$1.63/yd^3	463 yd^3	1200	1.75	2100
Concrete Structure	$4.57/ft^2	625 ft^2	4460		included
Net Costs Installed			5730		2140
Total Installed Cost			7870		

*Cost factor ($ 1975/1968) is 1.56.

8.6 Evaporator Design and Cost Estimation

The general procedure for designing evaporators is outlined by Kern (19). All boiling point temperatures were assumed to correspond to 1 atm total pressure. The evaporator surface area for heat transfer was calculated by

$$Q = U_D A \Delta T \qquad (15)$$

or

$$A = \frac{Q}{U_D \Delta T} \qquad (16)$$

where:

$$\Delta T = T_{steam} - T_{bp} \qquad (17)$$

U_D was assumed to be 700 Btu/hr-ft^2-°F. A plot of correction factors, ε, for U_D as a function of ΔT was obtained from Kern (19). Then,

$$A = \frac{Q}{\varepsilon U_D (T_{steam} - T_{bp})} \qquad (18)$$

In designing the evaporator for char wash and the first decanter the calculation is

$$A = \frac{(968{,}750 \text{ lb/hr})(970 \text{ Btu/lb})}{(0.85)(700 \text{ Btu/hr-ft}^2\text{-°F})(300 - 212 \text{ °F})} = 17{,}947 \text{ ft}^2$$

To estimate the capital cost of such an evaporator, the capital cost estimating technique outlined by Guthrie (14) was used. From tabulation in Guthrie's paper, the cost of the evaporator was $216,000 in mid 1968. Thus, the cost of the evaporator (December 1975) is,

$$C = C_B I_p = (\$216{,}000)(1.76) = \$3.8 \times 10^5$$

8.7 Filter Cost Estimates

The capital cost for filters is based on prelininary design data supplied by Dorr Oliver, Stamford, Conn., for filtration equipment for this process application (26). Based on an average filtration capacity per unit area for a rotary drum filter, 500 lb/ft^2-hr, the total filter area necessary to remove 10,342 tons/day of solids in filter No. 2 is

$$\frac{(10{,}342\ \text{ton/day})(1\ \text{day}/24\ \text{hr})(2000\ \text{lb/ton})}{500\ \text{lb/ft}^2\text{-hr}} = 1724\ \text{ft}^2$$

Since the surface area of the largest rotary drum filter is 300 ft^2, the number of filters needed is

$$\frac{1724\ \text{ft}^2}{300\ \text{ft}^2/\text{filter}} = 6\ \text{filters}$$

At an approximate cost of $750,000/filter plus 50% for labor, piping, and associated equipment (26), the total installed cost is approximately $4.5 million for materials plus $2.25 million for labor. Since each filter also requires a vacuum system costing $130,400 plus $53,000 for labor (6), the total cost for filter No. 2 is $7,850,100. Since each filter is equipped with a 25 H.P. motor (26), and the vacuum system consumes 800 H.P. (6), the rate of electricity consumption is 825 H.P.

8.8 Pump Cost Estimates

The sizes of pumps needed for the major streams in the process were based on stream flow rate and a total discharge head of 20 psig. The cost for each pump was then determined from a correlation by Guthrie (13) which relates the product of pump capacity and total discharge head to the total cost of the pump, motor, and supports. The design capacity of a pump for stream 7 is 2272 tons/day, corresponding to 378 gal/min. For a 500 gpm pump the 1968 cost is $1,110 plus 71.5% for extra materials and 69.7% for labor. The total 1975 cost for the installed pump is the total 1968 cost adjusted to 1975 dollars (2, 3).

$$\begin{aligned} C &= C_B(E + m + L)(I_p) = (\$1110)(1.00 + 0.715 + 0.697)(1.83) \\ &= \$5000 \end{aligned}$$

The power consumption of pump motors can be approximated by the brake horsepower which is related to the theoretical work required of a pump or hydraulic horsepower (23).

$$H = \frac{H_p G}{1714} = \frac{(20)(1000)}{1714} = 11.7 \qquad (19)$$

The brake horsepower is determined by the power required to pump the fluid times the motor efficiency.

$$\text{pump efficiency} = \frac{H}{\text{brake horsepower}} \tag{20}$$

For an efficiency of 0.45 the total power is

$$\left(\frac{11.7}{0.45}\right) = 26 \text{ H.P.}$$

8.9 Selective Precipitation Calculations

To calculate the amount of calcium oxide necessary to precipitate the aluminum and iron in reactor No. 6, the allowable hydroxide ion concentration must be calculated. First, the number of moles of zinc in the reactor must be calculated.

$$\text{gmole Zn} = \left(353\ \frac{\text{ton } ZnCl_2}{\text{day}}\right)\left(\frac{2000\text{ lb}}{\text{ton}}\right)\left(\frac{454\text{ g}}{\text{lb}}\right)\left(\frac{1\text{ gmole } ZnCl_2}{136.3\text{ g}}\right)$$

$$= 2.35 \times 10^6 \text{ gmoles/day}$$

Now, this can be converted into an ion concentration through dividing by the volume of water present in the reaction stream.

$$\text{volume } H_2O = \left(2526\ \frac{\text{tons}}{\text{day}}\right)\left(\frac{2000\text{ lb}}{\text{ton}}\right)\left(\frac{454\text{ g}}{\text{lb}}\right)\left(\frac{10^{-3}\text{ liter}}{\text{g}}\right)$$

$$= 2.29 \times 10^6 \text{ liter/day}$$

The zinc ion concentration is

$$[Zn^{+2}] = \frac{2.35 \times 10^6 \text{ gmole/day}}{2.29 \times 10^6 \text{ liter/day}} = 1.03 \text{ gmole/liter}$$

