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INVESTIGATION OF FREEZE CONCENTRATION AS A
PROCESS FOR INDUSTRIAL ENERGY CONSERVATION
IN BLACK LIQUOR, ACETIC ACID AND CITRUS JUICE
APPLICATIONS

Final Report

July 1979

Work Performed Under Contract No. AC01-78CS40034

Concentration Specialists, Inc.
Andover, Massachusetts

U. S. DEPARTMENT OF ENERGY

Division of Industrial Energy Conservation

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CONSERVATION IN BLACK LIQUOR, ACETIC ACID
AND CITRUS JUICE APPLICATIONS

FINAL REPORT

CONCENTRATION SPECIALISTS, INC.
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JULY 1979

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THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. EM-78-C-01-4130

ABSTRACT

One of the largest consumers of energy in industrial processing is the equipment that concentrates weak aqueous solutions to stronger more sellable or reusable concentrations. This study establishes the technical and economic feasibility of applying freeze concentration (that is, crystallization and removal from solution of pure solvent -- water) as an alternative to heat evaporation (or distillation) to three industrial applications. For each of the applications -- pulp mill black liquor concentration, acetic acid recovery and orange juice concentration -- the economic analyses indicate that the energy savings achievable by freezing justify the respective capital investments with pay out periods of generally one to three years. Past freeze concentration operations have been in the 10,000 to 100,000 gallons per day range for sea water desalination. Research and development work will be required to adapt this work to the three industrial applications.

ACKNOWLEDGEMENTS

The results of the work reported herein represent the contributions and accomplishments of many individuals on the staff of Concentration Specialists, Inc. and elsewhere. Valuable assistance was also provided by Mr. John R. Rossmeissl, Project Manager, Division of Industrial Energy Conservation, End Product Industries Branch, U.S. Department of Energy. Concentration Specialists also wishes to thank the industrial participants involved in the Technology Transfer seminars.

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ABBREVIATIONS

ACFM	actual cubic feet per minute	L	length
act	actual	l	liter
AD	air dry	lb	pound
ad	adiabatic	Liq	liquid
atm	atmosphere	Lmtd	logarithmic mean temperature difference
BBL	barrel	LTV	long tube vertical
BL	black liquor	M	thousand
bls	black liquor solids	m	meter
BOD	biochemical oxygen demand	MM	million
BPR	boiling point rise	Mat'l	material
BTU	British thermal unit	max	maximum
BWG	Birmingham wire gage	MEE	multi-effect evaporator
°Bx	degrees Brix	MEK	methyl ethyl ketone
°C	degrees Celcius	mg	milligram
Comp	compressor	min	minute or minimum
CONC	concentrate	N	number
CONC'R	concentrator	OD	outside diameter
Cond	condenser	O&M	operating and maintenance
Conv	conversion	op pres	operating pressure
Crys	crystals	P&ID	piping and instrument diagram
CS	carbon steel	Pres	pressure
des pres	design pressure	Prod	product
Deq	equivalent diameter	psi	pounds per square inch
dia	diameter	psia	pounds per square inch absolute
disch	discharge	psia	pounds per square inch gage
Dist'n	distillation	PVC	polyvinyl chloride
DOE	Department of Energy	°R	degrees Rankine
dp	deep	Recirc	recirculation
DS	dry solids	R&D	research and development
ea	each	Refin	refinery
Eff	efficiency	Rej	rejection
equiv	equivalent	Req'd	required
EVAP	evaporator	S	entropy
°F	degrees Fahrenheit	sec	second
ft	foot	Select.	selectivity
gal	gallon	Sep	separator
gpm	gallons per minute	Sq P	square pitch
H	head	SS	stainless steel
h	enthalpy	ST	stage
HA _c	acetic acid	Suct	suction
hr	hour	T	temperature
hp	horsepower	TASTE	thermally accelerated short tube evaporator
HT	heat		
HXR	heat exchanger		
ID	inside diameter		
Impur	impurity		
in	inch		
kg	kilogram		
KW	kilowatt		
kw-hr	kilowatt-hour		

ABBREVIATIONS /
(Cont'd)

TDS	total dissolved solids
TPD	tons per day
Tri P	triangular pitch
VC	vapor compression
W Col	wash column
wt frac	weight fraction
yr	year

EXECUTIVE SUMMARY

PURPOSE AND OBJECTIVES

One of the largest consumers of energy in industrial processing is the equipment that concentrates weak aqueous solutions to stronger more sellable or reusable concentrations or effects the separation of a product from weak mixture. The concentration is usually accomplished by boiling off the water and leaving behind the concentrate. Normally this concentration is accomplished with various configurations of evaporators and distillation columns -- processes which operate on steam and, as used in most industrial applications, are quite energy inefficient separators. Typical applications involve large flow volumes even within a single plant, and because of their wide spread use, these heat separation processes account for a large amount of industrial energy usage.

In addition to process applications, pollution abatement standards and the increasing scarcity of water will require concentration processes and their attendant energy requirements. If these effluent streams were concentrated, in many cases by-products could be recovered and water produced for reuse back in the plant. Again, if heat operated, inefficient concentration processes are used for these applications, a further strain will be placed on our energy supplies.

The objective of this work was to determine the technical and economic applicability of the more energy efficient freeze concentration process to three typical industrial applications presently utilizing heat evaporation (or distillation) for concentration or separation. The applications were chosen such that on a national basis they represent a large total usage of energy and potential for conservation and secondly, they are chemically and functionally similar to many other potential industrial applications. Specifically, the program consists of:

- o selecting three industrial separation applications,
- o developing a preliminary design for a freeze separation process for each application, and then,
- o developing the economics of the freeze separation process compared to the conventional process.

APPROACH

THE BASIS OF FREEZE SEPARATION

Freeze crystallization is a concentration/separation process based on the known scientific principle that when a solution containing dissolved solids is cooled to its freezing point, only pure water is frozen out, leaving behind a concentrated solution of the dissolved solids. As more pure crystals form, the remaining solution becomes more and more concentrated. Since usually only one component in the solution crystallizes (water), this permits separation in a single theoretical stage -- as contrasted to the incremental separation and multistage processes needed in vapor-liquid evaporation separations. The energy efficiency of the freeze separation process results both from this single-stage capability and from the lower latent heats associated with the solid-liquid phase change; crystallization latent heats are one-half to one-tenth those of vaporization.

Freeze crystallization is adaptable to concentrating organic, inorganic and mixed organic/inorganic aqueous solutions.

INDUSTRY AND APPLICATION SELECTIONS

In conjunction with the Department of Energy's Office of Industrial Programs, the following industrial applications were selected for evaluation:

<u>INDUSTRY</u>	<u>APPLICATION</u>	<u>ESTIMATED NATIONAL ENERGY CONSUMPTION</u>		
		<u>YEAR</u>	<u>10^{12} BTU/YR</u>	<u>EQUIVALENT BBL OIL/YR</u>
Pulp and Paper	Black Liquor Concentration	1977	189	33,800,000
Chemical	Acetic Acid Recovery	1976	10.9	1,950,000
Food	Orange Juice Concentration	1973	1.63	291,000

CONCENTRATION PROCESS CHARACTERIZATION AND COMPARISONS

For each of the above applications, the following information was developed to test the economic feasibility of freeze concentration compared to current industry practice:

Conventional Concentration Processes -

- o Current engineering practice
- o Unit energy consumption
- o National energy consumption
- o Representative, average or typical plant or unit size
- o Capital investment required
- o Annual energy costs (representative, unit steam and electrical energy costs were determined for each application separately)

Freeze Concentration Processes -

- o Preliminary engineering design based on projected solid-liquid phase chemistry and measured freezing point depressions and solution viscosities when available
- o Unit energy consumption
- o Potential national energy savings
- o Capital cost estimates based on process equipment component sizing
- o Annual energy costs

This information is the basis of the economic comparisons of (1) a replacement case where freezing is substituted for existing evaporator or distillation separation capacity, (2) an expansion case where both freezing and conventional concentration methods are being considered for a future plant expansion and (3) special applications such as concentration of black liquor spills.

TECHNOLOGY TRANSFER

Many government funded development programs have provided technology that has never been adopted commercially. Technology transfer groups in the various federal agencies have been formed to disseminate information once developed. This, however, only addresses part of the problem. Input from the prospective beneficiaries of government development programs can direct whether and how development should be undertaken in the first place. Thus, an important aspect of this contract was to provide information needed by the prospective industrial end users to evaluate the potential of freeze separation processing. Industries' feedback, obtained at technology transfer seminars at their facilities, was incorporated into the designs and economic evaluations of this program. Concentration Specialists feels strongly that the participation of industry in this project has measurably added to the relevance, applicability and accuracy of this analysis' basis and results.

CONCLUSIONS AND RECOMMENDATIONS

GENERAL ECONOMIC FEASIBILITY

This program examined three applications for freeze separation processing in place of existing conventional technology. Significant energy reductions are possible in all of the applications. Economic analyses indicate that, in all cases, the energy savings justify the expense of the freeze separation system with pay out periods of generally one to three years. Because of the differences in the three applications, the more detailed results and conclusions are discussed separately below. A brief description of each application is also presented.

BLACK LIQUOR CONCENTRATION

In 1975, the U.S. pulp and paper industry purchased an average 18 million BTU's/ton of dried product in fossil fuel and energy. The industry ranks first in fuel oil consumed and fifth in total energy consumed by all manufacturing industries in the nation. One of the largest consumers of energy in the pulping operation is the concentration of black liquor, which is the waste stream resulting from the chemical separation of wood fibers in the wood pulping operation. Black liquor is concentrated conventionally with multi-effect evaporators and then burned to (1) recover inorganic chemicals for reuse and (2) utilize the heating value of the concentrate to generate high pressure steam and electricity and for other process uses.

In evaluating freezing processes as alternatives to the current industry practice of using multiple effect evaporators, particular emphasis was given to absorption freezing -- a process capable of using low level waste heat as a source of energy. Comparison was also made with a mechanical refrigeration freezing process (utilizing a conventional heat pump refrigeration cycle) and a vapor compression evaporator.

The Expansion Case

One case considered was the expansion of a 1,000 tons per day (TPD) pulping operation by 350 TPD using freezing as a pre-evaporator to the current multiple effect evaporator train which would continue the concentration to the required 65% for incineration. This application would probably be the first full size application of freezing technology in the industry because no existing equipment needs to be replaced.

Table ES-1 shows that if an absorption freezing system was used for concentrating black liquor, the energy savings alone would pay out the additional capital cost of the process in less than one year of operation. With the expected near and long-term continued rising of energy costs, the pay out period of the mechanical freezing system can be expected to surpass that of the waste heat absorption system. Concentration Specialists feels therefore that the absorption system possesses the greatest long-term potential in this application. Additionally, 0.84 barrels of oil would be saved for each ton of pulp produced. The national impact of this savings is enormous since the industry is expanding by approximately 1,000,000 tons/year. Using absorption freezing for this expansion would save 840,000 barrels of oil a year. Extrapolating this rate of expansion 21 years to the year 2000 means that absorption freezing could save 17,640,000 barrels of oil per year. This is almost the equivalent of one day's current oil demand for the entire United States. Because of the development and time required to transfer freezing technology into the industry, savings of this magnitude are impossible in this time frame. However, this projection certainly demonstrates the potential future energy savings.

TABLE ES-1

BLACK LIQUOR CONCENTRATION EXPANSION CASE ECONOMIC SUMMARY

Basis: 350 tons per day expansion
 8,000 hours per year operation
 \$3.00/10⁶ BTU steam cost*
 \$0.025/kw-hr electrical energy cost*

	<u>BASE CASE: EVAPORATORS</u>	<u>ABSORPTION FREEZING WITH WASTE HEAT</u>	<u>MECHANICAL FREEZING</u>	<u>VAPOR COMPRESSION EVAPORATORS</u>
<u>CAPITAL COSTS</u>				
Capital Cost (10 ⁶ \$)	2.45	4.10	3.38	4.56
Incremental Cost Over Base Case (10 ⁶ \$)	-	1.65	0.93	2.11
<u>ENERGY COSTS AND SAVINGS</u>				
Annual Energy Cost (10 ⁶ \$/yr)	5.09	3.19	3.44	3.92
Savings Compared to Base Case (10 ⁶ \$/yr) -		1.90	1.65	1.17
<u>PAY OUT</u>				
Expansion Case- Incremental Capital Cost Paid Out by Energy Savings in:	-	0.87 yrs.	0.56 yrs.	1.80 yrs.

* Representative Industry Cost-East Coast Plant December 1978

The Replacement Case

This case considers alternatives of using freezing processes to replace the current multiple effect evaporator in a 350 ton per day pulping operation. Calculations were made using freezing both for concentration from 15% black liquor solids to 25% and 15% to 45%. Multiple effect evaporators currently in existence were used for the remaining concentration to 65%. 45% is probably a higher concentration than a freezing process can achieve because of the high viscosity of the cold black liquor, but concentrations greater than 25% are probable and the 45% case will give an indication of maximum possible savings.

The economics indicate approximately a three year pay out of capital costs by energy savings. If absorption freezing was used to pre-evaporate black liquor for the entire current U.S. pulp production, 10,800,000 barrels of oil a year could be saved on a national basis. If freezing could achieve 45%, the savings would be 18,300,000 barrels of oil a year.

Black Liquor Spills

Currently black liquor spills from the digesters and other portions of the pulping operation are cleaned up by washing the spill area with water and sewerage the discharge to the waste treatment system. The economics show that an absorption freezing system could concentrate a 60,000 gallons per day spill stream from 6% to 30%, for an energy cost one-tenth that of a 6-effect evaporator. The remaining concentration from 30% to 65% would be accomplished in the current evaporator train prior to burning the concentrate. Considering the credit for the fuel value recovered, the economic pay out for the freezing system is 3 to 3½ years. This analysis makes no allowances for further credits accrued because of additional chemical recovery or reduction in pollution control costs, both of which could account for significant additional savings.

Recommendations for Black Liquor Concentration

The comments received during the technology transfer seminars may be summarized as follows: If freeze crystallization were a developed and demonstrated technology, the pulp and paper industry couldn't afford not to look at it for black liquor concentration and other applications. The savings appear significant, but the risks and costs are too great for a private company to undertake. There needs to be operating plants in the industry before widespread use of the technology. Concentration Specialists, Inc. believes that a program supported by the Department of Energy can transfer this technology from its present developmental status into widespread use in the industry. The program is long range and would move slowly at first until there were one or two commercial installations, but proven installations would encourage widespread use.

ACETIC ACID RECOVERY

In 1976, acetic acid production in the United States was approximately 2.4 billion pounds. Most of the acid is produced by three reaction routes; two of these processes were chosen for detailed investigation in this program:

- o Vapor phase acetaldehyde oxidation, and
- o Methanol carbonylation.

The range of unit energy consumption, BTU per pound of acetic acid produced, represented by these two processes is such that the economics developed should bracket those of the third production route.

Energy Comparisons

The estimated energy consumption of the conventional, distillation refining sections of the methanol and acetaldehyde derived crude acid processes is 1400 to 9000 BTU/lb acetic acid respectively. The energy consumption for the prospective freeze refineries is projected to be about 95 percent less for these two crude acids. The salient difference between the freeze separation processes designed to purify the acetic acid from the two reaction routes is the need for water removal from the crude produced from acetaldehyde. Where the crude acid contains over 40% water there is a preliminary freeze dehydration step and then acetic acid is crystallized at the eutectic with simultaneous ice production (eutectic means the composition and temperature at which this simultaneous crystallization occurs). Crude from the methanol process, containing little water or impurities, is crystallized without any simultaneous co-precipitation, lowering energy consumption and equipment size.

Economic Benefits of Freezing

As shown in Table ES-2, the economics of freeze refining provide an attractive pay out period even where the freeze process would replace an existing fractional distillation refinery. This justification is based totally on energy savings. So, justification for freezing in new installations does not require any consideration of alternative capital costs; they are, however, presented here as a point of comparison.

TABLE ES-2

ACETIC ACID REFINING ECONOMICS SUMMARY

Basis: 100 million pounds of acetic acid per year
 8,000 hours per year operation
 \$3.50/10⁶ BTU steam cost*
 \$0.04/kw-hr electrical energy cost*

	<u>ACETALDEHYDE OXIDATION</u> <u>(30% Acid-70% Water)</u>	<u>METHANOL-CARBONYLATION</u> <u>(98% Conv.-96% Select.)</u>
<u>CAPITAL COSTS</u>		
Fractional Distillation Refinery (10 ⁶ \$)	3.5	3.3
Freeze Refinery (10 ⁶ \$)	2.1	0.9
<u>ENERGY COSTS AND SAVINGS</u>		
Fractional Distillation Refinery (10 ⁶ \$/yr)	3.1	0.48
Freeze Refinery (10 ⁶ \$/yr)	0.2	0.051
Savings by Freezing (10 ⁶ \$/yr)	2.9	0.43
<u>PAY OUT</u>		
Replacement Case		
Freezing's Capital Cost		
Paid in Energy Savings in	0.72 year	2.1 years

* Representative Industry Cost - East Coast December 1978

Recommendations for Freeze Crystallization in the Chemical Industry

None of the chemical companies with which we held technology transfer seminars was interested in a joint development/demonstration program with the government. Industry feels that if the economics justify adoption of this technology, they would develop it and no further incentive would be necessary. The role of the Department of Energy, therefore, should be one of coordinator and disseminator of information.

ORANGE JUICE CONCENTRATION

In 1973, 1.75 billion pounds of citrus concentrate was produced in the United States; orange juice alone making up nearly 80 percent of the total volume. Presently, the water is separated by evaporation. Evaporators concentrate orange juice from 10 degrees Brix (10°Bx) to 65°Bx (°Bx equals weight percent dissolved sugar content). However, orange juice concentrate is sold commercially at 45°Bx. One reason for this is that during evaporation concentration some of the volatile juice components are driven off and lost. In order to improve taste, single strength (dilute) juice is added-back and the resultant mix is therefore blended to 45° Bx prior to packaging.

Alternatively, the freeze concentration process we envision for this application is an indirect process in which the cooling occurs across a heat transfer surface. The refrigerant does not come in contact with the juice being concentrated, thus no loss of volatiles results. Concentration would be directly to 45° Bx; no add-back would be required. On the basis of the storage volume needed, freeze concentration would be equivalent to present systems.

Energy Comparison

The energy consumption of the 6-effect Thermally Accelerated Short Time Evaporator (TASTE), utilized to minimize steam consumption, is 260 BTU per pound of water separated. The mechanical freezing system would consume about 114 BTU per pound in the form of fuel converted to electrical energy.

Economic Benefits of Freezing

Table ES-3 shows that freezing provides an attractive pay out period for the case where both freezing and evaporation would be considered for a plant expansion. The replacement case appears marginal due in large part to the relatively low number of operating hours per year. The pay out period however can be expected to decrease as:

- o Energy costs continue to rise and
- o Freezing system capital costs decrease with further development and optimization.

Recommendations for Freeze Concentration in the Citrus Juice Industry

With the incorporation of the design features more fully explained in Chapter 5 of this report, we feel that many of the problems associated with past juice freezing processes utilizing scraped-surface heat exchangers (for freezers) and centrifuges (for crystal separators) can be eliminated. We expect that many of the outstanding research and development needs can be fulfilled by process testing on a small scale.

TABLE ES-3

ORANGE JUICE CONCENTRATION ECONOMICS SUMMARY

Basis: 60,000 lb water separated per hour
 3,600 hours per year
 \$3.50/10⁶ BTU steam cost*
 \$0.035/kw-hr electrical energy cost*

	<u>6-EFFECT EVAPORATOR^a</u> <u>(TASTE UNIT)</u>	<u>MECHANICAL</u> <u>FREEZING^b</u>
<u>CAPITAL COSTS</u>		
Capital Cost (\$)	710,000	906,000
Incremental Capital Cost of Freezing (\$)	-	196,000
<u>ENERGY COSTS</u>		
Annual Energy Cost (\$/yr)	206,000	86,000
Savings by Freezing (\$/yr)	-	120,000
<u>PAY OUT</u>		
Expansion Case - Incremental Capital Cost Paid Out by Freezing in Energy Savings in	-	1.6 yrs.
Replacement Case - Freezing's Capital Cost Paid Out in Energy Savings in	-	7.6 yrs.

^a To 65°Bx; volatile juice components lost, add-back required.

^b To 45°Bx only, volatile juice components retained, add-back not required.

* Representative Industry Cost - Florida - December 1978

CHAPTER 1
PROGRAM METHODOLOGY AND BASIS

INDUSTRY AND APPLICATION SELECTION

Three concentration/separation applications were chosen for study that:

- o on a national basis represent a large total usage of energy
- o offer technical applicability to freeze crystallization technology
- o are chemically and functionally similar to many other potential industrial applications.

An additional characteristic was defined as desirable for any application that would replace conventional heat evaporation or distillation with a freeze separation process. The application should be relatively large and diverse (i.e., a number of plants, with numerous companies involved, with a large annual output). This and the above criteria should insure the following advantages in the commercialization stage that would logically follow this study:

- o the energy savings would justify comparatively large capital expenditures relative to the conventional concentration methods.
- o the technology and its benefits would then be available to a large number of companies.
- o the total energy conservation from large-scale implementation would be more significant, even though any one application could make only an unnoticable mark on the energy consumed in such a diverse industry.
- o a large number of companies would be exposed to the technology in such a manner as to force their close attention to its benefits and capabilities.

In conjunction with the Department of Energy's Office of Industrial Programs, the following selections were made:

TABLE 1-1
INDUSTRY AND APPLICATION SELECTIONS

<u>INDUSTRY</u>	<u>APPLICATION</u>
Pulp and Paper	Black Liquor Concentration
Chemical	Acetic Acid Recovery from Weak Solutions
Food	Orange Juice Concentration

Information on the technical applicability of freeze concentration to these industrial processes is presented in the individual respective chapters that follow. Table 1-2 presents here the estimated total annual energy consumption for the three applications by the convential evaporation or distillation technology.

TABLE 1-2
SUMMARY OF ENERGY CONSUMPTION BY PRESENT
EVAPORATION AND DISTILLATION METHODS

<u>APPLICATION</u>	<u>YEAR</u>	<u>EST. NATIONAL ENERGY CONSUMPTION</u>	
		<u>(10¹² BTU/YR)</u>	<u>(EQUIV. BBL OIL/YR)</u>
Black Liquor Concentration	1977	189	33,800,000
Acetic Acid Recovery	1976	10.9	1,950,000
Orange Juice Concentration	1973	1.63	291,000

These figures give an indication of the large energy conservation potential for freeze concentration separation technology.

ECONOMIC ANALYSES

CAPITAL COSTS

The capital costs of the respective freezing systems for the three applications were developed from preliminary engineering designs which included equipment component sizing. For the purposes of this study, we are assuming a developed technology rather than a first of a kind installation which would have a great deal higher engineering cost associated with it. Base equipment costs were derived from references 1, 2, 3 and 4 and were updated with standard escalation indices to mid-1978. These were supplemented by equipment vendor quotes. The base equipment costs were then multiplied by appropriate factors to arrive at installed freezing system costs.² Installed equipment costs, particularly for units utilized by conventional evaporation and distillation were supplied by industry sources.

Indirect charges² have been added to the above installed costs only when needed to put comparisons between freezing and conventional concentration technology on an equal basis. Summarizing:

<u>Costs Included</u>	<u>Costs Not Included</u>
Process equipment	Site preparation
Installation materials and labor	Building
	Incremental facility costs for:
	electrical distribution
	cooling tower
	administration building
	Contingency
	Royalties, fees
	Indirect charges (except as noted)

OPERATING COSTS

The operating costs in this study are limited to the energy costs of the respective concentration processes. Other operating and maintenance costs for the conventional and freezing technologies were assumed equal.

ECONOMIC PARAMETERS

The economic parameters used as the basis for the comparisons of concentration processes were developed from industrial sources. These parameters were determined separately for the three applications. The following summarizes the criteria:

TABLE 1-3
BASIS FOR ECONOMIC EVALUATION

<u>ECONOMIC PARAMETER</u>	<u>APPLICATION</u>		
	<u>BLACK LIQUOR</u>	<u>ACETIC ACID</u>	<u>CITRUS JUICE</u>
Representative Plant or Unit Size	350 Tons/Day dry pulp ^a	100 Million lb/yr acetic acid	60,000 lb water separated/hr
Operating Level (hrs/yr)	8,000	8,000	3,600
Steam Cost (\$/10 ⁶ BTU)	2.76-3.00 ^b	3.50	3.50
Electrical Energy Cost (\$/kw-hr)	0.025	0.04	0.035
Waste Heat	No Cost	-	-

COST COMPARISONS DEVELOPED

To determine the economic feasibility and incentive for freeze concentration in the three industrial applications, we have made comparisons to the conventional processing. Annual projected savings in energy costs by freezing are related to capital costs in terms of the pay out period necessary to make up the capital investment. This is determined for the representative plant size noted above for:

1. Replacement Case - The existing evaporators or distillation units are to be shut down. Freezing is substituted for the appropriate water separation capacity.
2. Expansion Case - The plant facility is to be expanded by capacity equal to the representative plant or unit size. Both freezing and the conventional concentration methods are being considered. The pay out period is determined for any differences in capital investment required.
3. Special Applications - For example, recovery of the fuel value of black liquor lost in spills. Freeze concentration is evaluated as an alternative to waste disposal treatment.

^a An additional 60,000 gallons/day black liquor spill application is also evaluated.

^b Depends on steam quality and end-use; see cost derivation in Chapter 3.

TECHNOLOGY TRANSFER - INDUSTRY INVOLVEMENT

Many previous government funded development and demonstration programs have provided technology that has never been adopted commercially. Technology transfer groups in the various federal agencies have been formed to disseminate information once developed. This, however, only addresses part of the problem. Input from the prospective beneficiaries of government development programs can direct whether and how development should be undertaken in the first place. Thus, an important aspect of this contract was to provide the information needed by the industrial end users to evaluate the potential of freeze separation processing. This information was incorporated in a program that was presented to various industrial groups at their facilities. Concentration Specialists feels strongly that the participation of industry in this program has measurably added to the relevance, applicability and accuracy of this analysis' basis and results.

REFERENCES:

1. Perry, R. H., Editor, Chemical Engineers' Handbook, 5th edition, McGraw-Hill Book Company, New York, 1973.
2. Guthrie, K. M., Process Plant Estimating, Evaluation and Control, Craftsman Book Company of America, Solana Beach, CA, 1974.
3. Peters, M. S. and K. D. Timmerhaus, Plant Design and Economics for Chemical Engineer's, McGraw-Hill Book Company, New York, 1968.
4. Popper, H. Editor, Modern Cost-Engineering Techniques, McGraw-Hill Book Company, New York, 1970.

CHAPTER 2

GENERALIZED FREEZE CONCENTRATION PROCESS DESCRIPTION

STATUS

Freeze concentration processes must be considered developmental at this time. Plants have been constructed for sea water desalting, paraxylene separation and coffee and juice concentration, but there is no major commercial plant in operation today from which published data is available. The various components that make up a freeze crystallization process have been developed and demonstrated. Freeze sea water desalting plants have successfully and reliably operated producing over 125,000 gallons of fresh water per day with an energy consumption of less than 45 kw-hr/1000 gallons.¹ However, much adaptive work remains to demonstrate that freeze concentration can be used for applications such as black liquor concentration. The major purpose of this economic feasibility study is to determine if further applications work is justified from both a cost and energy savings point of view.

Appendix A describes the various types of freeze concentration processes, their relative merits and components. Freezing processes, are based on the physical fact that when a solution containing dissolved solids is frozen, only the pure water freezes, leaving behind a concentrated solution (this is analogous to an evaporator where the pure water is boiled off, leaving behind the concentrate). If the freezing process forms relatively small ice crystals (200 to 300 microns), there is no entrapment of impurities and the crystals are pure. Once the ice crystals are formed, the concentrate adhering to the outside of the crystals is washed off in a wash column, using a very small portion of the pure water produced and the concentrate is separated from the ice. The washed ice is then melted which recovers much of the refrigeration accounting for the process' high efficiency and produces a stream of pure water (approximately 100-200 ppm total dissolved solids, TDS).

Freeze crystallization separation processes are distinguished by the method of freezing. There are three basic types:

1. Indirect - The ice crystals are formed in a heat exchanger with the ice on one side of the heat transfer surface and the refrigeration on the other.
2. Vacuum - The solution to be concentrated is reduced in pressure to its triple point where both ice crystals are formed and water vapor given off. Refrigeration is provided by either mechanical compression or absorption of the water vapor.

3. Secondary Refrigerant - A secondary refrigerant such as n-butane or halocarbons is directly mixed with the solution to be concentrated and refrigeration is provided by the evaporation and compression of the secondary refrigerant.

Concentration Specialists, Inc. is currently designing and fabricating pilot plants using each of these processes. Applications include sea water desalting, juice and milk concentration, the concentration of dilute acetic acid waste streams, and a multi-purpose unit for industrial demonstrations.

FREEZING PROCESS OPERATION

A freezing process can be divided into two functions: the concentration system and the refrigeration system. The refrigeration system (some type of a heat pump) removes the heat from the feed solution, thus forming ice, and raises its energy level up to the point where it can be recovered by melting the ice. The concentration system takes the ice crystals that are formed and grows them into crystals that can be washed, then washes them thus effecting the separation and concentration.

Refrigeration Systems

Either a mechanical or absorption refrigeration system can be used. A mechanical system is simpler and more conventional, but uses a high form of energy: electricity or steam turbine for its motive force. An absorption system can use relatively low quality heat -- either hot water (180°F min.) or low level steam to supply its power.

Mechanical System - In a mechanical system a conventional refrigeration compressor is used to compress a refrigerant vapor (either ammonia or a halocarbon) from the freezer as shown in Figure 2-1 to the melter where the majority of the refrigerant is condensed and then recirculated back to the freezer. Due to process inefficiencies the cooling capacity of the ice is not sufficient to condense all the vapor and an auxiliary or heat rejection compressor is used to compress the excess vapors up to a pressure such that they can be condensed on cooling water. This usually represents 10-15% of the refrigeration energy requirement.

MECHANICAL REFRIGERATION
SYSTEM
FIGURE 2-1

Absorption Systems -

Selection of Absorbents

The requirements for an absorbent in a freezing process are different from the usual absorbent refrigeration process in that the operating temperature is much lower, and the desired regeneration temperature is as low as possible. These requirements are contradictory in themselves, i.e., the lower the temperature required, the lower the vapor pressure that is required in the absorber. Such low vapor pressures are associated with high concentrations of the solute, which in turn means a high boiling point rise (BPR) and high generator temperature.

The most common absorbent used today is lithium bromide, which solidifies at the required vapor pressures. An extensive search for suitable absorbent solutions was made in this study. Three absorbents were found which could be used and were considered in the study -- sodium hydroxide, sulfuric acid and aqueous ammonia. Sulfuric acid was eliminated because of the high cost materials that would have to be used to prevent corrosion. Sodium hydroxide required less costly materials than sulfuric acid, but more costly than ammonia. The ammonia process also eliminated the possible solidification of the absorbent during an abnormal shutdown and was thus selected. Also considerable data is available on ammonia systems, permitting a credible design at the present, even if further studies might indicate a more suitable absorbent.

The Absorption Cycle

A simplified absorption system consists of two basic operations: absorption and regeneration as shown in Figure 2-2. In the absorber, vapor from the fluid being cooled is absorbed in a solution of absorbent which has a lower vapor pressure than the vapor being absorbed. This absorption heats up the absorbent and increases the concentration of the compound being absorbed in the absorbing solution. The heat is removed by cooling the absorber as shown. The concentration of the absorbent is maintained by pumping the absorbent to a generator (a concentrating evaporator) where the compound that was absorbed is vaporized, thus restoring the absorbent to its original concentration prior to being recycled to the absorber. A heat exchanger is used between the absorber and generator to increase the efficiency of the cycle.

SIMPLIFIED ABSORPTION SYSTEM

FIGURE 2-2

Concentration Process

For all processes, a general process description can be applied (Figure 2-3). The feed water passes through a heat exchanger and is cooled to within a few degrees of its freezing point by the melt and concentrate streams leaving the process. The feed enters a freezer where heat is removed, thus forming ice crystals. The resulting ice-concentrate slurry flows out of the freezer to a wash column (see Appendix A, page 3 for details) where the concentrate is displaced from the ice by a portion of the melt. The ice is transferred to a melter where the heat removed in the freezer, after being elevated in temperature by a compressor or absorption refrigeration cycle, is reapplied to the ice to accomplish the melting.

FIGURE 2-3
GENERAL CONCENTRATION PROCESS SCHEMATIC

Several recycle streams (not shown above) would be mixed with the cooled feed to provide seed ice crystals for the freezing process and to maintain a pumpable slurry. Crystal growth tanks (following the freezer) providing hydraulic detention time to produce optimal ice crystal size for satisfactory washing are required when freezing certain solutions. These and other specific features are more fully described in the three following chapters which deal separately with the industrial applications noted above.

REFERENCES:

1. Heist, James A., "Freeze Crystallization", Chemical Engineering, May 7, 1979.

CHAPTER 3

BLACK LIQUOR CONCENTRATION BY FREEZE CRYSTALLIZATION

PULP AND PAPER INDUSTRY PROFILE

CURRENT PRACTICE

In 1975, the U.S. pulp and paper industry purchased an average 18 million BTU's/ton of dried product in fossil fuel and energy. The industry ranks first in fuel oil consumed and fifth in total energy consumed by all manufacturing industries in the nation.² One study considering eight industrial sectors pinpointed Kraft pulping as the process accounting for the greatest energy loss of any single industrial process -- a total lost work of 1.29×10^{15} BTU's/year.³

The industry is healthy and expanding which will put an even greater strain on available energy supplies. The following information from the American Paper Institute⁴ shows the current and projected growth of Kraft pulp production.

	<u>TOTAL KRAFT PULP PRODUCTION</u>	<u>CHANGE FROM PREVIOUS YEAR</u>
1977	36,930,000 U.S. Tons	-
1978	38,022,000 " "	1,092,000 U.S. Tons
1979	39,917,000 " "	895,000 " "
1980	39,901,000 " "	984,000 " "
1981	40,919,000 " "	1,018,000 " "

Using an average of 18×10^6 BTU's/ton of dried product, this growth means that the industry will use approximately 18×10^{12} BTU's or the equivalent of 3.2×10^6 additional barrels of oil each year if further energy conservation methods are not developed and used. Extrapolated to the year 2000, this would mean an additional 67.5×10^6 barrels of oil a year increase over current consumption.

One of the largest consumers of energy in the pulping operation is the concentration of black liquor by multi-effect evaporation prior to burning. Once the wood fibers from which paper will be made are chemically separated from the wood by dissolving the lignins and other binding agents, the remaining liquid, called black liquor in the Kraft processes, containing these wastes and the chemicals used for dissolving the pulp is then concentrated

prior to incineration. This waste stream is called black liquor and the concentration is effected by removing water with multi-effect evaporators to minimize steam consumption.

The concentrate is then fired in a furnace much like fuel oil. The burning of the concentrate serves two purposes: (1) recovery of the chemicals for reuse -- this is an economic necessity, (2) utilization of the heating value of the concentrate to make high pressure steam for the generation of electricity and process uses. The greater the amount of water removal from the dilute black liquor, the higher its heating value. Even though extensive use is made of cogeneration using steam for conversion to electricity prior to its use for process applications such as black liquor concentration, paper making and pulp digesting, additional fuel and electricity are purchased to supplement the heating value of the concentrated black liquor. There are also a few pulp and paper mills that use supplemental fuel to generate 100% of their electricity.

Energy usage has always been a significant expense for the paper industry, and the industry has done a great deal to economize its use. The industry was among the first to use widespread cogeneration, and there is currently a move to higher steam temperatures and pressures. Six and seven stage multi-effect evaporators have been in use for many years. In locations where low cost electricity is plentiful, vapor compression evaporation, a more energy efficient process, is currently being used to replace the first stage of the multi-effect evaporators. There are industry efforts to reduce the size and danger of the Tomlinson furnace by replacing it with hydrolysis or going to higher concentrations for increased fuel value. In spite of all these efforts, energy needs will continue to increase for the pulp and paper industry because of expansion and increasingly stringent pollution controls requiring more energy.

There is one source of energy available to a pulp and paper mill that would both conserve energy and reduce costs for the industry; that source is low level waste heat from low grade process steam or hot water. If a process could be found to operate on this low level waste heat, which now exists in great quantity in all pulp and paper mills, essentially a third level of cogeneration could be achieved with a corresponding decrease in the total supplemental energy that must be supplied to the mill.

KRAFT MILL PROCESS DESCRIPTION

The following is a general outline of the process in a Kraft mill from logs to finished paper. (See Figure 3-1 for process diagram.)

In preparation for pulping, logs are debarked and broken into chips.

In the pulping plant these wood chips are fed to a large tank called the digester, mixed with pulping chemicals (white liquor) and heated under pressure. The heat and chemical action breaks down the lignin which holds the separate wood fibers together. This process is called cooking. After cooking the contents of the digester (pulp) is ejected under pressure into the blow tank which is at atmospheric pressure. This sudden release of pressure also causes the wood chips to expand and helps separate them into more or less separate fibers. The wood fibers are screened to separate the larger pieces, which are refined and sent back to the digester. The screened pulp is sent to the brown stock washers where the spent cooking liquor (black liquor) is separated by countercurrent washing. The washed pulp is then sent on to the bleach plant. An important auxiliary process in the pulping plant is the Kraft liquor recovery system. The pulping chemicals in a Kraft pulping mill are recovered from the black liquor and reused in the digester. This is accomplished by concentrating the black liquor from the brown stock washers and burning it in a recovery furnace. The smelt (burned black liquor) from this furnace is then redissolved to form white liquor. Enough heat is produced in the recovery furnace to supply the energy needs of the pulping plant and also provide some steam and electricity to other parts of the mill. The operation of the black liquor recovery system is described in greater detail in another portion of this report.

Washed pulp from the pulping plant goes to the bleach plant. In the bleach plant the pulp goes through a series of bleaching stages and washers. In each bleaching stage the pulp is treated with a bleaching chemical which is generally manufactured in a bleach plant in an auxiliary process. Various bleaching chemicals are used in different stages at different times depending on pulp qualities and the degree of bleaching desired.

After bleaching, the pulp goes to either the pulp dryer or to paper making.

For market pulp, either in a non-integrated pulping mill or an integrated mill which also produces market pulp, the pulp is sent to the pulp dryer. In order to reduce shipping costs, market pulp is usually dried. In drying market pulp it is first pressed to remove as much water as possible by mechanical means and the remaining water is removed by vaporizing the moisture, usually through steam heat. Drying pulp uses a considerable amount of energy.

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JOB _____ OF _____
ANALYZED BY S. Thompson DATE 2/13/78
REF. NO. _____ CHKD. BY _____ DATE _____
SUBJECT KRAFT MILL PROCESS DIAGRAM

MAIN PROCESS

SECONDARY PROCESS

OPTIONAL PROCESS

FIGURE 3-1

In the paper making section, pulp is taken from the bleach plant and is mixed and prepared for papermaking. Purchased market pulp can also be used in paper making, either by itself or mixed with pulp from an attached plant. Purchased pulp is re-slurried in a pulper and then prepared for the paper making machine. In the paper making machine the pulp is deposited on a wire screen to form a thin sheet and water is drained off to form a wet mat (web). This web is then delivered to the press. In the press section the paper is passed between sets of cylindrical rollers where as much water as possible is squeezed out. The paper then goes to the dryer where the rest of the water is removed. As mentioned before, drying is a highly intensive user of energy. This energy is supplied as steam and is estimated to be approximately 5.3×10^6 BTU/air dry ton of paper. (The steam from the driers is one possible source of low level waste heat for an absorption freeze concentration process.) After drying, the paper goes to the calender where it is again passed between sets of cylindrical rollers. The calender rollers give the paper its finish and improve its dimensional consistency.

BLACK LIQUOR RECOVERY SYSTEM

In a conventional Kraft pulp mill black liquor is separated from the pulp in the brown stock washers. Some of this is returned directly to the digester, the rest goes to multiple effect evaporators, six effects being the most common number. The multiple effect evaporators concentrate the black liquor from 14-18% total solids to about 45-50% total solids. The concentrated black liquor then goes to the direct heat evaporator which is located in the upper part of the recovery furnace. (In more modern operations, steam operated concentrators are used instead of direct contact evaporators.) There moisture is removed by direct contact with flue gases and the black liquor is dried to about 60-70% total solids. The black liquor then falls into the recovery furnace proper where it is burned. About 45-55% of the wood that is dissolved in digestion is contained in this residual liquor and the heat generated when it is burned is considerable. Most of the heat generated in the furnace is used to produce steam. Figure 3-2 shows a typical mass and heat balance for the various processes in a Kraft pulping operation. Note cogeneration use of the steam where it is first used to generate electricity and then taken from the high pressure turbine at 135 psi for process use and at 35 psia for the evaporators. While this heat recovery represents a considerable amount of energy, additional supplemental fuel is needed to meet drying and other process requirements.

The smelt is dissolved in water to form green liquor. This green liquor is slaked, causticized, and clarified to make the white liquor for the digester. Make up chemicals are added either to the green liquor or to the black liquor just before burning.

Approximate heat balance in alkaline pulp mill,⁵ based on 1 ton of air-dry pulp (1,800 lb of oven-dry pulp). Datum temperature, 80°F; assumed boiler feedwater at 250°F obtained from returned condensate.

FIGURE 3-2

THE CURRENT POWER CYCLE

ASSUMPTIONS

The modern Kraft pulp and paper mill is an exceedingly complex operation that varies substantially from plant to plant and is strongly influenced by local economic and resource conditions. Trying to account for these variations in an economic feasibility study would produce such a wide bank of results that the comparisons would be meaningless. What we have chosen to do instead is to define a set of assumptions that might be typical of a mill and carefully show the development of our costing rationale, based as closely as possible on typical industry numbers in order that a knowledgeable reader could take our methodology and substitute conditions appropriate to his application and make his own feasibility determinations.

The typical case we have chosen is a 350 ton per day Kraft pulp mill or plant expansion. The assumption is that the plant purchases both supplemental fuel for steam process needs and additional commercial electricity. The steam conditions are 650 psia and 700°F -- these conditions are probably high for a mill as small as 350 TPD and low for a 350 TPD expansion in a large 1000 TPD modern, energy conscious plant.

The previous section described developed projected costs for a freezing process while this section of the report discusses current black liquor concentration practice, showing the derivation of energy costs from the given assumptions, and projected capital costs of both multi-effect and vapor compression evaporators based on actual installed costs obtained from industry sources.

MULTI-EFFECT EVAPORATORS

Normally the evaporators used are combined into a multi-effect system in order to economize energy usage. In a multi-effect system the steam or vapor is reused, as shown in Figure 3-3, to heat the liquor for the next body or effect. A single effect requires essentially one pound of steam to evaporate one pound of water. In a multi-effect system the economy is increased by roughly the number of effects installed after allowing for radiation, pressure losses, etc. Thus, a triple effect system will evaporate slightly under three pounds of water per pound of steam. The number of effects feasible depends on the operating costs for steam versus the added capital costs of additional effects. Also a controlling factor to consider in multi-effect systems is the available

MULTI-EFFECT EVAPORATOR⁸

FIGURE 3-3

LONG TUBE VERTICAL EVAPORATOR⁹

FIGURE 3-4

temperature drop (ΔT) across the system. The "driving force" of any evaporator is this (ΔT). This is the difference between the temperature of the steam into the first effect and the temperature of the vapor (steam) out of the last effect. This temperature difference is limited by (1) the pressure of the steam available, (2) the temperature limit of the material in process, and (3) the temperature and quantity of condenser water available.

In practice rarely is more than a septuple (seven) effect evaporator installed for the reasons discussed above.⁸

A typical evaporator used for black liquor concentration is a long tube vertical (LTV) evaporator which has a vertical heater as shown in Figure 3-4, integral with the vapor head. This compact design, which is usually self-supporting is quite economical to install particularly, when large heat transfer areas are required. Heat transfer areas approaching 40,000 square feet can be built into the heating element of this type evaporator. Tube lengths are normally in the range of 20-28 feet and tube diameters are 1½-2 inches. This type is commonly installed as a multi-effect system.

Feed liquor flows into the bottom liquor box and enters the vertical tubes, boiling at an ever-increasing rate as it rises through the tubes, then discharging at high velocity into the vapor head. Liquor inventory or hold up is minimal in this design. A vapor-liquor separation is made in the vapor head with the liquor being pumped from the bottom of the vapor head and the vapor exiting from the top through an entrainment separator. As vapor is generated from boiling in the tubes, relatively high tube velocities occur. This results in good heat transfer rates particularly for low viscosity liquors having low scaling tendencies.⁹

The following paragraphs describe the operating economy of a multi-effect evaporator.

Energy Cost Derivation for Evaporation

Cogeneration - The pulp and paper industry was one of the first to use widespread cogeneration of electricity and process steam. Typical practice is to generate high pressure steam in the recovery furnace and to use it for a high pressure turbine for electricity prior to process use. Steam is taken from the high pressure turbine at approximately 135 psi for process use and 60 psia for the evaporators. Condensing turbines are often used to generate additional electricity and to balance plant energy loads. A typical pulp and paper mill is not energy self sufficient and additional fuel and electricity must be purchased to meet process steam and electricity demands.