Now, the allowable hydroxide ion concentration can be found from the solubility constant for zinc hydroxide.

$$\text{solubility constant} = [Zn^{+2}][OH^-]^2 = 1.2 \times 10^{-17}$$

$$1.2 \times 10^{-17} = [1.03][OH^-]^2$$

$$[OH^-] = 3.41 \times 10^{-9} \text{ gmole/liter}$$

The aluminum and ferric ion concentrations in the solution containing this hydroxide ion concentration can be calculated using their respective solubility constants.

$$1.3 \times 10^{-33} = [Al^{+3}][OH^-]^3 = [Al^{+3}][3.41 \times 10^{-9}]^3$$

$$[Al^{+3}] = 3.28 \times 10^{-8}$$

and

$$4.0 \times 10^{-38} = [Fe^{+3}][OH^-]^3 = [Fe^{+3}][3.41 \times 10^{-9}]^3$$

$$[Fe^{+3}] = 1.01 \times 10^{-12}$$

These low concentrations are small enough to be considered zero. The fact that the iron (III) and aluminum can be separated from each other by selective precipitation can be seen by inspection.

8.10 Nomenclature

A	surface area, ft^2
$[Al^{+3}]$	concentration of aluminum ion, moles/liter
C	updated cost, dollars
C_B	base cost, dollars
D	diameter, ft
F	volumetric flow rate, ft^3/min
$[Fe^{+3}]$	concentration of ferric ion, moles/liter
F_m	cost adjustment factor for material of construction, dimensionless
F_p	cost adjustment factor for pressure, dimensionless
G	flow rate, gal/min

H	hydraulic horsepower, H.P.
h	height, ft
H_p	dynamic head, psi
I_F	price index for fabricated equipment, dimensionless
I_p	price index for pumps and pipes, dimensionless
$[OH^-]$	concentration of hydroxide ion, moles/liter
Q	heat load, Btu/hr
ΔT	apparent temperature difference, °F
T_{steam}	temperature of steam, °F
T_{bp}	boiling temperature of solution, °F
U_D	average heat transfer coefficient for steam, Btu/ft^2-hr-°F
V	volume of reactor, ft^3
$[Zn^{+2}]$	concentration of zinc ion, moles/liter
ε	correction factor for heat transfer coefficient, dimensionless
θ	residence time in reactor, min

8.11 References

1. Burger, personal communication, Bureau of Commerce, Washington, D.C., May 5, 1976.

2. *Chemical Engineering*, *75*(14), 162 (1968).

3. *Chemical Engineering*, *82*(26), 182 (1975).

4. Chemical Marketing Reporter, Schnell Publishing Co., New York, N.Y., April 12, 1976.

5. Chilton, C.H., "Process Labor Requirement," in "Data and Method for Cost Estimation," McGraw-Hill, New York (1952).

6. Cuny, Roy, personal communication, Nash Engineering Co., Norwalk, Conn, May 11, 1976.

7. Dean, J.A., "Lange's Handbook of Chemistry," 11th ed., p5-7, McGraw-Hill, New York (1973).

8. Duecker, W.W., "The Manufacture of Sulfuric Acid," p. 362-363, ACS Monograph Series (1959).

9. Elan, A., personal communication, AMOCO, Chicago, Ill., May 4, 1976.

10. Franklin, personal communication, Martin Marietta, Colorado, May 17, 1976.

11. Garmus, B., personal communication, Dupont, Wilmington, Delaware, May 5, 1976.

12. Guthrie, K.M., "Capital Cost Estimating," Modern Cost-Engineering Technique, p. 90-91, McGraw-Hill, New York (1970).

13. <u>Ibid.</u>, p. 93.

14. <u>Ibid.</u>, p. 96-99.

15. <u>Ibid.</u>, p. 103.

16. Hale, B.H., personal communication, ORNL Cost Engineering, Oak Ridge, TN, May 4, 1976.

17. Hurley, personal communication, Martin Marietta, Maryland, May 17, 1976.

18. Katz, D.L., "Evaluation of Coal Conversion Process to Provide Clean Fuels," EPRI Project 206-0-0.

19. Kern, D.O., "Process Heat Transfer," pp. 382-83, McGraw-Hill, New York (1950).

20. McCabe, W.L., and J.C. Smith, "Unit Operations of Chemical Engineering," p. 271, McGraw-Hill, New York (1967).

21. O'Rourke, B., personal communication, Stauffer Chemical, Westport, Conn., May 17, 1976.

22. Perry, J.H., "Chemical Engineers' Handbook," 4th ed., p. 1-36, McGraw-Hill, New York (1963).

23. <u>Ibid.</u>, p. 6-2.

24. <u>Ibid.</u>, p. 26-31.

25. Sajkowsky, S.D., personal communication, Knoxville Utility Board, Knoxville, TN, May 9, 1976.

26. Tursega, G., personal communication, Dorr Oliver, Stamford, Conn., May 6, 1976.

27. Williams, E., personal communication, Texaco, New York, May 2, 1976.

28. Wilson, T.C., personal communication, Y-12 Plant, Union Carbide, Oak Ridge, May 9, 1976.

29. Wood, R.E., "The University of Utah's Coal Hydrogenation Process, Summary Report for the Second Contract Period 1969-1975," U.S. Dept. of Interior, Office of Coal Research.

30. Wood, R.E., personal communication, University of Utah, May 3, 1976.

31. Wood, R.E., and W.H. Wiser, "Coal Liquefaction in Coiled Tube Reactors," I&EC Proc. Des. Dev., 15(1), 146 (1976).

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