Any attempt at energy costing must take into account cogeneration. Figure 3-5 shows a simplified Enthalpy versus Entropy diagram for the selected example of a 350 TPD pulp operation with high pressure steam conditions of 650 psia, 700°F. This figure shows the following conditions:

X ₁ - High Pressure Steam	- 650 psia 700°F	h ₁ = 1342 BTU's/# Steam
X ₂ - Turbine Exit	- 60 psia 400°F	h ₂ = 1234 BTU's/# Steam
X ₃ - Saturated Vapor	- 15 psia 213°F	h ₃ = 1151 BTU's/# Steam
X ₄ - Saturated Liquid	- 15 psia 213°F	h ₄ = 181 BTU's/# Water
X ₅ - Final Evaporation Cond.- Liquid	200°F	h ₅ = 168 BTU's/# Water
X ₆ - Condensing Turbine End Condition	- 3% Vapor @ 120°F	h ₆ = 1082 BTU's/#

Δh_a is the amount of energy available for high pressure electrical generation in the present power/evaporation cycle and Δh_b is the amount used for evaporations. Δh_c is the energy available for power generation using a condensing turbine if the evaporator were not being used. Specifically:

Δh_a - Energy used for high pressure power generation - X ₁ -X ₂	= 108 BTU's/# Steam
- Energy actually used for Evaporation - X ₃ -X ₅	= 983 BTU's/# Steam
- Energy lost because of evaporation - X ₂ -0	= 1234 BTU's/# Steam
- Energy available for power generation by condensing turbine if evaporator wasn't used - X ₂ -X ₆	= 152 BTU's/# Steam
Δh_c - Energy available for power generation if evaporator wasn't used - X ₁ -X ₆	= 260 BTU's/# Steam

Evaporator Energy Consumption - A 6-effect evaporator train is assumed with an economy ratio of 4.75 pounds of water evaporated per pound of steam. This is typical of industry practice for large mills. The amount of energy used for evaporation is:

$$\frac{X_3 - X_5}{4.75} = 207 \text{ BTU's/#H}_2\text{O Evaporated}$$

The actual energy used for the entire evaporation cycle is:

$$\frac{X_2 - 0}{4.75} = 260 \text{ BTU's/#H}_2\text{O Evaporated}$$

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SUBJECT _____

FIGURE 3-5
MOLLIER DIAGRAM
ENTHALPY VERSUS ENTROPY

Legend

Δh_a - Present Power Cycle : X_1-X_2

Δh_b - Present Evaporator Cycle: $X_2-X_3-X_4-X_5$

Δh_c - High Pressure Turbine plus Condensing Turbine for Electricity Generation without Evaporator: $X_1-X_2-X_6$

Value of Steam Used for Evaporation

The actual cost of steam varies widely with the type of fuel used and accounting practices on how the costs are allocated for generation equipment and process use. We have assumed that supplemental fuel is used to generate high pressure steam for the evaporators and that it has a generated value of \$3.00 per million BTU's. Using a world price of fuel oil of \$12.92/barrel at this writing and projected increases in the order of 15% to \$14.85 yields a fuel cost of \$2.31/10⁶ BTU's:

$$\left(\frac{\text{(Price per barrel)}}{5.6 \times 10^6 \frac{\text{BTU's}}{\text{barrel}}} \right)$$

To the direct fuel cost, additional cost must be added to account for boiler inefficiencies (on the order of 15%), the depreciated cost of the boiler and other generating equipment and manpower. Therefore \$3.00/10⁶ BTU's seems a reasonable conservative estimate for the value of the high pressure steam generated from supplemental fuels.

Since the high pressure steam is used with cogeneration, the cost of the steam must be apportioned between electrical generation and evaporation. Our assumption is the division can be best made by attributing the BTU's used for each operation divided by the total BTU's available. Referring again to the Mollier Diagram:

Assume cost of high pressure steam = \$3.00/10⁶ BTU's

Portion of steam value used for electricity = $\frac{X_1 - X_2}{X_1 - 0} = 8\%$

Portion of steam value used for evaporation = $\frac{X_2 - 0}{X_1 - 0} = 92\%$

Cost of steam for evaporation = .92 x \$3.00/10⁶ BTU's = \$2.76/10⁶ BTU's

Cost of Electricity Generated Without Evaporation

One question we wondered about as we proceeded with this study was since pulp mills already generate electricity along with producing process steam, why doesn't industry generate 100% of their electrical power using purchased fuel directly instead of buying additional power. The following calculation shows the answer. If the evaporator was not being used and both the high pressure and condensing turbine were being used for electrical generation, the fuel cost of this electricity is:

$$\text{Cost/kw-hr} = \frac{\text{Cost of Steam}}{\frac{\text{kw-hr}}{\# \text{ Steam}}}$$

$$\text{Where } \frac{\text{kw-hr}}{\# \text{ Steam}} = \left[\frac{X_1 - X_6}{3413 \frac{\text{BTU's}}{\text{kw-hr}}} \right] [\text{Generator Eff}] = \left[\frac{260}{3413} \right] [.95] = .0724 \frac{\text{kw-hr}}{\# \text{ Steam}}$$

$$\text{Cost/kw-hr} = \frac{1342 \text{ BTU's}}{\# \text{ Steam}} \times \frac{\$3.00}{10^6 \text{ BTU's}} \times \frac{1}{.0723 \frac{\text{kw-hr}}{\# \text{ Steam}}} = \$.0557/\text{kw-hr}$$

Without taking into consideration capital costs and operating costs, the cost per kilowatt-hour is greater than the cost of purchased electricity in most parts of the country.

There are some mills that do generate all or most of their own electricity. Usually these mills are in remote locations where the cost of obtaining commercial electricity is excessive or where they have low cost hydropower available. Large plants generating their own electricity have been among the leaders in going to higher temperature and pressure operating steam conditions, which would substantially lower the generation fuel costs.

Evaporator Capital Costs

Obtaining exact estimates for the installed capital costs of multi-effect evaporators is difficult because each mill has different conditions that must be incorporated into the final evaporator design and installation. Table 3-1 shows the capital costs for two actual installations obtained from industry sources. Actually, the installed costs are relatively similar, particularly if inflation is taken into account. The installed costs shown range from \$5.1 million to \$5.8 million for an installed capacity of 700,000 to 783,000 # of water evaporated per hour.

In order to develop capital costs for the comparison with freezing, these costs must be scaled to the relatively small capacity evaporator (116,000 #H₂O Evaporated/hr) that would be used to concentrate black liquor from 15% to 25% in a 350 ton/day pulp mill. During our discussions with industry representatives, we found rule of thumb cost capacity scaling factors in use of 0.6 to 0.7 with 0.65 being most common. (The same factor was also used for costing various size freezing and vapor compression plants from the base cases.)

The capital costs used in our comparisons for a 6-effect evaporator is \$1.68x10⁶.

TABLE 3-1

TYPICAL EVAPORATOR COSTS

A. 6-EFFECT EVAPORATOR (1978)

- Capital Cost/Installed - \$5.8 Million
- Materials - Carbon Steel Shells with 304 SS Domes and 304 SS Tubes - All Effects
- Economy Ratio - 4.5 lbs H₂O/lb Steam, 65# Gage
- Evaporating Cost - \$1.81/lb Solids Concentration
- Inlet Concentration - 13%
- Outlet Concentration - 55%
- 3.2 Million #/Day of Black Liquor Solids
- Capacity - 783,000 # H₂O Evaporated/Hr.
- Pulp Capacity - Approximately 1,000 Tons/Day

B. 6-EFFECT EVAPORATOR (2nd QUARTER 1974)

- Capital Cost - \$5.1 Million
- Installation Cost - \$3.0 Million
- Materials - First 3-Effects - All 316 SS
- Last 3-Effects - Carbon Steel Shells with 316 SS Tubes (clad)
- Economy Ratio - 5 lbs H₂O/lb Steam, 50 psig
- Inlet Concentration - 15%
- Outlet Concentration - 45%
- Capacity - 700,000 #H₂O Evaporated/hr.

VAPOR RECOMPRESSION

System Description

Vapor recompression in evaporation is just what the name implies. It consists of taking vapor exiting from a vapor head and compressing it to a higher pressure suitable for use as steam in the heating element.¹⁰ See Figure 3-6.

Vapor recompression can provide attractive operating economics providing the material being evaporated has a relatively low boiling point rise which will allow a low compression ratio. Power and steam costs are important considerations in evaluating the economic feasibility of vapor recompression.

A mechanical recompression vapor compression evaporator is particularly attractive in geographical areas, such as the Pacific Northwest, with particularly low electrical energy costs. Because of boiling point elevation, the maximum achievable concentration of black liquor is approximately 25%.

Figure 3-7 shows a flow diagram of a very advanced vapor compression concept for concentrating black liquor to 25% and recovering methanol for additional fuel value and to eliminate a significant pollution load. This is an excellent example of efficient energy use in the paper industry. The system is fully described in the references.¹¹⁻¹³

Capital and Energy Costs

According to Mr. Patrick J. Hurley* of Tacoma, Washington, a consultant to the pulp and paper industry, the installed capital cost of a vapor compression evaporator is extremely dependent on installation factors, but suggests that approximately \$3,500,000 is a reasonable installed cost for a vapor compression unit with a capacity of 300,000 lb of H₂O evaporated/hour. The estimated capital cost for a 116,000 lb/hr unit is $\$1.89 \times 10^6$. The energy required to operate such a system evaporating black liquor from 15% to 25% is 95 kw-hr/1000 gal.

* See Resume Appendix C

MECHANICAL RECOMPRESSION¹⁰

FIGURE 3-6

FIGURE 3-7

WEYERHAEUSER VAPOR COMPRESSION EVAPORATION/
DISTILLATION BLACK LIQUOR CONCENTRATOR¹¹⁻¹³

SK-1106

FREEZE CONCENTRATION

POTENTIAL OF FREEZE CONCENTRATION

The ideal freeze concentration process would utilize low level waste heat which currently must be disposed of in condensers or cooling towers for an energy source, reduce overall energy usage, possibly increase the BTU's available in the black liquor by eliminating inorganic build up and possibly reduce pollution energy requirements by more efficient treatment or eliminating pollution sources. The economic advantages, to the Forest Products Industry if such a process could be developed and demonstrated, are summarized in a personal communication from Dr. D. R. Raymond, Manager, Energy Fiber Products R&D, Weyerhaeuser Company, Tacoma, Washington:

"The concentration of black liquor in the Forest Products Industry is of major significance in many ways. The present state-of-the art requires concentration through multiple-effect evaporators and more recently through vapor recompression evaporation. The switch from multiple-effect to vapor recompression achieves an economy of thermal energy at the expense of electrical energy. Therefore, a measurable negative impact on total fossil energy is apparent if the fossil fuel used by the electric power industry is considered.

"Another situation is the rather large amounts of low level energy present in effluent streams and in the exhaust from steam hoods and from thermal mechanical and chemical mechanical pulping processes. These streams and others result in considerable hot water and low pressure steam which is discharged without use. In many cases, especially in the South, it is necessary to employ cooling towers at the expense of even more electrical energy in order to achieve a thermally acceptable level of discharge into the receiving water.

"As mills in the industry are closed up and as new mills built in a more closed fashion, there are at least three significant problems that freeze concentration could perhaps uniquely address. These three problems are and will continue to be critical to the Forest Products Industry over the foreseeable future.

"First, the need to collect both concentrated and dilute spills of black liquor and process these spills through some system of ultimate recovery of chemical and energy value is evident. The present approach is to utilize increased evaporator capacity which must be supplied with energy from fossil fuel. The absorption freeze concentration approach could apparently accomplish this utilizing waste heat in a more cost-effective manner.

"The second problem is associated with what the industry refers to as dead load on its recovery systems. This can best be explained by the cycling of inorganics through the recovery boiler which decrease substantially the heating value of the black liquor being burned, and therefore increase substantially the amount of fossil fuel which has to be burned to make up the difference. Freeze concentration could apparently achieve a preferential removal of these inorganics and therefore substantially raise the heating value of the black liquor and again accomplish this improvement with waste heat.

"The third problem is associated with color discharge from Kraft mills where a substantial amount of the color has been demonstrated to be from the black liquor escaping to the receiving water. Again, the most common solution to this problem utilizes collection and evaporation generally from fossil fuel as the energy source. Utilizing waste heat, freeze concentration could alleviate this problem.

"To place the impact that might be possible with this approach in perspective, within Weyerhaeuser there are 4×10^6 tons of Kraft black liquor dry solid processed per year. The average heating value of this black liquor is 5800 BTU/lb DS. Heating value could be improved in the order of 10% if the dead load were removed. Also, within Weyerhaeuser estimates indicate that 165×10^6 gallons/year of dilute Kraft black liquor are collected and reprocessed through evaporation as a result of spill and color control. Projections are that this will increase by 20% over the next decade as environmental laws become more stringent.

"Weyerhaeuser feels the development of freeze concentration techniques for the above and other applications is important and may constitute a unique way to utilize otherwise useless low level energy sources plentiful within many of its operations."

This study tests the economic feasibility of freeze concentration processes for concentrating black liquor, by comparing freezing processes to the current industry practice of using multiple effect evaporators. Particular emphasis was given to absorption freezing -- a process capable of operating on low level waste heat. The comparison is done by using a 350 ton per day pulping operation as an example and developing comparison costs and data from industry sources as much as possible. No attempt is made to consider all the possible variables in choosing a black liquor concentration system, but sufficient information is given on our methodology so a reader could make an approximate feasibility estimate of his application.

Freeze concentration processes have been demonstrated desalting sea water and some smaller applications in the chemical and fruit juice industries. However, the process must be considered developmental, particularly for an application such as black liquor, and further applications research is necessary before the technology could be expected to be transferred.

PROCESS CONSIDERATIONS AND SELECTION

Maximum Achievable Black Liquor Concentration

We do not know what is the maximum achievable concentration of black liquor by a freezing process. Concentration in a freezing process is limited by two variables.

1. Viscosity - Some solutions, especially organics, become extremely viscous at high concentrations and low temperatures and become impossible to pump or to separate the ice crystals from the concentrate. At some concentration this will certainly be the case with black liquor and a heat process will have to be used in conjunction with freezing to achieve the concentration required for black liquor incineration.
2. Freezing Point Depression - The freezing point depression determines the operating economics of a freezing system just as the boiling point elevation determines the operating cost of a vapor compression evaporator. The major energy cost is the refrigeration required to raise the energy from the temperature required to freeze the ice to where its recovered by melting the ice. Freezing point depression varies with chemical composition and concentration. For the concentration of black liquor, viscosity is certainly the limiting factor as the freezing point depression at any possible concentration is well within demonstrated technology.

There are other factors that also affect the maximum achievable concentration. There is a possibility that sodium sulfate crystals may precipitate from the black liquor as the concentration increases and the solubility limit is exceeded. In fact, it is the separation of these crystals that Dr. Raymond of Weyerhaeuser discusses above that would remove inorganic buildup and increase the heating value of black liquor. Removal of these inorganics could also have a favorable effect on viscosity. Another factor is the presence of volatiles in the concentrate. Unlike an evaporator where the volatiles evaporate along with the water, the freezing system chosen for black liquor could retain them in solution. A third factor is that ice crystal size decreases with concentration which causes the need for crystal growth tanks and staging of the wash columns. By staging the wash columns, the concentrate can be drained from the second stage without washing and the ice recycled with feed to the crystal growth tank and first stage wash column where the ice is separated and washed from the more dilute feed. This technique is still experimental but the literature reports some excellent results.⁶ The capital costs shown in the previous section includes provisions for crystal growth tanks and staged wash columns. The concentration system is described in greater detail later in this chapter.

Appendix B shows viscosity measurements and freezing point depressions of various black liquor samples that we have had performed for us by Drew Forest Chemicals Laboratory. Based on our extensive experience testing various viscous solutions with freezing systems, we believe that achieving a 25% concentration is within demonstrated technology and that 45% concentration with freezing is probably impossible. The maximum achievable black liquor concentration probably lies between these two values and can only be determined experimentally on a freezing pilot plant with actual black liquor samples.

In order to account for the unknown maximum concentration most of our cost comparisons are shown at the 25% level. Since energy costs are directly proportional to the amount of water removed, this would account for 40-50% of the water removed from the black liquor. It is also approximately the same concentration that vapor compression evaporators are currently being used for as an energy saving measure. A typical plant expansion would also probably use a new energy saving method for the first stage of concentration and retain the present, depreciated multi-effect evaporators for the final stages of concentrations. We have done some calculations showing 45% concentration by freezing to show the economic advantages of using freezing at a maximum possible concentration.

Process Selection

The freeze concentration process chosen for comparison with evaporators for black liquor concentrations was two versions of an indirect process:

1. Indirect with mechanical refrigeration
2. Indirect with absorption refrigeration using low level waste heat as an energy source.

Indirect processes were chosen because of their relative simplicity, easy adaption to a waste heat cycle, complete separation of the refrigeration system from the concentration mechanisms and retention of volatiles. The fact that a compressor is not needed in the waste heat cycle is a definite reliability plus. Vacuum freezing systems can be adapted to waste heat applications and are attractive because of their extremely high heat transfer rates in the freezer and lower capital cost because of elimination of a set of heat transfer surfaces. However worries of contaminating the absorbent and volatile carryover with the water vapor eliminated consideration at this time. Because of its inherent advantages, we still feel the vacuum freezing waste heat absorption process is worthy of further study to search for economical methods of handling the volatiles carryover, but the greater technical risk and limited time lead us to restrict consideration to the indirect

process in this study. Secondary refrigerant processes were rejected because they cannot be adapted to operate from low level waste heat and we believe that a low level waste heat process is extremely important for black liquor concentration because of the large amount of waste heat available in a pulp and paper mill.

PROCESS DESCRIPTION

The Concentration Process

A two stage washing process and crystal growth tank is used in conjunction with the freezer to accomplish the concentration as shown in Figure 3-8. Feed water is used to fluidize the ice scraped off of the first wash column. This serves the purpose of reducing the concentration and viscosity of the water adhering to the ice crystals and thus make them easier to wash in the second wash column. (A description of the operation of the wash column and mechanism of washing is found in Appendix A). The liquid displaced from the second wash column then forms the feed to the freezer. Water is frozen in the freezers in the form of tiny ice crystals. In order to wash these crystals they must be grown to at least 200 microns (.008") in size. This is accomplished by providing residence time in a crystal growth tank and recycling a slurry through the freezer. In the crystal growth tank the larger crystals increase in size, while the slurry recycle provides nuclei for crystal growth, thus minimizing the number of new crystals formed.

Refrigeration System

Mechanical Refrigeration - The conventional refrigeration compressor cycle is described in Chapter 2 (see also Figure 2-1).

Absorption Refrigeration - The general characteristics of the absorption cycle are described in Chapter 2 (see also Figure 2-2). Features specific to the ammonia system employed for this application are discussed below.

In ammonia systems one characteristic should be kept in mind that is opposite of most other absorption systems. The ammonia is vaporized in the generator rather than the water. The following description uses exact operating conditions shown on Figure 3-9 to make the explanation clearer, although these conditions are only typical. Pure ammonia is sprayed over the freezer tubes at 7°F and 37 psia. Ammonia evaporates from the freezer and is absorbed (similar to being condensed) in a 55% NH₃ solution entering the absorber @ 51°F, and leaving the absorber @ 60% and 40°F. The absorber operates at 36 psia providing a 1 psia driving force for absorption. The absorber is cooled primarily by the ice from the system -- thus accomplishing the melting function.

BLACK LIQUOR CONCENTRATION PROCESS

FIGURE 3-8

-49-

CONCENTRATION SPECIALISTS, INC.
ANDOVER, MASS.

SCALE: NONE

APPROVED BY

DRAWN BY RJP

DATE: 10-27-78

INDIRECT WASTE HEAT CYCLE USING
AMMONIA AS ABSORBENT

FIGURE 3-9

DRAWING NUMBER
7004-2002

Auxiliary cooling must also be supplied by an auxiliary absorbent loop (absorbent cooler #1 in Figure 3-9) which provides 30°F ammonia for cooling as well as for precooling the feed. The concentrated ammonia in the absorber (#2000) is heated by dilute absorbent from generator #2, and then sprayed over the tubes of the condenser for generator #1 where it is cooled by cooling H₂O and enriched in ammonia from generator #1. The purpose of spraying ammonia over the surface of absorbent cooler #3 is to reduce the pressure in this vessel. This significantly reduces the pressure and thus the temperature of generator #1, thus permitting either a lower level of heat input or an increased ΔT and correspondingly less surface area.

The liquid from absorbent cooler #3 is heated up by the dilute absorbent and auxiliary heat before entering the primary generator where the majority of the NH₃ that was absorbed is vaporized and condensed. The condensed NH₃ is returned to the cooling loops for reuse. A similar but smaller cycle is used to precool the feed and supply the auxiliary cooling to the main absorber.

CAPITAL AND ENERGY COSTS

Ammonia Absorption Cycle

Table 3-2 summarizes the capital cost and operating power requirements for an ammonia absorption freeze concentration process using low level waste heat as an energy source. Also included is an equipment list describing the size and materials of the major components, Table 3-3. The calculations shown are for a plant to concentrate the black liquor output of a 350 ton per day pulp operation from 15% to 25% (291,000 #/hr black liquor feed and 116,000 #/hr of pure water output). A cost-capacity scaling exponent of 0.65 is used in this study to obtain capital costs for various capacity plants.

The installed costs of standard equipment were obtained from Perry's Chemical Engineering Handbook⁷ and updated with standard escalation indices. Specialty components such as wash columns and freezers are estimates based on Concentration Specialists, Inc. experience with freezing pilot plants. For purposes of this study, we are assuming a development technology and not the first of a kind installation, which would have a great deal more engineering cost associated with it.

TABLE 3-2

CAPITAL COSTS
BLACK LIQUOR FREEZE CONCENTRATION VIA
AMMONIA ABSORPTION CYCLE

<u>ITEM</u>	<u>INSTALLED COST⁷</u> \$
1. Absorbent Cooler 1	84,800
2. Absorbent Cooler 2	122,800
3. Absorbent Cooler 3	78,900
4. Generator 1	84,200
5. Generator 2	134,500
6. Inter Cooler 1	57,300
7. Inter Cooler 1A	10,200
8. Inter Cooler 2	86,500
9. Inter Cooler 3	29,200
10. Inter Cooler 3A	33,900
11. Condenser	104,000
12. Freezer	122,800
13. Feed Exchanger	175,000
14. Pre-Cooler	17,000
15. Pumps	152,000
16. Crystal Tank	139,000
17. Wash Columns	143,000
18. Process Controls	200,000
TOTAL INSTALLED COSTS	<u>\$1,776,100</u>

TOTAL HORSEPOWER REQUIRED - 513 hp

TABLE 3-3

EQUIPMENT LIST FOR BLACK LIQUOR FREEZE CONCENTRATION
VIA AMMONIA ABSORPTION CYCLE

	<u>SURFACE AREA</u> (ft ²)
1. Serial No. 1000, Absorbent Cooler 1, Shell & Tube Exchanger (1-2), Material: Carbon Steel/Carbon Steel, Pressure Capacity (400 psia), Shell I.D. 4'+2' Entrainment, Tube O.D. 3/4" L=20', 1" sq. Pitch, N=1,463.	6,664
2. Serial No. 2000, Absorbent Cooler 2, Shell & Tube Exchanger (1-2), Material: Carbon Steel/Carbon Steel, Design Pressure (400 psia), Shell I.D. 5'+2' Entrainment, Tube O.D. 3/4" 1" Tri Pitch L=20' (N=1,786 Ammonia), N=876	12,128
3. Serial No. 3000, Absorbent Cooler 3, Shell & Tube Exchanger (1-2), Material: Carbon Steel/Carbon Steel, Design Pressure (400 psia), Shell I.D. 45'+2' Entrainment, Tube O.D. 3/4", 1" Sq. Pitch L=20', N=1,353.	6,167
4. Serial No. 4000, Generator 1, Shell & Tube Exchanger (1-2), Material: Carbon Steel/Carbon Steel, Shell I.D., 48'+2' Entrainment, Tube O.D. 3/4", 1" Sq. Pitch, L=20, N=1,453.	6,621
5. Serial No. 5000, Generator 2, Shell & Tube Exchanger (1-2), Material: Carbon Steel/Carbon Steel, Shell I.D. 5'+2' Entrainment, Tube O.D. 3/4", 1" Tri Pitch, L=20', N=2,900.	13,210
6. Serial No. 6000, Inter-Cooler 1, Shell & Tube Exchanger (2-4), Material: Carbon Steel/Carbon Steel, Design Pressure (400 psia), Shell I.D. 42", Tube O.D. 3/4", 1" Sq. Pitch, L=20', N=1,056.	3,751
7. Serial No. 6500, Inter-Cooler 1A, Shell & Tube Exchanger (1-2), Material: Carbon Steel/Carbon Steel, Shell I.D. 23 1/4", Tube O.D. 3/4", 1" Sq. Pitch, L=5', N=283	322
8. Serial No. 7000, Inter-Cooler 2, Shell & Tube Exchanger (3-6), Material: Carbon Steel/Carbon Steel, Shell I.D. 48", Tube O.D. 3/4", 1" Sq. Pitch, L=20', N=1,483.	6,756
9. Serial No. 8,000, Inter-Cooler 3, Shell & Tube Exchanger (2-4), Material: Carbon Steel/Carbon Steel, Shell I.D. 23 1/4", Tube O.D. 3/4", 1" Sq. Pitch, L=20', N=309.	1,408

TABLE 3-3 (Continued)
EQUIPMENT LIST FOR BLACK LIQUOR FREEZE CONCENTRATION
VIA AMMONIA ABSORPTION CYCLE

	<u>SURFACE AREA</u> (ft ²)
10. Serial No. 9000, Inter-Cooler 3, Shell & Tube Exchanger (1-2), Material: Carbon Steel/Carbon Steel, Shell I.D. 27", Tube O.D. 3/4", 1" Sq. Pitch, L=20', N=456	1,903
11. Serial No. 10,000, Condenser, Shell & Tube Exchanger (Horizontal), Material: Carbon Steel/Carbon Steel, Shell I.D. 78", Tube O.D. 3/4", 1 1/4" Tri Pitch, L=20', N=3,200.	9,065
12. Serial No. 11,000, Freezer, Shell & Tube Exchanger, Material: Carbon Steel/Carbon Steel, Shell I.D. 66" + 2' Entrainment, Tube O.D. 1", 1 1/4" Tri Pitch, L=20', N=2,032.	10,639
13. Serial No. 12,000, Feed Exchanger, Plate & Frame Exchanger, Material: 316 S.S., De=.026', No. of Plates = 1,112.	5,986.4
14. Serial No. 13,000, Pre-Cooler, Shell & Tube Exchanger, Material: Carbon Steel/Stainless Steel, Shell I.D. 35", Tube O.D. 1", 1 1/4" Sq. Pitch, L=5', N=477.	624
15. Pumps (Centrifugal), Serial No. 13,100-13,900, No. 13,100 hp = 77 No. 13,200 hp = 131 No. 13,300 hp = 66 No. 13,400 hp = 125 No. 13,500 hp = 17 No. 13,600 hp = 19 No. 13,700 hp = 12 No. 13,800 hp = 2 No. 13,900 hp = 64 TOTAL hp 513	
	<u>VOLUME</u>
16. Crystal Tank, Carbon Steel, Serial No. 14,000 25' I.D., 75' Height Insulation 2" Polyurethane	36,815 ft ³ 5,890 ft ²
17. Wash Column, Serial No. 15,000, Fiberglass, 10' I.D. 21.3' Height, Cylindrical Screen 2' Height at Mid-section, Internals: Piping and Metal Scraper with Motor.	1,671 ft ³

Mechanical Refrigeration System

Capital costs for a mechanical freeze concentration system are described in detail in Chapter 5 of this report. For the concentration of black liquor we have assumed that the process would be very similar, and we assumed that the capital cost would vary with the 0.65 power of capacity. For concentrating black liquor from a 350 ton pulp mill from 15 to 25%:

$$\begin{aligned} \left(\begin{array}{c} \text{Capital Cost} \\ \text{Black Liquor Conc.} \end{array} \right) &= \left(\frac{\text{Capacity-Black Liquor}}{\text{Capacity-Orange Juice}} \right)^{.65} \left(\begin{array}{c} \text{Capital Cost} \\ \text{Orange Juice Conc.} \end{array} \right) \\ \text{Capital Cost} &= \left(\frac{116,000 \text{ /hr}}{60,000 \text{ /hr}} \right)^{.65} \times \$905,900 = \$1,390,000 \\ \text{Black Liquor Conc.} & \end{aligned}$$

The orange juice study produced a calculated energy rate of 95 kw-hr/1000 gal. of pure water. At 25% concentration, black liquor has a much less freezing point depression than orange juice at 40% to 50%, and therefore, we are using a power consumption of 70 kw-hr/1000 gal. of pure water. These values are in line with Concentration Specialists operating experience with past pilot plants in other applications, but with similar freezing point depression. Actual power consumption can vary from liquor to liquor.

ENERGY USAGE COMPARISON - FREEZE CONCENTRATION VS. EVAPORATION

ASSUMPTIONS

Plant Capacity

350 ton/day mill - 3000 # solids/ton of air dry pulp

- Plant purchases both supplemental fuel and electricity.

Operating Factor

8,000 hours/year

Cost of Steam

- High pressure = \$3.00/10⁶ BTU's
- 60 psia steam = \$2.76/10⁶ BTU's

Cost of Purchased Electricity

- \$.025/kw-hr

Evaporation Steam Entrance Conditions

- 15 psia @213°F

Economy Ratio

- 4.75 or 260 BTU's/#H₂O Evaporated

Evaporation Capacity

- 15% to 25% - 116,000 #/hr. or 335,800 GPD
- 25% to 45% - 78,000 #/hr. or 225,900 GPD
- 15% to 45% - 194,000 #/hr. or 561,700 GPD

Concentration Processes Compared

Indirect Mechanical Refrigeration Freezing - 15% to 25% Concentration
Indirect Absorption Freezing - 15% to 25% Concentration
Indirect Absorption Freezing - 15% to 45% Concentration*
6-Effect Evaporation - 15% to 25% Concentration
6-Effect Evaporation - 15% to 45% Concentration
Vapor Compression - 15% to 25% Concentration

Cases to be Compared

1. Replacement of evaporators in a 350 TPD mill with freezing or vapor compression evaporators
2. Expansion of 1000 TPD mill to 350 TPD capacity using freezing vapor compression for the 15% to 25% preevaporation concentration to present multi-effect evaporator train.
3. Special Cases:
 - a. Black liquor spills
 - b. Ultra high concentrations
 - c. Hydropyrolysis

INTERPRETATION OF ENERGY SAVINGS

If evaporation capacity is replaced with a freezing system or vapor compression and the amount of high pressure steam generated correspondingly reduced, additional electricity must be purchased from outside to replace the electricity that would have been cogenerated along with the evaporation. As the calculations in above show, 108 BTU's of electricity are produced for each 1234 BTU's of energy used for evaporation and this loss must be accounted for in any calculations of energy savings. For purposes of this study savings will be defined as:

* As explained earlier in this chapter, this probably exceeds the maximum possible concentration with a freezing process, but is used to show the maximum possible savings.

Energy Savings in \$ = + Cost of high pressure steam that would be used for power generation and evaporators.

- Cost of replacing electricity not being generated.

+ Cost difference in pump power.

Savings in BTU's

+ BTU's currently used.

- BTU's to generate electricity at utility
at 10,000 $\frac{\text{BTU's}}{\text{kw-hr}}$ generated

+ BTU's difference to generate pump power.

REPLACEMENT CASE

This case represents the substitution of a freezing process or a vapor compression evaporator for a portion of the concentration currently being accomplished with a 6-effect multi-effect evaporator in a 350 ton per day pulping operation. The current multi-effect evaporator will then be used to complete the concentration to the 45% required for the direct contact evaporator. Energy consumption comparisons are calculated only up to 45% concentration, since the direct contact evaporation stage is common to all comparisons. Cogeneration is accounted for as described previously. The effect of tall oil separation is neglected for this study. Figure 3-10 shows the comparison cases and Tables 3-4, 3-5 and 3-6 summarize the calculations of energy cost and BTU savings for the various cases. Table 3-4 also shows the capital cost for each case.

FIGURE 3-10

REPLACEMENT COMPARISON CASES

Base Case for Comparison - Conventional 6-Effect Evaporators:

Case 2 - Use of Freezing Processes or Vapor Compression for Preevaporation

Case 3 - Use of an Absorption Freezing Process for Concentration to 45%*

* NOTE: As explained previously, 45% probably exceeds the maximum possible concentration achievable with a freezing process. However, the calculation does indicate the relative value of going to a concentration greater than 25% with a freezing process. Although the maximum possible concentration will have to be demonstrated, Concentration Specialists, Inc. believes it to be from 30 to 40%.

TABLE 3-4

REPLACEMENT CASE ENERGY SAVINGS — TON/DAY MILL

	STEAM DEMAND BTU's/HR	NET POWER DEMAND (PRODUCTION) kwh/h	NET POWER DEMAND (PRODUCTION) BTU's @ POWER PLANT/hr	TOTAL NET BTU's REQUIRED BTU's/yr	BTU SAVINGS OVER BASE CASE BTU's/yr	STEAM @ \$3.00/10 ⁶ BTU's \$/yr	NET PURCHASED POWER INCREASE (CREDIT) @\$.025/kwh \$/yr	TOTAL YEARLY ENERGY COSTS \$/yr	COST SAVINGS OVER BASE CASE \$/yr
<u>BASE CASE - 6-EFFECT EVAPORATION TO 45%</u>									
Base Case	54.7x10 ⁵	(998)	(9.98x10 ⁶)	358x10 ⁹	-	1,312,800	(199,600)	1,113,200	-
<u>CASE I - PREEVAPORATION TO 25% + 6 EFFECT EVAPORATION 25 to 45%</u>									
Absorption Freezing & 6-Effect Evap.	22.1x10 ⁵	(15)	(15x10 ⁶)	176x10 ⁹	182x10 ⁹	530,400	(3,000)	527,400	585,800
Vapor Compression & 6-Effect Evap.	22.1x10 ⁵	932	9.32x10 ⁶	251x10 ⁹	106x10 ⁹	530,400	186,400	716,800	396,400
Mechanical Refrig. & 6-Effect Evap.	22.1x10 ⁵	582	5.32x10 ⁶	223x10 ⁹	135x10 ⁹	530,400	116,400	646,800	466,400
<u>CASE II - ABSORPTION FREEZING TO 45%</u>									
Waste Heat		637	6.37x10 ⁶	51x10 ⁹	307x10 ⁹	Waste Heat	127,400	127,400	985,800

INSTALLED CAPITAL COSTS

for - Preevaporation Concentration to 25% - Evaporation Capacity = 116,000 #/hr

BASE CASE - 6-Effect Vaporation - \$1.68x10⁶

CASE I - Absorption Freezing - \$1.78x10⁶
 Vapor Compression - \$1.89x10⁶
 Mechanical Refrigeration - \$1.40x10⁶

TABLE 3-5

REPLACEMENT CASE ECONOMIC CALCULATION

	EVAPORATION RATE #H ₂ O/hr	STEAM DEMAND BTU's/hr@ 650 psia-700°F	CONCENTRATION POWER DEMAND kwh/h	BY PRODUCT POWER PRODUCTION kwh/h	NET POWER DEMAND (PRODUCTION)	YEARLY STEAM @ \$2.00/10 ⁶ BTU's \$	OPERATING COST NET PURCHASED POWER INCREASE @\$.025 kwh ABOVE BASE CASE (CREDIT)	TOTAL YEARLY COST \$
<u>BASE CASE</u>								
<u>CONVENTIONAL 6- EFFECT EVAP. 15-45%</u>	194,000	54.7x10 ⁶	292	1,290	(998)	1,312,800	(199,600)	1,113,200
<u>FREEVAPORATION PROCESSES</u>								
<u>ABSORPTION FREEZING 15-25%</u>	116,000	Waste Heat	381	0	381	Waste Heat	76,200	76,200
<u>MECHANICAL FREEZING 15-25%</u>	116,000	-	978	0	978	0	195,600	195,600
<u>VAPOR COMPRESSION 15-25%</u>	116,000	-	1,328	0	1,328	0	265,600	265,600
<u>25%-45% CONCENTRATION</u>								
<u>MULTI-EFFECT EVAPORATOR 25-45%</u>	78,000	22.1x10 ⁶	125	521	(396)	530,400	(79,200)	451,200
<u>15%-45% CONCENTRATION COMBINED PROCESSES</u>								
<u>ABSORPTION FREEZING/6-EFFECT EVAP. 15-45%</u>	194,000	22.1x10 ⁶	506	521	(15)	530,400	(3,000)	527,400
<u>MECHANICAL FREEZING 6-EFFECT, 15-45%</u>	194,000	22.1x10 ⁶	1,103	521	582	530,400	116,400	646,800
<u>VAPOR COMPRESSION/6-EFFECT 15-45%</u>	194,000	22.1x10 ⁶	1,453	521	932	530,400	186,400	716,800
<u>ALL FREEZING</u>								
<u>ABSORPTION FREEZING 15-45%</u>	194,000	Waste Heat	637	0	637	Waste Heat	127,400	127,400

TABLE 3-6

BLACK LIQUOR CONCENTRATION REPLACEMENT CASE SUMMARY

	<u>BASE CASE</u>	<u>CASE I</u>			<u>CASE II</u>
	6-EFFECT EVAP. TO 45%	PRE-EVAPORATION TO 25% & 6-EFFECT EVAPORATION 25-45%			ABSORPTION FREEZING TO 45%
		ABSORPTION FREEZING & 6-EFFECT EVAPORATION	MECHANICAL FREEZING & 6-EFFECT EVAP.	VAPOR COMPRESSION & 6-EFFECT EVAP.	ABSORPTION FREEZING
	<u>MULTIPLE EFFECT</u>	<u>6-EFFECT EVAPORATION</u>	<u>6-EFFECT EVAP.</u>	<u>6-EFFECT EVAP.</u>	<u>FREEZING</u>
Net Yearly Fuel Demand BTU's/yr	358x10 ⁹	176x10 ⁹	233x10 ⁹	251x10 ⁹	51x10 ⁹
Net Yearly Fuel Savings BTU's/yr	-	182x10 ⁹	135x10 ⁹	106x10 ⁹	307x10 ⁹
Net Yearly Fuel Savings Barrels of oil/yr	-	32.5x10 ³	24.1x10 ³	18.9x10 ³	54.8x10 ³
Yearly Energy Costs - \$/yr Electricity Cost = \$.025/ kw-hr, Fuel Cost = \$3.00/10 ⁶ BTU's	1,113,200	527,400	646,800	716,800	127,000
Yearly Energy Savings = \$/yr Electricity Cost = .025/kw-hr Fuel Cost = \$3.00/10 ⁶ BTU's		585,800	466,400	396,400	985,800
Replacement Capital Cost = \$	1,680,000	1,780,000	1,400,000	1,890,000	-

Total Energy Savings if Applied to all Pulp Production

Assume - 38,917,000 tons production/year for 1979.

$$\text{Energy Savings} = \frac{\text{Yearly BTU Savings Over Base Case}}{350 \text{ Tons/Day}} \times \frac{38,917,000 \text{ Tons/Year}}{333 \text{ Days/Yr } 5.6 \times 10^6 \text{ BTU's barrel Oil}}$$

CASE I - Preevaporation to 25% + 6-Effect Evaporation 15 to 25%

$$\text{Absorption Freezing} = \frac{182 \times 10^9 \times 38.917 \times 10^6}{350 \times 333 \times 5.6 \times 10^6} = 10.8 \times 10^6 \text{ barrels/yr}$$

$$\text{Vapor Compression} = \frac{106 \times 10^9 \times 38.917 \times 10^6}{350 \times 333 \times 5.6 \times 10^6} = 6.3 \times 10^6 \text{ barrels/yr}$$

$$\begin{array}{l} \text{Mechanical} \\ \text{Refrigeration} \end{array} = \frac{135 \times 10^9 \times 38.917 \times 10^6}{350 \times 333 \times 5.6 \times 10^6} = 8.03 \times 10^6 \text{ barrels/yr}$$

CASE II - Absorption Freezing to 45%

$$= \frac{307 \times 10^9 \times 38.917 \times 10^6}{350 \times 333 \times 5.6 \times 10^6} = 18.3 \times 10^6 \text{ barrels/yr}$$

EXPANSION CASE

Because of the extremely high capital cost of new pulp and paper mills, the most common method of meeting new production demands is to expand existing facilities. This would also be the most likely route of introducing new freeze concentration technology into the industry because it would permit retention of present, depreciated equipment while substantially reducing energy consumption at comparable capital costs to conventional expansion.

In order to insure using reasonable costs parameters for the economic feasibility evaluation of using freezing processes for the concentration of black liquor in a plant expansion, Concentration Specialists, Inc. asked Mr. Patrick J. Hurley, a consultant to the pulp and paper industry, to perform the study. Concentration Specialists, Inc. provided the information on freezing systems for Mr. Hurley's calculations, while he provided the information on evaporation processes from his industry background. His report and calculations follow:

Description of Expansion Alternatives

Figures 3-11, 3-12, 3-13, and 3-14 show four alternative methods of expanding capacity in pulp mill: (1) A conventional system using multi-effect evaporation and systems using, (2) mechanical freezing, (3) absorption freezing using waste heat and (4) vapor compression evaporation all as preevaporators for the existing multi-effect system. In the conventional system sketch, the lower set of sextuple evaporators and concentrator #2 would be added to existing equipment to process the solids flow from the expansion. In the sketches for the other three systems, the multiple effect evaporator (MEE) line and #1 concentrator are identical to the upper set of MEE's and #1 concentrator of the conventional system. The #2 concentrator shown is identical for each system. Number labels are put on the steam flows on each sketch, and the calculated flows for each of these streams are identified by these same labels in the calculation sheets, power demand for evaporation is taken from an article authored by Hank Lankenau of Unitech (sextuple LTV system). Power demand for freeze concentration is from information supplied by Concentration Specialists.

The choice of 650 psia high pressure steam is arbitrary and fits many existing pulp mills. New mills generally will have 900 to 1,300 psia systems.

Conventional technology in the evaporation area would be a new sextuple MEE, followed by a single effect concentrator (#2). Vapors from the concentrator would be fed into the MEE's to allow, typically, 3-effects of evaporation. Each effect is estimated to evaporate 0.8 lb H₂O per lb of vapor from the concentrator. Steam applied at the first effect is estimated to evaporate 4.8 lb H₂O/lb steam. MEE product liquor flash tanks are not shown. Steam economy of the concentrator was calculated to be 0.78 lb based on concentration from 52 to 65% solids, 200BPR, 14.5 psia operating pressure and 55 psia steam supply.

Application of freeze concentration or vapor compression technology as a pre-evaporation step would permit the weak liquor from the expansion and existing tonnage to be raised in concentration ahead of the MEE's. Concentrator (#2) would be needed due to the higher solids flow. Two systems are shown using freeze concentration. All the systems used to preconcentrate the liquor from 15 to 25% show a very large drop in steam demand at the first effect of the MEE. The evaporation heat use shown approaches the minimum that would be expected with these systems.

FIGURE 3-11

EXPANSION ALTERNATIVE: CONVENTIONAL EVAPORATORS

SK-1107

FIGURE 3-12

EXPANSION ALTERNATIVE: MECHANICAL FREEZE PRECONCENTRATION

FIGURE 3-13

EXPANSION ALTERNATIVE: ABSORPTION FREEZE PRECONCENTRATION

FIGURE 3-14

EXPANSION ALTERNATIVE: VAPOR COMPRESSION PRECONCENTRATION

Effective operation of this system might require that the MEE be operated as a quint or quad unit, i.e., this or alternate steps would be required to return evaporation rate per ft.² of evaporating surface nearer to design. The difference in the MEE steam economy that would result from the higher feed % solids and slightly lower feed temperature would be small, and is ignored.

The vapor compression unit shown in Figure 3-14 is used as a preconcentrator similar to the freezing systems. There are several installations using vapor compression pre-evaporation technology now in operation -- particularly in areas where the price of electricity is low in relation to other fuels.

Calculation Basis

High pressure steam: 650 psia, 700°F: h = 1,347
 Turbine exhaust @70% eff.: 60 psia, h = 1,197
 Saturated steam @ evaporation: 55 psia, h = 1,176
 Condensate from evaporators and deaerator: h = 257
 Ratio, turbine exhaust/saturated steam: 0.97 lb/lb
 Steam rate to 60 psia: 22.76 lb/kw-hr

Black liquor solids flow: 3,000 lb/ton Pulp

from existing 1,000 TPD: $125,000 \frac{\text{lb bls}}{\text{hr}}$

from incremental 350 TPD: $43,750 \frac{\text{lb bls}}{\text{hr}}$

Weak liquor, % solids - 15

Concentrator, % solids -

feed - 52

product - 65

Evaporator and concentrator power¹-

Approximately $\frac{20 \text{ kw-hr}}{100,000 \text{ lb water evaporated}}$

Heat capacity of dry black liquor solids - $\frac{0.3 \text{ BTU}}{\text{lb-}^\circ\text{F}}$

¹ Varies with type and configuration

Calculate Conventional System (Figure 3-11)

Vapor flow from concentrator #1:

$$125,000 \frac{\text{lb bls}}{\text{hr}} = \left(\frac{1}{.52} - \frac{1}{.65} \right) = 48,077 \frac{\text{lb}}{\text{hr}}$$

Steam flow to concentrator #1:

$$48,077 \frac{\text{lb}}{\text{hr}} \left(\frac{1 \text{ lb steam}}{0.78 \text{ lb vapor}} \right) = 61,637 \frac{\text{lb}}{\text{hr}} \quad (2)$$

Water evaporated by vapors from #1 concentrator:

$$48,077 \frac{\text{lb}}{\text{hr}} \left(\frac{0.8 \text{ lb vapor}}{1 \text{ lb-effect}} \right) 3\text{-effects} = 115,384 \text{ lb}$$

Total H₂O evaporation required on existing 1,000 TPD system, 15 to 25%:

$$125,000 \frac{\text{lb}}{\text{hr}} \left(\frac{1}{.15} - \frac{1}{.52} \right) = 592,948 \text{ lb}$$

Water to be evaporated by steam flow to first effect:

$$592,948 - 115,384 = 477,564 \frac{\text{lb}}{\text{hr}}$$

Steam flow to first effect:

$$477,564 \frac{\text{lb}}{\text{hr}} \left(\frac{1 \text{ lb steam}}{4.8 \text{ lb H}_2\text{O}} \right) = 99,493 \frac{\text{lb}}{\text{hr}} \quad (3)$$

The following calculations apply to the new evaporator and concentrator equipment, installed for 350 pulp TPD. They are ratio'd from existing 1,000 TPD equipment.

Steam flow to concentrator #2:

$$61,637 \frac{\text{lb}}{\text{hr}} \left(\frac{350 \text{ TPD}}{1,000 \text{ TPD}} \right) = 21,573 \frac{\text{lb}}{\text{hr}} \quad (4)$$

Steam flow to first effect:

$$99,493 \frac{\text{lb}}{\text{hr}} (0.350) = 34,822 \frac{\text{lb}}{\text{hr}} \quad (5)$$

(1), Total steam flow to the evaporation area is:

$$(2) + (3) + (4) + (5)$$

$$61,637 + 99,493 + 21,573 + 34,822 = 217,225 \frac{\text{lb}}{\text{hr}} \quad (1)$$

Power Consumption:

$$\left(125,000 \frac{\text{lb bls}}{\text{hr}} \right) \left(\frac{1,350 \text{ TPD}}{1,000 \text{ TPD}} \right) \left(\frac{1}{.15} - \frac{1}{.65} \right) \left(\frac{20 \text{ kw-hr}}{10^5 \text{ lb evaporation}} \right) = 170 \text{ kw-hr}$$

Power generated due to evaporation plant steam demand:

$$217,225 \frac{\text{lb}}{\text{hr}} \left(\frac{0.97 \text{ Turb. Exh.}}{1.0 \text{ Sat. Stm.}} \right) \left(\frac{1 \text{ kw-hr}}{22.67 \text{ lb}} \right) = \frac{9,295 \text{ kw-hr}}{\text{hr}}$$

Total heat to power and process:

Heat to power:

$$9,295 \text{ kw-hr} \left(\frac{3,414 \text{ BTU}}{\text{kw-hr}} \right) \left(\frac{1}{.98 \text{ eff.}} \right) = 32.38 \times \frac{10^6 \text{ BTU}}{\text{hr}}$$

Heat to process:

$$217,225 \frac{\text{lb}}{\text{hr}} (0.97) (1,197-257) \frac{\text{BTU}}{\text{lb}} = 198 \times \frac{10^6 \text{ BTU}}{\text{hr}}$$

Total:

$$198 + 32.38 = 230.5 \times \frac{10^6 \text{ BTU}}{\text{hr}}$$

Fuel, @ 80% boiler efficiency:

$$230.5 \times 10^6 \frac{1}{0.8} = 288.1 \times 10^6 \frac{\text{BTU}}{\text{hr}}$$

Calculate System with Mechanical Freeze Preevaporation (Figure 3-12)

NOTE: The MEE line & #1 concentrator are the existing evaporation plant.

Vapors from 1 and 2 concentrator will be same as calculated for conventional.
Steam flows to these units will also be the same.

$$\text{Steam to \#1 concentrator: } 61,637 \frac{\text{lb}}{\text{hr}} \quad (2)$$

$$\text{Steam to \#2 concentrator: } 21,573 \frac{\text{lb}}{\text{hr}} \quad (4)$$

Water to be evaporated by steam supply to the first effect:

Water evaporated by concentrator vapors:

$$\frac{\text{Due to \#1 concentrator}}{115,384 \frac{\text{lb}}{\text{hr}}} + \frac{\text{Due to \#2 concentrator}}{115,384 \frac{\text{lb}}{\text{hr}} \left(\frac{350}{1,000} \right)} = 155,768 \frac{\text{lb}}{\text{hr}}$$

Water removed to freeze unit:

$$168,750 \frac{\text{lb b1s}}{\text{hr}} \left(\frac{1}{.15} - \frac{1}{.25} \right) = 450,000 \frac{\text{lb}}{\text{hr}}$$

Total water removed between 15 to 52%:

$$168,750 \frac{\text{lb bls}}{\text{hr}} \left(\frac{1}{.15} - \frac{1}{.52} \right) = 800,480 \frac{\text{lb}}{\text{hr}}$$

Water evaporated due to first effect steam flow:

$$800,480 - 450,000 - 155,768 = 194,713 \frac{\text{lb}}{\text{hr}}$$

Steam flow to first effect:

$$194,713 \frac{\text{lb}}{\text{hr}} \left(\frac{1 \text{ lb steam}}{4.8 \text{ H}_2\text{O}} \right) = 40,565 \frac{\text{lb}}{\text{hr}} \quad (3)$$

∴ (1) Total steam flow to the evaporation area:

$$(2) + (3) + (4)$$

$$61,637 + 21,573 + 40,565 = 123,775 \frac{\text{lb}}{\text{hr}} \quad (1)$$

Power Consumption:

At freeze unit:

$$450,000 \frac{\text{lb}}{\text{hr}} \left(\frac{8.4 \times 10^{-3} \text{ kw-hr}}{\text{lb}} \right) = 3,780 \frac{\text{kw-hr}}{\text{hr}}$$

At Evaporation:

$$\left[168,750 \frac{\text{lb bls}}{\text{hr}} \left(\frac{1}{.15} - \frac{1}{.65} \right) - 450,000 \right] \left[\frac{20 \text{ kw-hr}}{10^5 \text{ lb-evap.}} \right] = 85 \text{ kw-hr}$$

Total power for concentration:

$$2,700 + 85 = 3,865 \frac{\text{kw-hr}}{\text{hr}}$$

Power generated due to evaporation plant steam demand:

$$123,775 \frac{\text{lb}}{\text{hr}} (0.97) \left(\frac{1 \text{ kw-hr}}{22.67} \right) = 5296 \frac{\text{kw-hr}}{\text{hr}}$$

Total heat to power process:

Heat to power:

$$5,296 \text{ kw-hr} \left(\frac{3,413 \text{ BTU}}{\text{kw-hr}} \right) \left(\frac{1}{0.98 \text{ eff.}} \right) = 18.45 \times \frac{10^6 \text{ BTU}}{\text{hr}}$$

Heat to process:

$$123,775 \frac{\text{lb}}{\text{hr}} (0.97) (1,197-257) \frac{\text{BTU}}{\text{lb}} = 112.86 \times \frac{10^6 \text{ BTU}}{\text{hr}}$$

Total:

$$112.86 + 18.45 = 131.31 \times \frac{10^6 \text{ BTU}}{\text{hr}}$$

Fuel @ 80% Efficiency:

$$131.31 \times 10^6 \left(\frac{1}{0.8} \right) = 164.1 \times 10^6 \frac{\text{BTU}}{\text{hr}}$$

Calculate System with Absorption Freeze Preconcentration (Figure 3-13)

Note: The MEE line and #1 concentrator are the existing evaporation plant.

- (1) Total steam flow to evaporator area will be the same as the mechanical refrigeration cases:

$$(2) + (3) + (4)$$

$$61,637 + 40,565 + 21,573 = 123,775 \frac{\text{lb steam}}{\text{hr}}$$

(1)

Power Consumption

At freeze unit (1 effect regeneration absorption from process comparisons, $\frac{27 \text{ kw-hr}}{10^3 \text{ gal.}}$)

$$450,000 \frac{\text{lb}}{\text{hr}} \left(\frac{27 \text{ kw-hr}}{10^3 \text{ gal.}} \right) \left(\frac{1 \text{ gal.}}{8.34 \text{ lb}} \right) = 1,470 \frac{\text{kw-hr}}{\text{hr}}$$

At Evaporators:

$$168,750 \frac{\text{lb bls}}{\text{hr}} \left(\frac{1}{.15} - \frac{1}{.65} \right) - 450,000 = 415,384 \frac{\text{lb}}{\text{hr}}$$

$$415,384 \frac{\text{lb}}{\text{hr}} \left(\frac{20 \text{ kw-hr}}{10^3 \text{ lb}} \right) = \frac{85 \text{ kw-hr}}{\text{hr}}$$

Total:

$$1,470 + 85 = 1,555 \frac{\text{kw-hr}}{\text{hr}}$$

Total Heat to Power and Process:

Power generation due to evaporation plant steam demand:

$$123,775 \frac{\text{lb}}{\text{hr}} (0.97) \left(\frac{1 \text{ kw-hr}}{22.67 \text{ lb}} \right) = 5,296 \frac{\text{kw-hr}}{\text{hr}}$$

Heat to power:

$$5,296 \text{ kw-hr} \left(\frac{3,413 \text{ BTU}}{\text{kw-hr}} \right) \left(\frac{1}{0.98} \right) = 18.45 \times \frac{10^6 \text{ BTU}}{\text{hr}}$$

Heat to process:

$$123,775 \frac{\text{lb}}{\text{hr}} (0.97) (1,197-257) \frac{\text{BTU}}{\text{hr}} = 112.86 \times \frac{10^6 \text{ BTU}}{\text{hr}}$$

Total:

$$112.86 + 18.45 = 131.31 \times \frac{10^6 \text{ BTU}}{\text{hr}}$$

Fuel @ 80% Efficiency:

$$131.31 \times 10^6 \left(\frac{1}{0.8} \right) = 164.1 \times \frac{10^6 \text{ BTU}}{\text{hr}}$$

Calculate System with Vapor Compression Evaporation Preconcentration (Figure 3-14)

Note: The MEE line and the #1 concentrator are the existing evaporation plant.

- (1) Total steam flow to evaporator area will be the same as the mechanical refrigeration case.

Power Consumption:

At vapor compression unit - 95 kw-hr/1000 gal:

$$450,000 \frac{\text{lb}}{\text{hr}} \left(\frac{95 \text{ kw-hr}}{10^3 \text{ gal}} \right) \left(\frac{1 \text{ gal.}}{8.34 \text{ lb}} \right) = 5,126 \frac{\text{kw-hr}}{\text{hr}}$$

Evaporator power demand - same as mechanical refrigeration case = 85 kw-hr

Total Power Consumed =

$$5,126 + 85 = 5,211 \frac{\text{kw-hr}}{\text{hr}}$$

Total heat to power and process - same as mechanical case

$$\text{Heat to power} = 18.45 \times \frac{10^6 \text{ BTU}}{\text{hr}}$$

$$\text{Heat to process} = 112.86 \times \frac{10^6 \text{ BTU}}{\text{hr}}$$

$$\text{Total} = 131.31 \times \frac{10^6 \text{ BTU}}{\text{hr}}$$

Total Fuel @ 80% Efficiency:

$$164.1 \times \frac{10^6 \text{ BTU}}{\text{hr}}$$

Capital and Energy Cost Comparisons

350 ton per day expansion of a 1,000 ton per day pulp mill. Costs do not take into account concentrator #2 which would be required with all processes. Base costs and scaling factors are discussed in previous sections of this chapter.

Base Case - Multi-Effect Evaporation

$$\text{Capital Cost} = \left(\frac{208,000 \frac{\#H_2O \text{ Evap.}}{hr}}{783,000 \frac{\#H_2O \text{ Evap.}}{hr}} \right)^{.65} \times \$5.8\text{MM} = \$2,450,000$$

Preevaporation

$$\text{Absorption Freezing} = \left(\frac{450,000}{116,000} \right)^{.65} \times \$1.7\text{MM} = \$4,100,000$$

$$\text{Mechanical Freezing} = \left(\frac{450,000}{116,000} \right)^{.65} \times \$1.4\text{MM} = \$3,380,000$$

$$\text{Vapor Compression} = \left(\frac{450,000}{300,000} \right)^{.65} \times \$3.5\text{MM} = \$4,500,000$$

Pay Out Periods - The pay out period in years is given by:

$$\text{Pay Out} = \frac{\text{Cost of Alternative Expansion} - \text{Cost of Base Case Evap.}}{\text{Energy Savings per Year}}$$

$$\text{Absorption Freezing} = \frac{\$4,100,000 - \$2,450,000}{\$1,899,200/\text{yr}} = 0.87 \text{ years}$$

$$\text{Mechanical Freezing} = \frac{\$3,380,000 - \$2,450,000}{\$1,653,200/\text{yr}} = 0.56 \text{ years}$$

$$\text{Vapor Compression} = \frac{\$4,560,000 - \$2,450,000}{\$1,168,000/\text{yr}} = 1.80 \text{ years}$$

Energy requirements, costs, savings and economic summaries are shown in Tables 3-7, 3-8 and 3-9.

National Impact of Fuel Savings

For a 350 ton/day pulp mill expansion using an absorption freezing plant operating on low level waste heat. 8,000 operating hours per year.

TABLE 3-7

EXPANSION CASE ENERGY SAVINGS

BASIS: 150 Ton/Day Expansion of 1000 ton/day Mill
 Black Liquor Concentration is from 15 to 65%
 8,000 hours/year
 \$3.00/10⁶ BTU Fuel Cost

	1	2	3	4	5	6	7	8	9	10	11	12
	FUEL DEMAND BTU/hr	COGENERAT. POWER PRODUCED BTU/hr	POWER REQUIRED FOR CONC. BTU/hr	NET FUEL DEMAND BTU/hr 1-2+3	NET YEARLY FUEL DEMAND BTU/yr	FUEL SAV. OVER BASE CASE BTU/yr	COST OF NET YR. FUEL DEMAND \$/YEAR	YR. CCST SAV. CVER BASE CASE \$/YEAR	UTILITY CONDENSER POWER DISPLACED BTU/hr 2-3	UTILITY FUEL DISPLACED BTU/hr 10,000 BTU/ kw-hr	NET SYS. FUEL IMPACT BTU/hr	NET SYS. YR. FUEL SAVINGS BTU/yr
BASE CASE - Expansion with multiple effect evaporation												
Base Case	288.1x10 ⁶	32.38x10 ⁶	.59x10 ⁶	256.3x10 ⁶	2.05x10 ¹²	-	6,150,000	-	31.79x10 ⁶	93.12x10 ⁶	194.98x10 ⁶	-
CASE I - Expansion with Freeevaporation												
Absorption Freezing	164.1x10 ⁶	18.45x10 ⁶	5.4x10 ⁶	151.1x10 ⁶	1.21x10 ¹²	.84x10 ¹²	3,625,000	2,525,000	13.05x10 ⁶	38.22x10 ⁶	125.88x10 ⁶	0.55x10 ¹²
Mechanical Freezing	164.1x10 ⁶	18.45x10 ⁶	13.2x10 ⁶	158.9x10 ⁶	1.27x10 ¹²	.78x10 ¹²	3,810,000	2,340,000	5.25x10 ⁶	15.38x10 ⁶	148.72x10 ⁶	0.37x10 ¹²
Vapor Compression	164.1x10 ⁶	18.45x10 ⁶	18.2x10 ⁶	163.9x10 ⁶	1.31x10 ¹²	.74x10 ¹²	3,930,000	2,220,000	.25x10 ⁶	.73x10 ⁶	163.67x10 ⁶	0.25x10 ¹²

TABLE 3-8

EXPANSION CASE ECONOMICS OF ENERGY SAVINGS

BASIS: 350 Ton/Day Expansion of 1000 ton/day Mill
 Black Liquor Concentration is from 15 to 65%
 8,000 Hours/Year

	1	2	3	4	5
	FUEL DEMAND @\$3.00/10 ⁶ BTU \$/YEAR	COGENERATED POWER PRODUCED CREDIT @ \$.025/kw-hr \$/YEAR	POWER REQUIRED FOR CONCENTRATION @\$0.025/kw-hr \$/YEAR	YEARLY ENERGY COST \$/YEAR 1-2 + 3	YEARLY COST SAVINGS OVER BASE COST \$/YEAR
BASE CASE - Expansion with multiple effect evaporator	6,914,400	1,857,000	34,000	5,089,400	-
CASE I - Expansion with preevaporation					
Absorption Freezing	3,938,400	1,059,200	311,000	3,190,200	1,899,200
Mechanical Freezing	3,938,400	1,059,200	557,000	3,436,200	1,653,200
Vapor Compression	3,938,400	1,059,200	1,042,200	3,921,400	1,168,000

TABLE 3-9
BLACK LIQUOR CONCENTRATION EXPANSION CASE SUMMARY

	<u>BASE CASE CURRENT PRACTICE</u>	<u>ABSORPTION FREEZING w/ WASTE HEAT</u>	<u>MECHANICAL FREEZING</u>	<u>VAPOR COMPRESSION EVAPORATOR</u>
Net System Fuel Demand - BTU's/hr	194.98x10 ⁶	125.88x10 ⁶	148.72x10 ⁶	163.67x10 ⁶
Net System Yearly Fuel Savings - BTU's/yr	-	.55x10 ¹²	.37x10 ¹²	.25x10 ¹²
Net System Yearly Fuel Savings - Barrels of Oil/yr	-	9.8x10 ⁴	6.6 x10 ⁴	4.5x10 ⁴
Yearly Energy Costs - Electricity at \$.025/kw-hr + Fuel @\$3.00/ 10 ⁶ BTU's	\$5,089,400	\$3,190,200	\$3,436,200	\$3,921,400
Yearly Energy Savings - Electricity Cost = \$.025/kw-hr, Fuel Cost = \$3.00/10 ⁶ BTU's	-	\$1,899,200	\$1,653,200	\$1,168,000
Expansion Capital Cost	\$2,450,000	\$4,100,000	\$3,380,000	\$4,560,000

Yearly fuel savings over expanding with multi-effect evaporation:

$$= \frac{.55 \times 10^{12} \text{ BTU's/Year/350 ton per day expansion}}{5.6 \times 10^6 \text{ BTU's/barrels of fuel oil}} =$$

$$0.098 \times 10^6 \text{ barrels of oil/year}$$

or

$$\frac{0.98 \times 10^6 \text{ barrels of oil/year}}{350 \text{ tons/day} \times 333.3 \text{ days/year}} = .84 \text{ barrels of oil/ton of pulp}$$

Since the industry is expanding at approximately 1,000,000 tons/year, using absorption freezing black liquor concentration to expand pulp production would save 840,000 barrels of oil each year. Extrapolated 21 years to the year 2000, this would mean a savings of 17,640,000 barrels of oil a year in the year 2000 if absorption freezing were used for black liquor preevaporation instead of multi-effect evaporation. If freeze concentration technology could be developed to achieve higher concentrations than the 25% assumed in this study, the energy savings would be even greater.

SPECIALIZED BLACK LIQUOR CONCENTRATION APPLICATIONS

BLACK LIQUOR SPILLS

One of the most interesting near term applications of the freeze concentration of black liquor is black liquor spills. Currently the spills from the digesters and other portions of the pulping and concentrating process are cleaned up by washing the spill area with water and sewerage the discharge to the waste treatment system. The washing dilutes the black liquor from 15% to approximately 6%. In spite of the relatively low volume and dilution of these wastes, they are high in BOD content and contribute a significant loading and cost to the waste disposal system. In addition the fuel value in the black liquor, if concentrated and burned as in conventional practice, is lost.

Figure 3-15 describes this application and shows comparable costs of freezing and multi-effect evaporation for concentrating 60,000 gallons per day of black liquor spills from 6% to 30% and then putting the concentrate into the current evaporator train. To put this flow into perspective, the feed flow of black liquor to the evaporator train of a 1,000 ton per day mill is over 2,300,000 gallons per day.

FIGURE 3-15

BLACK LIQUOR SPILLS

6% to 30% Concentration

60,000 gallons/day (20,825 #/hr)

Feed Capacity

Ambient Temperature

<u>COSTS</u>	<u>WASTE HEAT ABSORPTION FREEZING</u>	<u>6-EFFECT EVAPORATOR</u>
Evaporation Rate	16,600 #/hr	16,600 #/hr.
Steam @650 psia-700°F	0	4.71x10 ⁶ BTU's/hr.
Steam - Waste Heat 160°F	No Cost	-
Electricity	55 KW	25 KW

○

OPERATING COSTS/HR.

Steam @ \$2.76/10 ⁶ BTU	Waste Heat	\$13.00
Electricity @ \$.025	\$1.38	\$ 0.63

OPERATING COSTS/YR. - 8000 HRS/YR

Steam	Waste Heat	\$104,000
Electricity	<u>\$11,040</u>	<u>5,040</u>
	\$11,040	\$109,040

○

If absorption freezing using waste heat as an energy source were used to concentrate a 60,000 GPD spill stream, the following shows the recoverable fuel value:

Cost of 6% to 30% concentration - see Figure 3-15 \$11,040

Cost of concentration in present system - 30%-60%

= Water Evaporated x Cost

$$= 2082 \frac{\# \text{ Water Evaporated}}{\text{hr}} \times \frac{283 \text{ BTU's}}{\# \text{ Water Evap.}} \times \$3.00/10^6 \text{ BTU's}$$

$$\times 8,000 \text{ hrs.} = \frac{14,140}{\$25,180}$$

TOTAL ENERGY COSTS

$$\frac{14,140}{\$25,180}$$

This energy expense would return a fuel value of:

$$\text{Fuel Value} = \# \text{ Solids} \times \frac{6,600 \text{ BTU's}}{\# \text{ Solids}}$$

$$= 2082 \frac{\# \text{ Concentrate}}{\text{hr}} \times 60\% \times \frac{6,600 \text{ BTU's}}{\# \text{ Solids}} \times$$

$$\$3.00/10^6 \text{ BTU's} \times 8,000 \text{ hrs} = \$197,873$$

This says that a freezing process would return approximately \$173,000/year in increased fuel value for a system that would cost between \$500,000 to \$600,000 for a fully developed freezing system. This return makes no allowances for values accrued because of additional chemical recovery or reduction in pollution control costs, both of which would account for significant additional savings.

The concentration of black liquor spills could make an ideal first demonstration project for using freezing technology for black liquor prior to its adoption for full process adaptation. The size of the black liquor spill streams are small enough so that the capacity of freezing plant required is within the demonstrated technology for the desalination of sea water. Also, the spills are not critical to the main production of pulp. Since the streams are currently sewered, if a developmental problem occurred, as would be expected with a first of a kind plant, the wastes would be returned when necessary to the sewer until fully reliable operation was obtained. This could not be tolerated in the main production line, but such an application would serve as a model demonstration for a larger black liquor concentration. The application would also help economically solve a major pollution contribution to the industry. The final argument is that the application itself can show a positive payback in fuel, chemical and pollution control savings.

ULTRA HIGH CONCENTRATION OF BLACK LIQUOR

One extremely interesting new development we heard about in our discussions with industry people was strong interest in concentrating black liquor to very high concentrations (90% and above) in order to reduce the size and complexities of the furnace. Going to high concentrations could also decrease overall energy consumption by increasing the heating value of the concentrate by the removal of more water and by the more efficient use of steam.

The major problem in going to high concentrations is that the liquor becomes very tar-like and achieving acceptable heat transfer rates becomes exceedingly difficult. There is some evidence that scraped surface evaporators operating with high temperature steam can concentrate black liquor to these levels. As explained previously, freeze processes cannot be used at these concentrations, but an absorption freezing process operating on low level waste heat used as a preconcentrator to the evaporators would significantly improve the economics of the process. Because of the experimental nature of this application, no precise calculations were made for this application. However, approximate calculations indicate significant energy savings, but not as great as those accruing from the expansion case. Figure 3-16 shows how such a process could be arranged to minimize steam consumption by staging the concentration processes.

FIGURE 3-16

ULTRA HIGH CONCENTRATION OF BLACK LIQUOR

SK-1114

TECHNOLOGY TRANSFER

The preceeding sections show that if freeze crystallization was in widespread use for the concentration of black liquor in pulp mills, it would effect a significant energy saving large enough to have a national impact. The question remaining is how to develop this technology and put it into widespread use. As part of this study we had in-depth conversations with the personnel of several paper companies to discuss technology transfer. The companies contacted include:

Cheasapeake Corp.
ITT Rayonier, Inc.
St. Regis Paper Co.
Scott Paper Co.
Sonoco Products Co.
Weyerhaeuser Co.

A presentation to a regional meeting of the National Council
for Air and Stream Improvement

The comments and knowledge gained from these meetings contributed greatly to the details of this report, but basically their comments can be summarized: If freeze crystallization were a developed and demonstrated technology, the pulp and paper industry couldn't afford not to look at it for black liquor concentration and other applications. The savings appear significant, but the risks and costs are too great for a private company to undertake. There need to be operating plants in the industry before widespread use of the technology.

Concentration Specialists, Inc. believes that a long range, well thought out program supported by the Department of Energy can transfer this technology from its present developmental status into widespread use in the industry. The program is long range and would move slowly at first until there were one or two commercial installations, but proven installations would encourage widespread use.

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- ⁷ Perry, R. H. Editor, Chemical Engineers Handbook, 5th Edition, McGraw-Hill Book Company, New York, 1973.
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- ¹⁰ —, "Vapor Recompression" in Goslin Evaporators and Crystallizers, 11/75/5M, p. 8
- ¹¹ Dev, L. and P. W. Kelso, "Steam Stripping of Kraft Mill Condensate", CEP, Vol. 74, No. 1 January 1978, p. 72.
- ¹² Personal communication with L. Dev and P. W. Kelso, Weyerhaeuser Co.
- ¹³ Hugh and Sallec, TAPPI, Vol. 60, No. 2, February 1977, p. 83.

CHAPTER 4

ACETIC ACID RECOVERY

INDUSTRY PROFILE

CAPACITY

Acetic acid production in the United States is approximately 2.4 billion pounds per year (1976). There are fourteen producing companies with approximately 30 plant-sites. The largest plants have capacities up to 600 million pounds per year but the majority are in the 50 to 200 million pound per year range. This market grew at a 10% per year rate in the early 1960's but has grown at only half that rate in the last decade.

Most of the acetic acid is produced by three reaction routes: oxidation of acetaldehyde, oxidation of C₄ paraffins or olefins, and the reaction of methanol and carbon monoxide. At least three plants recover acetic acid as a by-product of other operations; from peracetic acid production, from glycerine production, and from neutral sulfite semi-chemical pulping operations. No facilities produce acetic from the destructive distillation of wood, once the predominant route. Recent worldwide trends have been toward the methanol-carbonylation process; it is very selective, has good conversion efficiency, and is much more energy conservative than the other processes.

The national demand for acetic acid could probably be met by recovering that in chemical industry waste streams. Numerous partial oxidation processes produce acetic acid by-product that is scrubbed from the system producing a weak aqueous waste (e.g., the reactions of isobutylene to methacrylic acid and xylene to terephthalic acid both produce aqueous 1 to 3% acetic acid waste streams). Similar waste streams result from the water bath used to produce synthetic fibers when the polymer solvent is acetic acid. No economical method for recovery of this waste acetic acid has yet been demonstrated; economic studies indicate, however, that preconcentration of these weak solutions by freeze separation followed by recovery in the freeze refining system described later in this chapter, can economically recover the acid from the waste streams.

PROCESSES

Two of the acetic acid processes were chosen for detailed investigation in this program:

- o Vapor phase acetaldehyde oxidation, and
- o Methanol carbonylation.

The acetaldehyde process was developed in the 1940's and was predominantly used in the industry until the methanol carbonylation process was introduced. The latter has become the predominant process in the 1970's. Methanol carbonylation has significant advantages including good selectivity and conversion, a crude acid that is relatively pure and therefore easy to refine, relatively low energy consumption, and low-cost raw materials. Predictably, nearly all of the new plants in the last decade have used this technology. The older acetaldehyde process plants will continue to compete because of the low fixed costs of already depreciated facilities.

Butane-butylene-naptha oxidation was not considered beyond initial evaluations for several reasons:

- o The process has poor selectivity, converting only half of the reactants to acetic acid and producing some fifty by-products, five of which are major.
- o The crude acetic acid refinery includes extensive systems for separating the other by-products, making any apportionment of energy between the products arbitrary, at best. (The value of the by-products makes this route economical.)
- o There are relatively few of these plants with little available information.
- o The unit energy consumption probably is greater than that of the methanol process but less than that of the acetaldehyde process. Therefore, economics indicated for the latter two should bracket the economics of a butane oxidation freeze refinery and the decision was made to study only the former two.

Process descriptions of the three production routes and the subsequent refining system follow in a succeeding section. Energy consumption in the refining systems for the acetaldehyde and methanol processes is discussed in the following paragraphs.

ENERGY ANALYSES

Conventional Systems

The methanol-carbonylation and acetaldehyde derived crude acid streams represent, respectively, the least and most energy efficient refining needs of the production routes; the butane-butene-naptha derived acids require energy consumption for refining somewhere between these lower and upper limits. By-product acetic acid recovery processes are small, some requiring energy on the low end of the spectrum, others using as much as in the acetaldehyde-derived crude acid refining case. The by-product processes are a very small portion of the industry so were not studied because of the complexities cited earlier.

Energy consumption of the refining sections of the acetaldehyde and methanol derived crude acids is summarized in Table 4-1. These are crude estimates and the numbers can vary significantly between plants. Based on numerous discussions with various industry groups we feel that these values are representative of most facilities. They are also in general agreement with energy consumption values published elsewhere. The energy consumption is broken down, in Table 4-1, into that used in specific areas of the conventional distillation refinery. A detailed description of the individual columns in the refineries is given below in the section entitled Acetic Acid Refining.

Freeze Refineries

Process descriptions of the freeze refineries are also given below. The energy consumption of these processes is summarized in Table 4-2. The salient difference between the freeze separation processes designed to purify the acetic acid from the two reaction routes is the need for water removal from the crude produced from acetaldehyde. Where the crude acid contains over 40% water there is a preliminary freeze dehydration step and then acetic acid is crystallized at the eutectic with simultaneous ice production. Crude from the methanol process, containing little water or impurities, is crystallized without any simultaneous co-precipitation, lowering energy consumption and equipment size. These details are explained more fully later.

ACETIC ACID REFINING

The three major routes to acetic acid produce quite different crude acid qualities that require totally different refining processes. Because of this diversity in refining requirements it is necessary to look at each as a totally separate application. As explained earlier the production routes studied in detail in this program were the acetaldehyde and methanol-carbonylation processes as they represent, respectively, the most and least energy-consumption refining requirements. A preliminary freeze refining process was defined for a generic butane-butene-naptha oxidation route to acetic acid and some comparisons to the freeze refineries for the other routes are made. To minimize confusion, the alternative conventional and freeze separation systems for crude acid refining are presented together for each of the production routes.

TABLE 4-1

CONVENTIONAL ACETIC ACID
REFINING ENERGY CONSUMPTION

<u>REFINING STEP</u>	<u>REACTION ROUTE</u>		
	<u>METHANOL- CARBONYLATION (BTU/lb HAc)</u>	<u>VAPOR PHASE ACETALDEHYDE OXIDATION (BTU/lb HAc)</u>	<u>OTHER PROCESSES (BTU/lb HAc)</u>
1. Water Removal (Azeotropic Distillation)	-	6,550	
2. Light By-Product Removal	50	150	
3. Acetaldehyde Recycle	-	100	
4. Catalyst Recovery	450	-	
5. Formic Acid Removal (Azeotropic Distillation)	100	1,000	
6. Refining Column	750	1,000	
7. Pumping (equiv. BTU's at 10,000 BTU/KW-HR)	10	20	
	<hr/> 1,360	<hr/> 8,820	5,100
o Equivalent Oil Use Per 100 Million Pound Per Year Plant, BBL	24,300	151,500	91,000
o Production From Each Process Route			
- 1976 Production 10 ⁶ lb/yr	684	338	1,378
- Energy Consumption BBL/yr	166,212	532,350	1,253,980
10 ¹² BTU/yr	0.931	2.981	7.022

1 BBL = 5.6 x 10⁶ BTU

TABLE 4-2

ACETIC ACID REFINING
ENERGY SUMMARY

	<u>METHANOL CARBONYLATION</u>	<u>VAPOR PHASE ACETALDEHYDE OXIDATION</u>
	(BTU per pound of product)	
1. Conventional Refining		
Column 1 - Water Azeotrope	-	6,550
Column 2 - Lights Removal	50	150
Column 3 - Acetaldehyde Removal	-	100
Column 4 - Catalyst Recovery	450	-
Column 5 - Formic Azeotrope Column	100	1,000
Column 6 - Refining Column	750	1,000
Pumps, KW-HR/#	.0012	.002
TOTAL (EQUIV. BTU/#)	1,360	8,820
2. Freeze Refining	(HP for 100 MM lb/yr plant)	
Compression Stage		
No. 1 (-45°F)	5.	9.
No. 2 (-25°F)	83.	168.
No. 3 (0°F)	-	478.
No. 4 (40°F)	-	100.
Heat Reject. (70°F)	8.	13.
Pumps	11.	85
TOTAL HP	107.	853.
TOTAL (EQUIV. BTU/#)	65.	500.
3. Energy Savings by Freezing		
BTU Per Pound	1,295	8,320
% Refining Energy Consumption Decrease	95%	94%

Capital costs for the conventional distillation processes were not developed in detail; estimates derived from the literature are presented. If the economics of the freeze refining alternative were such that it could compete only on new installations then an accurate analysis of the difference in capital cost would be important. As will be shown below, the economics of freeze refining provide an adequate return-on-investment even where the freeze process would replace an existing fractional distillation refinery; the justification is based totally on energy savings. So, justification for freezing in new installations does not require any consideration of alternative capital costs; they are, however, presented here as a point of comparison.

The economic summaries presented below (Table 4-3) are developed more fully in the succeeding paragraphs. The cost estimating logic and sources of raw data for capital costs are explained in Chapter 2. The operating costs were limited to comparisons of energy costs, the unit values adopted being also explained in Chapter 2. Other O&M costs were assumed equal for the distillation and freezing separation systems.

ACETALDEHYDE OXIDATION

Conventional Refining Technology

This vapor-phase process for producing acetic acid has seen widespread use for nearly four decades and was the first major synthetic process. It is widely used with a capacity in this country up to 650 million lbs/yr. Liquid-phase acetaldehyde oxidation uses less energy and is not detailed in this report. Liquid acetaldehyde is added to recycled crude acid and reacted with air at 80°C and 10 atm. The fraction of acetaldehyde in the feed is about .2 with conversions of 90% and selectivities of 90 to 95%. The chief impurities are formaldehyde and formic acid, but alcohols and ketones are also formed. In fact, sufficient methanol is formed to justify recovery of methyl acetate as shown in the refinery process diagram, Figure 4-1.

A typical refinery is depicted in this diagram. Two streams out of the reactor require treatment for acetic acid recovery. The inerts in the air stream pass through the reactor carrying the unreacted acetaldehyde, acetic acid and some other trace vapors. The bulk of the product is in the liquid stream out of the reactor; catalyst, some acetaldehyde, and by-products are also in this stream.

TABLE 4-3

REFINING ECONOMICS SUMMARY

BASIS: 100 million lb/yr product
 8,000 hours per year operation
 \$3.50/10⁶ BTU steam cost
 \$.04/kw-hr electrical energy cost

	ACETALDEHYDE OXIDATION (30% Acid-70% Water)	METHANOL- CARBONYLATION (98% Conv.-96% Select.)	BUTANE-BUTENE-NAPHTHA OXIDATION (50% Acid-10% Water, 40% Impurities)
CAPITAL COSTS			
- Fractional Dist'n. Refin.	\$3,500,000	\$3,250,000	\$4,000,000
- Freeze Refinery	2,100,000	900,000	900,000
- Difference	1,400,000	2,350,000	3,100,000

	AMOUNT	\$ VALUE/YR	AMOUNT	\$ VALUE/YR
ENERGY COSTS - CONSUMPTION				
- Distillation				
o Steam, BTU/# Acid	8,820	\$3,087,000	1,360	\$476,000
o Electricity kw-hr/# Acid	.002	8,000	.0012	5,000
- Freeze Crystallization				
o Electricity kw-hr/# Acid	.050	201,000	.0127	51,000
<hr/>				
SAVINGS	8,170 BTU/\$	\$2,894,000/yr	1,245 BTU/#	430,000/yr

PROCESS FLOW DIAGRAM
ACETIC ACID RECOVERY
ACETALDEHYDE ROUTE

FIGURE 4-1 7004-2007

The vapor stream is scrubbed, first with acetic acid and then with water, to remove the organics from the inert gases. Apparently some plants have a pretreatment stage that uses cooling water in an indirect contact partial condenser to reduce the water required for scrubbing. The acetic acid used for scrubbing is crude acid from the reactor and is either returned to the reactor or sent to the acetaldehyde recovery section. The scrubber water stream goes to the refining section for recovery of the scrubbed acid.

The liquid stream out of the reactor is stripped of unreacted acetaldehyde and then mixed with the scrubber water stream noted above for refining. The first step in refining is a light by-product removal step. A second step of lights removal is often used to recover a refined methyl acetate. Water can be removed either before or after light materials stripping. It is always taken out azeotropically as the volatility of the water-acetic acid stream precludes direct separation. The azeotroping agent can be either the by-product ethyl acetate or a more suited material added to the process. If ethyl acetate is used the water in the heavy phase from condensing the vapors overhead has to be stripped; ethyl acetate is soluble at about 8% in the water. The acetic acid can be refined in the dehydration column, taken off as a side-stream, or removed in a separate column. The bottoms out of the refining column contains the heavy by-product as well as the catalyst (a heavy metal salt). The catalyst is recovered in a liquid extraction step; a two-phase water aromatic stream is the extractant. The organics dissolve in the aromatic phase while the catalyst is preferentially absorbed by the water. The two phases are then decanted and the water-catalyst stream is returned to the reactor.

Formic acid formed as a by-product also has nearly the same volatility as the acetic acid. It is either removed in a separate azeotropic column or oxidized by the addition of potassium permanganate in the refining column.

Freeze Refining

Process Description - The size, cost and efficiency of the freeze refining process is greatly affected by the water content of the crude acid. Since the water-acetic acid eutectic composition is at 59 weight percent acid, any crude that is more dilute will require an initial stage of dehydration to concentrate to the eutectic. The dehydration step could occur in the eutectic freezing stage if the crude acid had 50 to 55 weight percent acetic acid or above.

In our conversations with the acetic acid industry we got reports of acids containing from 30% to over 70% acid (conversely, 70% to less than 30% water). The freeze refining process was designed for flexibility in giving energy consumption and cost analysis for all of the cases encountered. The general process is shown in Figures 4-2 and 4-3 and can best be understood by reference to the binary acetic acid-water phase diagram, Figure 4-4. This process

CONCENTRATION SPECIALISTS, INC.
ANDOVER, MASS.

SCALE: NONE	APPROVED BY	DRAWN BY JIP
DATE: 10-10-78		
FLOW DIAGRAM ACETIC ACID FREEZE REFINERY (ACETALDEHYDE OXIDATION REACTION PROCESS)		
DRAWING NUMBER		7004-2001

FIGURE 4-2

WATER-ACETIC ACID
PHASE DIAGRAM

FIGURE 4 - 4

NOTES

1) DATA SOURCE, INT'L
CRITICAL TABLES
1929, MCGRAW HILL

7004-1002

can refine the most dilute (30%) acetic acid, or by leaving off the first one or two dehydration stages is directly applicable to the higher concentration cases. This system was designed for a 30% acid feed that is concentrated to 39% in the first stage and then to just below the eutectic (59%) in the second stage. The third stage is a eutectic separator, simultaneously producing acetic acid crystals and ice. The achievable recovery of acetic acid in Stage 3 is limited by the build-up of impurities and the resulting freezing point depression. The total impurities at this point are about 40% of the flow. The fourth stage recovers more of the acetic acid from the impurities before they are finally purged from the system. The high level of impurities results in much lower temperatures in this stage than in the third. It was added to maintain good overall recovery of acid from the crude while not penalizing Stage 3 (relatively large capacity) with high refrigerant-compressor power. Values of power consumption for the freeze refining processes discussed below were developed on a per-stage basis so that any portion of this 4-Stage refining process can be used separately to meet the requirements of the several applications we have encountered.

Some recycle is required at various stages in the process, as shown in the flow diagram. Brine from the crystal slurry in the wash columns is recycled to the freezer as required to meet the specified recovery in each stage. The heat exchangers employed as freezers require that the circulating brine has a relatively large crystal fraction, so a crystal slurry recycle is employed. Interstage recycling is also required in the latter stages. The concentration of impurities and acetic acid inhibits the growth of the ice crystals so that they are difficult to drain or wash in a wash column. Therefore these ice crystals are separated in the eutectic separators and slurried back into the second stage where they are grown to sufficient size under better growth conditions and removed from the system in the wash column. No recycle lines were added for acetic acid because we feel that its crystal growth characteristics will be far superior to that of ice and will not require any recycle.

The refrigeration system is shown in Figure 4-5. It derives from the binary water-acetic acid phase diagram, at least in the middle stages of compression. The first two freezer stages operate with what is in essence a water-acetic acid solution. The operating temperatures for ice crystallization in the first two stages are derived directly from the binary phase diagram: at 40% acid the freezing point is +7°F and at 59% acid the freezer operates at -15°F. Operating temperatures in Stages 3 and 4 are more complicated to predict due to the effects of the impurities. We have assumed that the impurities induce a 5 F° freezing point depression of the eutectic in Stage 3 and that, at their higher concentrations, they depress the freezing point 25 F° in Stage 4.

The system is controlled to give specified temperatures in each of the freezers which in turn sets the concentrations of the major components leaving the freezer. Similarly, control of the wash columns is based on the temperature of the melt slurry; since quality of the final product is defined by its freezing point this control mode is especially meaningful.

Energy Consumption - The energy requirements for the 4-Stage refining process is summarized in Table 4-4. The table is structured to show the effect of the water in a 30% acetic acid in water solution. The feed pump is required regardless of the initial concentration and Stages 3 and 4 are relatively insensitive to the initial water content as they operate at the eutectic and are determined mainly by plant capacity. Stages 1 and 2 are required only for dehydration of the crude acid to the eutectic and thus would not be required if the crude acid arrived at 60% or higher concentration; Stage 1 would be eliminated if the crude feed was over 40% acid.

Energy consumption for crude streams starting with concentrations greater than 30% can be estimated from Table 4-4. Its use is best explained by an example, say a stream of 60% acid. Since this is very near the eutectic, the first two dehydration stages would not be used. The corresponding compression stages would not be totally eliminated since they were used both to compress the refrigerant from the lower-temperature stages as well as to provide the refrigeration for the dehydration freezers. The compressor power can be estimated from the refrigerant flow analysis provided in the second and third columns. The first stage compressor still sees the same flow but the second stage no longer has the load from Freezer Stage 2 and its load is reduced by the 76 hp. Similarly, the third stage compressor now only sees the refrigerant load from freezers 3 and 4 and its power requirement is reduced accordingly. The refrigerant load to compressor Stages 4 and 5 is that representing the refrigerant load to freeze the acetic acid plus that needed to carry heat added by inefficiencies out of the system. As a conservative measure these can be left unadjusted; this assumes that there is as much inefficient work put into the system as before, even though compressor Stages 2 and 3 are now much smaller. The feed pump and water melter recirculation pumps need to be adjusted for the reduced flows as well.

The significance of Table 4-4 is to show the energy required in dehydrating a 30% acid to its eutectic concentration. Over half of the energy is used to remove the water. The results of the table, using the procedure illustrated above, can be used to calculate the energy requirements for refining other strengths of acetic acid.

TABLE 4-4
ENERGY SUMMARY
ACETIC ACID FREEZE REFINERY - Acetaldehyde Route

	30% ACETIC ACID CRUDE		60% CRUDE ACETIC ACID
	POWER LOAD HP	REFRIGERANT FLOW TOTAL (lb/hr)	REFRIGERANT FLOW PREVIOUS STAGE (lb/hr)
1. COMMON EQUIPMENT			
o Feed Pump	3.75		2.0
o Heat Reject Compressor (Stage 5)	13.	518	13.
o Acetic Acid Melt Comp. (Stage 4)	101.	3,345	101.
o Acid Melt Circ'n. Pump	9.5	-	9.5
o Water Melt Circ'n. Pump	34.25	-	9.75
SUBTOTAL	<u>161.50</u>		<u>135.25</u>
2. FREEZER STAGE 4			
o Compressor Stage 1	8.75	367	8.75
o Circulation Pump	2.0		2.0
SUBTOTAL	<u>10.75</u>		<u>10.75</u>
3. FREEZER STAGE 3			
o Compressor Stage 2 (Partial)	92.0	3,920	92.0
o Circulation Pump	5.75		5.75
SUBTOTAL	<u>97.75</u>		<u>97.75</u>
4. FREEZER STAGE 2			
o Compressor Stage 2 (Partial)	76.25	6,184	0
o Circulation Pump	14.5		0
SUBTOTAL	<u>90.75</u>		<u>0</u>
5. FREEZER STAGE 1			
o Compressor Stage 3	478.	11,079	169.
o Circulation Pump	6.0		-
SUBTOTAL	<u>484.0</u>		<u>169.</u>
TOTAL	<u>849.</u>		<u>412.75</u>

Engineering Package - The summary of the engineering design activities for the freeze refinery is summarized in the following tables:

- o Table 4-5 - Major Equipment Lists
- o Table 4-6 - Pump List
- o Table 4-7 - Line Index

The tables are quite illustrative of the process and when used with the Flow Sheet and P&ID, define the four stage refining process developed in this project. The methods used to develop the package and some of the intermediate results that led to the final system definition are covered in the following paragraphs.

Energy Requirements

Recycle requirements were determined in the mass balance based on criteria for crystal concentration in the feed to the wash columns and in the recycle plus make-up flow into each freezing stage. The crystal concentration out of the freezer was set at 15%; the necessary quantity flows to the wash column to remove the product from that stage while the rest is recycled with the crystal-less feed and wash column brine. The quantity of crystals recycled was set to give a mixed stream with $7\frac{1}{2}\%$ crystals. The recycle from the wash column and freezer determine, with pressure drops through the freezer and wash column, the power requirements of the recycle pump. The pumping power heat is added to the flowing stream and, together with a heat gain from ambient, represent an added load on the corresponding refrigeration stages. Latent and sensible heat loads were calculated from the mass balances and together with this additional load formed the basis for sizing the refrigeration system.

Heat Transfer (Freezor and Melter/Condenser Sizing)

All tubes in the freezers and melters were assumed stainless steel. Properties of the solutions and refrigeratants were calculated if necessary or derived from the literature. The necessary properties were those involved in the Reynold's and Prandtl dimensionless equations. In all cases except the feed heat exchanger the shell side material is boiling or condensing refrigerant (ammonia). Process fluids - concentrated crude, product acetic acid, or pure water - are always the fluids on the tube side. Crystal slurries at high turbulence are involved so that fouling factors are low on the tube side. Using these properties the overall heat transfer coefficients shown in Table 4-8 were calculated.

When the freezers were sized an additional 20% of area was added to each. Eight pass exchangers were chosen to minimize the passes that the slurry would make through the pump. When the 20%-excess-

TABLE 4-5
MAJOR EQUIPMENT LIST
ACETIC ACID FREEZE REFINERY
Acetaldehyde Route

1. FEED HEAT EXCHANGER

- o FE-1
316-L stainless, plate & frame,
2 fluid (product acetic acid
& feed).
- o FE-2A
316-L stainless, plate & frame,
3 fluid (water, concentrate &
feed).
- o FE-2B
316-L stainless, plate & frame
2 fluid (concentrate & feed).

2. FREEZER #1

- o Shell & tube heat exchanger,
8-pass, 3284 ft.², 88 tubes per
pass, 1" $\emptyset$ x 20' long 316-L S.S.
tubes, sheets & head, CS shell
operating pres. = 30 psia,
vessel rating = 300 psia.
42-46" $\emptyset$ shell.
 - o Circulation pump, 316 S.S.,
pumping 8% slurry of ice and
concentrate. 215 gpm at 25 psi
head, 7.5 hp motor.
- Wash column, 32 ft.² (6.5 ft. $\emptyset$,
coated carbon steel vessel.
15 ft. tall, scraper mounted on
top, screens at 8 ft. level. Ice
slurry trough with 7.5 ft. ID x
3 ft. deep around periphery at
top of column w/6 spray nozzles.

3. FREEZER #2

- o Shell & Tube Heat Exchanger
8-pass, 2530 ft.², 68 tubes per
pass, 1" $\emptyset$ x 20' long 316-L S.S.
tubes, sheets, and heads. C.S.
shell. Design Pres.=30 psi
tube side & 300 psi shell side.
- o Circulation Pump,
316-L S.S. 8% slurry of ice &
concentrate 525 gpm at 25 psi,
15 hp motor.
- o Wash Column
56.4 ft.² (8.5' $\emptyset$) coated carbon
steel vessel. 15 ft. tall,
scraper mounted on top, screens
at 8' level. Ice slurry trough
9.5'0x3' deep around top
periphery of column w/9 spray
nozzles.

4. FREEZER #3

- o Shell-and-Tube Heat Exchanger
8-pass, 3043 ft.², 60 tubes/
pass, 1" OD x 20' 316-L S.S.
subes, and sheet. Head is
carbon steel. Op. pres. =
20 psia, vessel rating = 300
psia, 42-46" $\emptyset$ shell.
- o Circulation Pump
316-L S.S., pumps 8% slurry
of ice and concentrate. 260
gpm at 20 psi, 5.6 hp

TABLE 4-5 (Cont'd)
MAJOR EQUIPMENT LIST
ACETIC ACID FREEZE REFINERY
Acetaldehyde Route

4. FREEZER #3 (Continued)

- o Eutectic Separator
11' Ø x 15' h. lined carbon steel vessel. Inlet nozzle at bottom (distribution ring) & 4 equally spaced nozzles on periphery of tank at top of ice slurry collection.
- o Acetic Acid Dewatering Screen
4' wide inclined screen, with .01" screen slots. 316-L S.S. reslurry tank attached: 60" x 60" x 48" tall of coated C.S.

- o Acetic Acid Dewatering Screen
4 ft. wide inclined dewatering screen with .01" slots, all 316-L S.S.
Reslurry tank attached: 60" x 60" x 48" tall coated C.S.

ICE MELTER

- o Shell & Tube Heat Exchanger
6-pass, 1700 ft.² exchanger, 61 tubes per pass x 21 L x 1" Ø x 20 BWG 304 S.S. 31" shell.
- o Circulation Pump
550 gpm x 50 psi heat to pump 10% ice slurry. 304 S.S. construction & 50 hp motor

5. FREEZER #4

- o Shell & Tube Heat Exchanger
8-pass, 295 ft.², 8-1" Ø x 20' L tubes/pass. 316 L S.S. heads, tube sheets & tubes, CS shell, op. pres., 20 psi, des. pres. 300 psi, 15½" shell
- o Circulation Pump
316-L, S.S., 95 gpm at 20 psi head, 2.06 hp.
Pumping 12% slurry of crystals.
- o Eutectic Separator
5' ID x 10' tall lined C.S. tank. 1" feed header
1" single underflow line, & 4 ea.-1" overflow lines connected into a 1" line for recycle

7. ACETIC ACID MELTER

- o Wash Column
7' dia. x 15' h. vessel with side screens at 8' level & ice scraper at top. Carbon steel with polyester lining & 316-L screens. 9' dia. x 2½' dp trough at top to reslurry crystals in.
- o Melter (plus ammonia condenser)
Shell & tube heat exchanger, 1436 ft.² 316-L tubes, heads & tube-sheets, & carbon steel shell. Op. pres. is 130 psia, design pres: 300 psi.
- o Pump-Acetic Acid Wash Column Feed
225 gpm at 17 psi, 5 hp motor, 316 L S.S.
- o Pump-Acetic Acid Melter Reslurry
225 gpm at 37 psi, 10 hp motor, 316-L S.S.

TABLE 4-5 (Cont'd)
MAJOR EQUIPMENT LIST
ACETIC ACID FREEZE REFINERY
Acetaldehyde Route

8. REFRIGERATION SYSTEM

o Compressors

Five stages of compression for ammonia refrigerant. Normal operating conditions (100% load) as follows:

	STAGE 1	STAGE 2	STAGE 3	STAGE 4	STAGE 5
#/hr. NH ₃	367.6	6551	11,079	3,345	518.3
Pres. In	9.04	16.10	30.42	73.32	128.8
Pres. Cut	16.15	30.5	73.4	128.9	211.95
H ad	23,400	27,500	46,200	30,750	35,900
HP ad	4.72	90.85	258.02	54.32	7.03
HP act	8.75	168.25	477.83	100.60	13.03
T in	-45	-20	59	100	100
T out	69	114	280	251	226
ACFM	182	1838	1684	221	20

Each stage a centrifugal compressor with inlet guide vanes controlled by the temperature (or pressure) in corresponding freezer.

- o Ammonia Receiv
500 gal carb
normal opera
max. design.

o Intercoolers

All 3/4" x 18 BWG 304 S.S. tubes, 1" square pitch, 304 S.S. tube sheets, lined heads and carbon steel shells. Three intercoolers operating on the discharge of Stages 2, 3 & 4 compressors. An aftercooler/NH₃ condenser on Stage 5 discharge. Specifications as follows:

	INTER- COOLER 1	INTER- COOLER 2	INTER- COOLER 3	INTER- COOLER COND. 4
Q, BTU/Hr.	45,282	957,792	250,786	281,786
Lmt'd, °F	24.3	76.0	55.75	49.7/11
Area, ft. ²	39.3	204.	102	257.
No. of Tubes	32	52	52	124
Tube Length, ft.	10'	20'	10'	10'
Passes	1	1	1	2
Shell Dia., in.	8"	10"	10"	15½'
Baffle Space	4.5	5'	5'	5'

TABLE 4-6

PUMP LISTACETIC ACID FREEZE REFINERYAcetaldehyde Route

<u>PUMP NO.</u>	<u>DESCRIPTION</u>	<u>CAPACITY GPM</u>	<u>HEAD PSI</u>	<u>HP</u>
P-1	Feed to Freezer	76	45	3.75
P-2	First Stage Freezer Recycle	214	25	5.90
P-3	Freezer 2 Recycle	525	25	14.47
P-4	Freezer 3 Recycle	260	20	5.60
P-5	Freezer 4 Recycle	90	20	2.06
P-6	Ice Melter Recycle	530	50	34.35
P-7	Acetic Acid Wash Column	225	17	4.35
P-8	Acetic Acid Melter Slurry	225	37	9.45
TOTAL				79.93

TABLE 4-7

LINE INDEXACETIC ACID FREEZE REFINERYAcetaldehyde Route

<u>LINE</u>	<u>DESCRIPTION</u>	<u>MATERIAL</u>	<u>SIZE</u>	<u>MATERIAL IN LINE</u>
<u>FREEZER SYSTEM #1</u>				
1000	Feed to Freezer #1	316L SS	2½"	70% H ₂ O, 30% HAC
1010	Freezer Recycle Loop	" "	5"	Ice Slurry & W Col Brine & Feed
1011	Slurry to Recycle	" "	3"	12½% Ice Slurry
1020	Wash Column #1 Feed	" "	4"	12½% Ice Slurry
1021	W Col-1 Brine	" "	4"	Brine to Recycle
2000	Feed to Freezer #2	" "	2½"	61% H ₂ O, 39% HAC
<u>FREEZER SYSTEM #2</u>				
2010	Freezer Recirc. Loop	" "	6"	6.25% Ice, 43% H ₂ O
2011	Slurry Recycle	" "	4"	12.5% Ice
2020	Ice Wash Column #2 Feed	" "	4"	12.5% Slurry
2021	Wash Column #2 Brine	" "	4"	43% Acetic, 30.5% H ₂ O & 27.0% Impur.
<u>FREEZER SYSTEM #3</u>				
3000	Freezer #3 Feed	" "	4"	Same as 2021
3010	Freezer #4 Crystal Slurry	" "	6"	7.5% Crystal Slurry
3020	Eutectic Separator Feed	" "	4"	15% Crystal Slurry
3021	Acetic Acid Crystal Slurry	" "	3"	37% Acetic, 25% H ₂ O, 38% Impurities
	Solution Return			
3025	Ice Crystal Slurry to ST 2	" "	3"	15% Ice, Same as 3021
3026	Acetic Acid Crystal Slurry	" "	3"	15% HAC Crystals
	to Dewatering Screen			
<u>FREEZER SYSTEM #4</u>				
4000	Freezer #4 Feed	" "	1"	Same as 3021
4010	Freezer #4 Recycle	" "	3"	12% Slurry
4011	Freezer #4 Crystal Recyc	" "	2½"	15% Slurry
4020	Freezer #4 Eut. Sep. Feed	" "	1"	15% Slurry
4025	Eut. Sep'r. Ice Fraction	" "	1"	15% Ice
4026	Eut. Sep'r. Bottoms Flow	" "	1"	15% HAC Crystals
4050	Waste Material	" "	½"	50% Impurities, 30% Acetic, 20% H ₂ O
<u>FEED HEAT EXCHANGERS - SYSTEM 5000</u>				
All piping is included in other sections				
<u>ICE MELTER - Series 7000</u>				
7001	Slurry from W Col #1	304L SS	5"	5% Ice in H ₂ O
7002	" " " " #2	" "	6"	" " " "
7010	Slurry to Ice Melter	" "	8"	" " " "
7021	Slurry Water Return to	" "	5"	H ₂ O
	W Col #1			
7022	Slurry Water Return to	" "	6"	"
	W Col #2			
7050	Product Water to Feed HXR	" "	2"	"

TABLE 4-7 (Cont'd)

LINE INDEXACETIC ACID FREEZE REFINERYAcetaldehyde Route

<u>LINE</u>	<u>DESCRIPTION</u>	<u>MATERIAL</u>	<u>SIZE</u>	<u>MATERIAL IN LINE</u>
<u>ACETIC ACID MELTER-SYSTEM 8000</u>				
8000	Wash Column Feed	316 L.SS.	4"	10% Acetic Acid Crystals
8003	ST 3 HAc Crystal Slurry Pump Suct.	" "	5"	" " " "
8004	ST 4 HAc Crystal Slurry Pump Suct.	" "	1½"	" " " "
8010	Wash Column Brine Recycle	" "	5"	Acetic Acid Brine
8013	Brine Recycle to Stage 3	" "	5"	" " "
8014	" " " " "	" "	1½"	" " "
8020	Crystal Slurry to Melter - Pump Suct. - Pump Discharge	" " " "	5" 4"	Acetic Acid Slurry " " "
8021	Acetic Acid Recycle for Reslurry	" "	4"	" " "
8022	Make-up HAc to ST 3&4 Slurry Tanks	" "	1"	Acetic Acid Product
8050	Acetic Acid Product	" "	1½"	Product Acetic Acid
8070	Acetic Acid Recycle to Stage 3	" "	½"	Off-Spec. Acetic
<u>REFRIGERATION SYSTEM-SYSTEM 9000</u>				
9000	Liq Refrig to Freezers	CS	2½"	Liquid NH ₃
9001	" " " F-1	"	1½"	" "
9002	" " " F-2	"	1"	" "
9003	" " " F-3	"	1"	" "
9004	" " " F-4	"	½"	" "
9010	Freezer #4 Ammonia Vapor	"	3"	Vapor NH ₃
9011	Comp. ST 1 Discharge	"	2"	" "
9015	Comp. ST 1 By-Pass	"	3"	" "
9020A	Freezer ST 3 Ammonia Vapor	"	6"	" "
9020B	" " 2 " "	"	"	" "
9020	Comp. ST 2 Suction	"	8"	" "
9021	" " " Discharge	"	6"	" "
9025	" " " By-Pass	"	8"	" "
9030A	Freeze ST 1 Ammonia Vapor	"	6"	" "
9030	Comp. ST 3 Suction	"	10"	" "
9031	" " 3 Discharge	"	8"	" "
9035	Ice Melter NH ₃ Vapor Line	"	8"	" "
9036	" " " Liquid Line	"	2½"	Liquid NH ₃
9040	Comp ST 4 Suction	"	6"	Vapor "
9041	" " " Discharge	"	5"	" "
9045	Acetic Acid Melter Vapor Line	"	4"	" "
9046	Acetic Acid Melter Liquid Line	"	1"	Liquid "
9050	Comp ST 5 Suction	"	3"	Vapor "
9051	" " " Discharge	"	2½"	" "
9056	Ammonia Condenser Liq Line	"	1"	Liquid "

TABLE 4-8

HEAT TRANSFER SUMMARY
ACETIC ACID FREEZE REFINERY
Acetaldehyde Route

HEAT EXCHANGER DESCRIPTION	HEAT LOAD BTU/HR	INDIVIDUAL COEFFICIENTS & RESISTANCES				OVERALL HEAT TRANSFER COEFFICIENT BTU/HR-FT ² ·°F
		h_o	h_i	r_w	r_f	
Freezer No. 1 Ice removed to concen- trate HAC to 40%	2.873x10 ⁶	427	772	.00031	.001	200.
Freezer No. 2 Ice removed to concen- trate HAC to 59%	1.580x10 ⁶	353	542	.00031	.0015	153.
Freezer No. 3 Eutectic freezer concentrating impurities	1.914x10 ⁶	350	407	.00031	.001	151.
Freezer No. 4 Eutectic Freezing for final product recovery	.221x10 ⁶	350	407	.00031	.001	151.
Feed Heat Exchanger o Product to feed	.290x10 ⁶	1111.5	326	.00035	.002	158.
o Water to feed	1.833x10 ⁶	887	610.	.00035	.002	209.
Ice Melter Ice slurry is melted at 32°F & heated to 34°F	3.134x10 ⁶	217.	1066	.00035	.001	145.
Acetic Acid Melter Product acetic acid is slurried, melted at 60°F and heated to 62°F	1.509x10 ⁶	775	111.	.00031	.001	94.
h_o - Heat Transfer Coefficient Outside of Tubes		r_w - Tube Wall Resistance				
h_i - Heat Transfer Coefficient Inside of Tubes		r_f - Fouling Factor				

surface area was calculated the next largest standard 1" tubes x 1 5/16" square pitch heat exchanger was chosen for the service and used as the basis for the cost estimate.

Process Vessels

The only significant process vessels envisioned for this process are the wash columns, eutectic separators, and drainage screens. The screens selected are greatly oversized for a 100 million pound per year plant but are the smallest commercially available and were therefore used in the design and cost study.

The wash columns were sized for the full flow of crystals based on a 300 pound of crystal per hour per square foot of wash column performance rate. This is a common design criteria for ice wash columns and is thought to be conservative for acetic acid.

The eutectic separators were designed on the basis of differential rise and settling velocities of the ice and acetic acid crystals. This system is ideally suited for this kind of separation because of the densities of the liquid and crystals. An acetic acid solution at its eutectic has a specific gravity of about 1.03 while those of ice and crystal acetic acid are 0.90 and 1.05, respectively. Thus, a gravity settling device can be used to separate the crystals quite effectively. The critical sizing parameter for this device is the downflow velocity -- it has to be set small enough so that small ice crystals are not entrained with the flow of acetic acid crystals. With proper baffling in the separator all but the smallest ice nuclei should be segregated from the stream with the product acetic acid crystals.

Capital Cost Estimates - Installed capital costs were developed using the rationale and procedures that were outlined in Chapter 2. The cost estimate for the 100 million lb/yr system refining glacial acetic acid from a 30% solution is summarized in Table 4-9. This table, like the equipment list and energy summary tables, is arranged to allow direct estimate for other concentrations of crude acid.

METHANOL-CARBONYLATION CRUDE REFINING

Conventional Refining Technology

This reaction route was developed in the 1960's and for the past decade has been used almost exclusively in new plants. Two alternative options exist: high or low pressure systems. The advantage of this route generally, in addition to low raw material costs, is the high selectivity and conversion. Apparently, both processes have very similar refining systems, the general flow sheet shown in Figure 4-6.

TABLE 4-9
CAPITAL COST BREAKDOWN
ACETIC ACID FREEZE REFINERY
Acetaldehyde Route

	<u>INSTALLED COST</u> <u>\$</u>
STAGE 1	
Freezer #1	\$ 93,000
Ice Wash Column	75,025
Ice Melter (1/3)	27,375
Freezer 1 Circulation Pump	10,175
Ice Melt Circulation Pump	11,400
Compressor Stage 4	78,250
SUBTOTAL	<u>295,225</u>
STAGE 2	
Freezer #2	99,675
Ice Wash Column ($\frac{1}{2}$)	75,025
Ice Melter (1/3)	27,375
Freezer 2 Circulation Pump	12,700
Ice Melt Circulation Pump (1/3)	11,400
Compressor Stage 3	187,850
SUBTOTAL	<u>414,025</u>
STAGE 3	
Freezer #3	110,600
Ice Wash Column 2 ($\frac{1}{2}$)	75,025
Stage 3 Eutectic Separator	72,200
Acetic Acid Wash Column ($\frac{1}{2}$)	22,475
Ice Melter	27,375
Acetic Acid Melter ($\frac{1}{2}$)	36,225
Freezer 3 Circulation Pump	10,200
Ice Melt Circulation Pump (1/3)	11,400
Acetic Acid Wash Column Feed Pump ($\frac{1}{2}$)	5,275
Acetic Acid Melt Circulation Pump ($\frac{1}{2}$)	6,375
Acetic Acid Drain Screens	45,025
Compressor Stage 2	94,000
SUBTOTAL	<u>516,175</u>
STAGE 4	
Freezer #4	19,275
Stage 4 Eutectic Separator	27,025
Acetic Acid Wash Column ($\frac{1}{2}$)	22,475
Acetic Acid Melter ($\frac{1}{2}$)	36,225
Freezer 4 Circulation Pump	3,025
Acetic Acid Wash Column Feed ($\frac{1}{2}$)	5,275
Acetic Acid Melt Circulation Pump ($\frac{1}{2}$)	6,375
Stage Acetic Acid Drain Sc.	45,025
Compressor Stage 1	46,950
SUBTOTAL	<u>211,650</u>
COMMON EQUIPMENT	
Feed Heat Exchanger	13,650
System Feed Pump	3,025
Compressor Stage 5	46,950
SUBTOTAL	<u></u>
TOTAL DIRECT COST	1,500,700
(Stages 1-4 and Common Equipment)	570,200
INDIRECT COST	<u>\$2,070,900</u>
TOTAL

ACETIC ACID COMMERCIAL PRODUCTION PROCESS
METHANOL CARBONYLATION

FIGURE 4-6 7004-2006

The reactor off-gases, mostly carbon oxides and methane, are scrubbed with chilled methanol that then becomes the reactor feed. The crude acid is first stripped to remove the light by-products. The light materials (ethers, acetates and aldehydes) are the smaller portion of the by-products formed. Catalyst is separated from the crude by distilling the acetic acid and heavy by-products overhead in a second column. By-product water is removed in a third azeotropic column and then the acetic acid is purified in a final column. The heavy by-products out of the refining column contains some product that is sometimes recovered in a fifth, stripping column.

The literature values for energy consumption in these refineries are not very specific and quite variable, ranging from 2000 to 5000 BTU's per pound. To clear up the discrepancies we checked with various manufacturers who did little to quantify the actual usage. Several manufacturers informed us that even the low values were somewhat high. Apparently the energy crisis and higher energy costs have had some effect on this industry and new and retrofitted plants have been designed to minimize energy use. On this basis we tried to estimate minimum reflux ratios and consequent minimum energy use in these facilities. Our results, summarized earlier in Table 4-1 (approximately 1360 BTU/lb), represent the lowest anticipated consumption and is, apparently, being met by some, but not all, refineries processing crude from this reaction route.

Freeze Refining

The crude acid produced from this reaction route is relatively pure. Catalyst that flows forward with the product are present at about 1% or less. Propionic acid is apparently the predominant organic by-product, at $\frac{1}{2}$ to 1%. Ethyl and tar methyl alcohols at a fraction of a percent, convert in the crude material, to the acetates.

The starting point to define the freezing system is, once again, the phase diagram. The multi-component diagram would be the ideal starting point but the techniques for predicting multi-component solid-liquid equilibria are difficult, require binary data unavailable on this project, and are of questionable accuracy. Therefore, we were forced to start with binary data; for the acetic acid-water system, that is available in the literature, and for propionic and acetic acid, that should be predictable with reasonable accuracy because of the similarity of the two acids. The water-acid diagram was presented earlier (Figure 4-4) and the two-acid diagram as predicted by classical thermodynamics is shown in Figure 4-7. The binary diagrams show that the impurities must be concentrated many times before the eutectics are approached. In fact, the binaries indicate that over 98% of the acetic could be recovered without encountering simultaneous precipitation of any of the impurities. Based on 98% recovery, we predict that the resulting freezing point of the concentrated

SK-1115

impurities (11% water, 22% propionic, and 22% other impurities) would be about 10°F. It would be possible to remove all of the acetic acid in one freezing stage but the energy efficiency can be substantially improved by using two stages.

Process Descriptions - The flow diagram and P&ID are shown in Figures 4-8 and 4-9, respectively.

Crude acetic acid is fed to the first stage. Acetic acid is crystallized to concentrate the total impurities to about 21% of the remaining liquid, a value selected to give a freezing point midway between that of the second stage and the melting point of acetic acid. The operating temperature of 35°F represents the first approximation of optimal operating conditions.

The freezer is designed to operate with influent and effluent slurry concentrations of 7½% and 15%. The concentrated slurry is fed to the wash column and the brine that is separated then is partially recycled to the first stage freezer where more of the acetic acid is crystallized. The feed and recycle brine have no crystal content so some of the concentrated slurry out of the freezer is recycled to give a combined feed to the freezer with 7½% crystals.

Wash column size is governed largely by crystal size, a parameter that is unknown without testing and beyond prediction techniques. The freezer can be designed to separate the larger crystals for feed to the wash column, recycling the small particles to the freezer for additional growth. To some degree the crystal size can be controlled, providing the conditions for more optimum wash column operation. Our results in laboratory tests would indicate that acetic acid crystals grow more rapidly than do ice crystals, so that the acetic acid wash column in this application would operate better than the ice columns of the acetaldehyde-route acetic acid application.

Feed to the second stage is controlled by the operating temperature of the first stage crystallizer. Higher recovery produces a concentrate with a lower freezing point, while a too-low recovery has the opposite effect. Therefore, forward feed of concentrate and subsequent make-up of crude acid can be controlled by the temperature in the freezer-wash column section.

The second stage of this process functions nearly identically to the first stage. Operating temperature will be some 25°F lower. The freezer will still operate with a 7½% inlet ice slurry, increasing the concentration to 15% during its passage. The crystals formed in the second stage may be small or irregular, making them difficult to wash and purify. Rather than wash the small quantities produced in the second stage in a wash column,

-114-

CONCENTRATION SPECIALISTS, INC.
ANLOVER, MASS.

SCALE: NONE	APPROVED BY	DRAWN BY C. ZOLTY
DATE: 1 12 79		

FLOW DIAGRAM
ACETIC ACID FREEZE REFINERY FIGURE 4-8

METHANOL DERIVED CRUDE

DRAWING NUMBER
1004-2009

CONCENTRATION SPECIALISTS, INC.
ANDOVER, MASS.

SCALE: NONE	APPROVED BY	DRAWN BY C. ZOLTKO
DATE: 1-12-79		
P&ID ACETIC ACID FREEZE REFINERY FIGURE 4-9		
METHANOL DERIVED CRUDE		DRAWING NUMBER 7004-2008

these crystals will be drained (in a drainage column or on inclined screens) and then reslurried with brine from the first stage wash column. These reslurried crystals can then be pumped either directly to the wash column or recycled to the feed to Freezer 1, the passage through which will improve the size and distribution of the crystals. Ultimate blowdown would again be controlled by the operating temperature in the freezing stage.

The acetic acid melter services also as a refrigerant condenser; the thermodynamic advantage of recovering the heat of crystallization is somewhat reduced by the high melting temperature but is still worth doing.

The refrigeration system envisioned for this process would be a three-stage cascading ammonia system. The first stage draws vapor from the lowest temperature freezer (Stage 2) and compresses it to the saturated pressure corresponding to the Stage 1 freezer operating temperature. Refrigerant vapors from the Stage 1 freezer combine with the compressed stream to form the suction to a second compression stage. Superheat is removed from the compressed stream with cooling water and part of the ammonia is condensed in the melter-condenser. Melting acetic acid is the heat sink against which the refrigerant is condensed.

The melting heat sink can not condense all of the refrigerant; the remaining vapor has to be compressed so that it will condense against cooling water. This compressor and condenser comprise the heat rejection loop of the process.

Energy Consumption - The power requirements for refining this crude acetic acid illustrate the low energy demand of freeze separation processes under optimum process conditions. Table 4-10 summarizes the power required by the freeze refining operating on methanol-carbonylation crude acetic acid. Comparing the breakdown of power consumed in various sections of the plant with the flow diagrams shown earlier illustrates some of the reasons for this low energy consumption.

- o Since there is relatively little impurity, none of which would be crystallized, the latent heat load on the freezers is limited to that of the primary product.
- o The freezing point depression of the solution is relatively small, especially in the first stage freezer where half of the acetic acid is recovered.
- o The acetic acid crystals formed in both stages are pure and do not require melting and recrystallization. (This also is true in the other acetic acid cases. The literature shows some cases where solid solutions of organic compounds are formed, but they are not common and there is no indication that acetic acid is involved in any such situation.)

TABLE 4-10

ENERGY SUMMARYACETIC ACID FREEZE REFINERYMethanol Carbonylation Route

	<u>CAPACITY</u> <u>(lb/hr)</u>	<u>HEAD</u> <u>(psi)</u>	<u>HP</u>
PUMPING POWER			
Stage 1 Recirculation	132,097	16.	5.
Stage 2 Recirculation	16,874	14.5	.5
Stage 2 Crystal Reslurry	14,380	5.	.25
Wash Column Melter	126,840	15.3	5.
Refrigerant Pump	5,193	21.	.5
TOTAL HP - PUMPS			<u>11.25</u>

	<u>CAPACITY</u> <u>(lb/hr)</u>	<u>P_{out}/</u> <u>P_{in}</u>	<u>HP</u>
Stage 1	324	1.57	5.
Stage 2	2,052	2.40	83.
Heat Rejection	600	1.65	8.
TOTAL HP - REFRIGERATION			<u>96</u>

Total Plant kw	80.0
Equivalent kw-hr/Product	0.0065
Equivalent BTU's (at 10,000 BTU/kw-hr)	
BTU/lb Product	65.

Engineering Package - As with the acetic acid from acetaldehyde, the citrus and the black liquor freeze separation applications, a preliminary design and cost analysis was prepared for this case, where the methanol-derived acetic acid is being refined. The Flow Diagram and P&ID, Figures 4-8 and 4-9, were first prepared, representing our best estimate of the freeze process that would perform the necessary separations. From this, mass and energy balances were derived using the general criteria that were discussed in the previous sections. Individual component designs were then performed to adhere to the requirements of the balances. The design for the freeze refining process are summarized in the following tables:

- o Table 4-11 - Major Equipment
- o Table 4-12 - Pump List
- o Table 4-13 - Line Index

Energy Requirements

In this system the variables that most effect energy consumption are: recirculation pumping requirements, which in turn are determined by the assumptions of maximum crystal content in the freezer effluent (15%) and the minimum crystal fraction in the stream entering the freezer ($7\frac{1}{2}$); and the temperature difference across the refrigerant heat exchangers (10°F across both the freezers and 9°F across the melter-condenser).

Heat Transfer (Freezer and Melter/Condenser Sizing)

The refrigerant heat exchangers were sized with 1" OD x 20 BWG tubes of 316 L stainless steel. Since there is little data in the literature on details of the methanol carbonylation process we had to calculate all of the crude acid physical properties. Refrigerant properties were those for ammonia at the particular temperature and pressure of the individual heat exchangers. The freezers spray a thin film of ammonia on the shell side of the tubes and have a high velocity (7 ft./sec.) recirculating slurry on the tube side. Viscosities were those calculated for the brine conditions without any crystal; since slurries behave in a non-Newtonian manner the actual viscosity under flow conditions will be less than calculated and the tube-side coefficients will be higher. The required surface areas so calculated were then given an additional 20% contingency. Cost estimates assumed an eight-pass design with the 1 inch OD tubes on a 1 5/16 inch square pitch.

The melter-condenser is a horizontal tube exchanger with ammonia condensing on the shell side and a slurry of acetic acid circulating on the tube side. Again, an 8 pass exchanger with 15/16" square pitch 1" OD tubes was assumed. A summary of the heat transfer calculations is shown in Table 4-14.

TABLE 4-11

MAJOR EQUIPMENT LIST

ACETIC ACID FREEZE REFINERY

Methanol Carbonylation Process Crude

FEED HEAT EXCHANGERS

- o FE-1
316 L stainless steel, plate and frame, feed and product acetic acid, area of 316 ft.²
- o FE-2
316 L stainless steel, plate and frame, feed and concentrated impurities, total area of 7 ft.²

FREEZER #1

- o Shell and Tube Exchanger, total area required is 1,980 ft.² Shell dimensions 33" OD x 20' long. Tubes and head of 316 L stainless steel, shell of carbon steel. Working pressure 50 psi, max pressure 300 psi.
- o Circulation Pump, 4.4 hp, 260 gpm at 16 psia head. Pump of 316 L stainless steel.
- o Wash Column, to wash 12,700 lbs/hr of acetic acid crystals, 250 lbs/hr-ft.² crystal flux rate, 50 ft.² cross-sectional area (8 ft. Ø) x 15 ft. tall. Carbon steel construction with ½" PVC lining, brine withdrawal screens, a scraper assembly, slurry distribution and wash headers and a crystal reslurry trough (all wetted surfaces of 316 L stainless steel).

FREEZER #2

- o Shell and Tube Heat Exchanger, total area required is 250 ft.² Shell dimensions, 20" OD x 16 ft. long. Tubes and head of 316 L stainless steel, shell of carbon steel. Working pressure is 150 psi, design pressure is 300 psi.
- o Circulation Pump, .5 hp, 33 gpm at 14.5 psia total head. Pump construction is 316 L stainless steel.
- o Crystal Drain Screen, inclined 316 L stainless screen 4' width (smallest commercial size with 150 micro wedgewire).
- o Crystal Reslurry System, 500 gal. carbon steel tank, lined with PVC, and a ¼ hp pump, 35 gpm at 10 psia, 316 L stainless construction.

ACETIC ACID MELTER

- o Heat Exchanger, 8 pass shell and tube, total area is 530 ft.² Tubes and head of 316 L stainless, shell is carbon steel. Dimensions, 20 inch OD by 20 ft. long.
- o Melt Recirculation Pump, 5 hp, 250 gpm at 15.3 psia total head, constructed of 316 L stainless steel.

TABLE 4-11 (Cont'd)
MAJOR EQUIPMENT LIST
ACETIC ACID FREEZE REFINERY
Methanol Carbonylation Process Crude

REFRIGERATION SYSTEM

	<u>STAGE 1</u>	<u>STAGE 2</u>	<u>STAGE 3</u>
#/hr NH ₃	328.	2059.	600.
Pressure In, psia	34.3	53.5	128.8
Pressure Out, psia	53.9	128.9	212.
H _{ad}	18,987	41,179	25,405
HP _{ad}	3.15	49.65	7.70
HP _{act}	5.25	82.75	12.85
T _{in}	5°F	34°F	100°F
T _{out} actual	91°F	220°F	215°F
ACFM	4...	183.20	14.2

TABLE 4-12

PUMP LISTACETIC ACID FREEZE REFINERYMethanol Carbonylation Process Crude

<u>PUMP NO. & DESCRIPTION</u>	<u>MAT'L BEING PUMPED</u>	<u>FLOW RATE</u>		<u>HEAD</u> <u>psi</u>	<u>hp</u> <u>REQUIRED/</u> <u>CONNECTED</u>
		<u>#/hr</u>	<u>gpm</u>		
P-1 Feed Pump	Crude Acetic Acid	13,261	25	15.0	.41/.50
P-2 ST 1 Recirculation	ST 1 Recycle Slurry	132,079	254	16.0	4.4/5.0
P-3 ST 2 Recirculation	ST 2 Recycle Slurry	16,874	33	14.5	.5/1.0
P-4 ST 2 Crystal Reslurry Pump	ST 2 Crystals Plus Wash Column Con'te.	14,380	27	10.0	.3/.5
P-5 Melter Recirculation	Product Acetic Acid Crystal Slurry	126,840	250	15.3	4.0/5.0

TABLE 4-13

LINE INDEXACETIC ACID FREEZE REFINERYMethanol Carbonylation Process Crude

<u>LINE NO.</u>	<u>FLOW DESCRIPTION</u>	<u>MATERIAL OF CONSTRUCTION</u>	<u>SIZE</u>	<u>MATERIAL IN LINE</u>
1000	Feed to Refinery	316 L.SS	1½"	97% Acetic & Impurities
1010	ST 1 Freezer Recycle	" "	5"	75% Acetic 7½% Crys
1020	ST 1 W Col Feed	" "	4"	15% Crystal, 67% HAc
1021	ST 1 & 2 W Col Feed	" "	"	14% Crystal, 67% HAc
1022	Wash Column Brine	" "	"	67% HAc, 33% Impurities
1023	W Col Brine Recycle to ST 1	" "	3"	" " " "
1024	W Col Brine Recycle to ST 2	" "	2"	" " " "
1030	ST 1 Recirc Pump Suct.	" "	5"	8½% Crystal, 67% HAc
1031	ST 1 Crystal Recycle	" "	4"	15% Crystal, 67% HAc
1032	ST 1 Recirc Pump Disch	" "	5"	8½% Crystal, 67% HAc
2000	ST 2 Feed	" "	1"	67% HAc, 33% Impurities
2010	Freezer ST 2 Recycle	" "	2"	7½% Crystal, 50% Acetic
2020	Slurry to Dewatering Screen	" "	1½"	15% Crystal, 40% Acetic
2021	Screen Underflow	" "	1½"	40% Acetic, 60% Impur.
2025	Crystal Reslurry Pump Suct.	" "	2"	40% Crystal, 40% HAc

TABLE 4-14

HEAT TRANSFER SUMMARYACETIC ACID FREEZE REFINERYMethanol Carbonylation Process Crude

<u>HEAT EXCHANGER DESCRIPTION</u>	<u>HEAT LOAD BTU/HR</u>	<u>INDIVIDUAL COEFFICIENTS</u>				<u>OVERALL HEAT TRANSFER COEF., BTU/HR-FT²-°F</u>
		<u>h_o</u>	<u>h_i</u>	<u>r_w</u>	<u>r_p</u>	
FREEZER #1 Horizontal Tube, Spray Film NH ₃ on shell side, 7 ft/sec. velocity slurry on tube side	1.162x10 ⁶	450	333	.00031	.0015	141
FREEZER #2 Horizontal Tube, Spray Film NH ₃ on shell side, 7 ft/sec. velocity slurry on tube side	.186x10 ⁶	634	450	.00031	.0015	177
ACID MELTER Horizontal Tube, NH ₃ condensing on shell side, acetic acid slurry at 7 ft/sec. melting on tube side	.944x10 ⁶	775	111	.00031	.0015	90
FEED HEAT EXCHANGERS Plate & Frame, Deq. .026 ft.						
Unit A (FE-1) Feed/Product Exchanger	.226x10 ⁶	327	1112	.00035	.002	159
Unit B (FE-2) Feed/Concentrator Exchanger	.018x10 ⁶	327	348	.00035	.002	121

h_o - Heat transfer coefficient outside of tubes
 h_i - " " " " inside " "
 r_w - Tube wall resistance
 r_f - Fouling factor resistance

Process Vessels

The acetic acid wash column was sized assuming a crystal flux of 300 pounds per hour per square foot of cross sectional area. This is a capacity that should be achievable with crystals greater than about 250 microns major axis length.

The inclined screen used to dewater crystals in the second stage can be designed to insure adequate crystal size from that stage. The screen is sized to allow small crystals to pass through with the fluid for recycle while the large crystals are segregated and drained. The crystal reslurry tank is sized for a 5 minute retention of sufficient fluid to give a 5% slurry with the Stage 2 crystals.

Capital Cost Estimates

Capital costs for a freeze refining system, defined above, to produce 100 million pounds per year of product from methanol derived crude is summarized in Table 4-15.

BUTANE/BUTENE/NAPHTHA LIQUID PHASE OXIDATION

Conventional Refining Technology

This program did not evaluate freeze refining of crude acetic acid produced by butene oxidation with the same thoroughness as the two previous crudes. The reasons will be discussed in greater detail but the limited attention was primarily for two reasons:

- o The crude acetic acid produced from C₄ feedstocks includes significant quantities of by-products that must be recovered to make the process economically competitive. The total refining system is so enmeshed that it is difficult to assign that portion of the total savings that should be credited to the acetic acid.
- o Energy consumption in conventional refining processes is between that for the two processes studied in depth. Similarly, the savings possible with a freeze crystallization refinery, and the justification for it would be somewhere between these two extremes. The freeze equipment would be less complex than that for the acetaldehyde crude but more so than the methanol crude. Since both cases studied in depth indicated favorable economics for the freeze refining process, it seems justifiable to conclude that the same would be true of the butylene-process crude.

The butylene process was studied in sufficient depth to support these conclusions. A freeze refining system was conceived that would recover high quality acetic acid and produce a concentrated stream of by-products for subsequent refining. That process is described below. The immediate paragraphs discuss the reaction and conventional refining systems.

TABLE 4-15
CAPITAL COST
ACETIC ACID FREEZE REFINERY
Methanol Carbonylation Route

BASIS: 100 Million lb/yr Product

<u>ITEM</u>	<u>INSTALLED COST (\$)</u>
First Stage Freezer	\$130,000
Second Stage Freezer	30,000
Acetic Acid Melter	50,000
Acetic Acid Wash Column	112,500
Crystal Drain Screen	45,025
Feed Pump	2,000
Stage 1 Recirculation Pump	2,600
Stage 2 Feed Pump	2,000
Stage 2 Recirculation Pump	1,750
Stage 2 Reslurry Pump	1,750
Acetic Acid Melt Pump	2,400
Stage 1 Compressor	61,000
Stage 2 Compressor	125,000
Stage 3 Compressor	50,000
Feed Heat Exchanger	15,500
TOTAL DIRECT COST	631,525
INDIRECT COST	265,241
TOTAL	\$896,766

The butylene liquid phase oxidation system is unusual among the commercial acetic acid processes because of its lack of selectivity. The reaction can be performed in one or two stages. The feedstock is dissolved in recycle acetic acid and catalytically reacted at 15 to 25 atmospheres and 100 to 120°C to produce an intermediate butyl acetate. Conversion in this stage is 50 to 80%; a two-stage process allows intermediate separation of the unreacted feed so that by-products formation in the subsequent oxidation step is minimized. The second reaction step in a two-stage process occurs at 50 to 60 atmospheres and the exothermic heat of reaction is removed to control the temperature at 200°C. Again, conversion is not complete and unreacted butyl acetate is separated for recycle. Gases are stripped from the product, expanded in a turbine and combusted. Selectivity of the butylene to acetic acid is less than 50%, producing 1.0 to 1.2 pounds of by-product per pound of product acetic acid, in approximately the following ratio: Acetic Acid - 10, Formic Acid - 1.0, Acrylic Acid - 1.0, Methyl/Ethyl Acetate 3.0, MEK - 2.5, Water 1.0, Miscellaneous - 2.3. Over fifty organics have been identified as side reactions in this process but only those listed above are produced in recoverable quantity.

The refining process for this crude acid is relatively complex because of the various by-products that must be separated and purified. The process is shown in Figure 4-10. The first two steps in the refining process remove unreacted butene's and butyl acetate. The crude acid is first stripped of light by-products. This stream contains five major components: Acetone, Methyl Acetate, Ethyl Acetate, Methyl Ethyl Ketone, and Methyl Vinyl Ketone. Fractionation can be into two or three boiling-range mixtures or into the individual components, requiring one to four columns.

The crude acid has a substantial portion of water that is removed in a dehydration column. Volatilities of water and acetic acid are nearly identical so straight distillation is a very expensive dehydration technique; an azeotroping agent such as ethyl acetate is used.

The major by-product of similar or higher boiling point is formic acid, which also is difficult to separate from acetic acid. The formic acid by-product column uses an azeotroping agent such as chloroform or benzene. Product acetic acid remains in the sump of this column with the high boiling impurities. The acetic acid in refining overhead acids can be separated in further columns if economically justified.

Freeze Refining

Of the various applications studied in this program, the butylene derived crude acetic acid is unique in the large number of varied species that need to be separated into individual, pure components. Several aspects of this application are less than ideal for the state-of-the-art of freeze refining:

ACETIC ACID COMMERCIAL PRODUCTION PROCESSES
BUTANE/NAPHTHA OXIDATION

FIGURE 4-10 7004-2005

- o After some degree of acetic acid recovery, other material (water and then soon after acrylic and formic acids) will start to precipitate simultaneously. While the water can be separated relatively simply from the acid crystals, it is beyond the state-of-the-art to fractionate the individual acids with high degrees of resolution.
- o The large fraction of volatile acids and ketones will create a large freezing point depression. Commercial ammonia refrigeration systems can operate with a -60°F evaporator (the freezer) temperature. Lower temperature devices are commercially available but get quite expensive. Low compressor suction pressures also increase power consumption, so the relative economics of low temperature operation make freezing less attractive.

Because of these limitations it would seem that freezing would have limited application. Specifically, the freezing system would be used to perform only part of the separation. This is not a foreign or novel concept in chemical processing where individual processes are combined into total systems to take advantage of their specific capabilities. The question here becomes what can the freeze separation process do most advantageously.

Once again, the starting point is to look at the solid-liquid equilibria; a task that is complicated by the large number of components in significant concentrations. The best prediction techniques for multi-component equilibria require extensive vapor-liquid binary data, at least, and then are not reliable. A literature search failed to produce (a) solid-liquid equilibria data for any similar mixture, (b) solid-liquid equilibria for most of the binary combinations of the major constituents or (c) even vapor-liquid equilibria for most of the binary combinations. With such a vacuum, the only method assessing the solid-liquid equilibrium is a qualitative evaluation of ideal behavior. The assumption of thermodynamic ideality is generally poor, given the diverse nature of the stream and the large number of oxygenated, non-symmetrical molecules with large electronic forces. Usually ideality only holds, even loosely, for compounds with a similar functional groups. Since the predominant species are all acids and they are the compounds that present the possible precipitation/fractionation problems, the interactions of the binary acid systems warrant some consideration. The assumptions made in using ideal solid-liquid behavior to formulate a freeze crystallization system included:

- o The individual acids are affected equally by the non-acid by-products as well as by the other acids.
- o The ideal binary predictions are accurate in predicting eutectic compositions but estimate eutectic temperatures well below actual systems. (For example, compare the ideal projections in Table 4-16 for acetic acid and water to the actual binary data shown in Figure 4-4.

TABLE 4-16

BINARY SOLID-LIQUID EQUILIBRIA
IDEAL BEHAVIOUR BETWEEN VARIOUS ORGANIC ACIDS

BINARY SYSTEMS ACETIC ACID WITH	EUTECTIC CONDITIONS		
	TEMPERATURE (°F)	ACETIC WT. FRAC.	SECOND WT. FRAC.
Water	-24	.611	.389
Acrylic Acid	- 2	.516	.484
Butyric Acid	-17	.286	.714
Formic Acid	- 4	.516	.484
Propionic Acid	-33	.231	.769

SECONDARY ACID	RATIO OF ACETIC TO SECOND ACID COMPONENT		NO. OF TIMES SECOND ACID IS CONC'D BEFORE EUTECTIC PRECIP.	ACETIC ACID RECOVERY
	IN CRUDE ACID	AT THE EUTECTIC		
Water	5:1	1.5:1	3.33	70%
Acrylic	10:1	1:1	10.	90%
Butyric	10:1	1:3½	25.	96%
Formic	10:1	1:1	10.	90%
Propionic	>10:1	1:3	30.	97%

RATIO OF ACETIC ACID TO VARIOUS IMPURITIES
AT 70% ACETIC RECOVERY

IMPURITY	WT. FRAC. ACETIC ACID WITH THE IMPURITIES	
Water	1½# Acetic	1# Water
Acrylic	3	: 1
Butyric	3	: 1
Formic	3	: 1
Propionic	3	: 1

The analysis of the binary systems and projections of this data to a freezing system is summarized in Table 4-16. Using the weight ratio's of acetic acid to the other acids at the binary eutectic points, it was first assumed that the individual by-product acids could be concentrated to these ratios by the crystallization of acetic acid. This analysis indicates that 70% of the acetic acid can be recovered before the water eutectic is reached. Another 20% of the feed acid is then recovered by simultaneous (eutectic) precipitation. The eutectic temperature will be lowered by the impurities; probably by 10 to 20°F, perhaps by more. In the eutectic freezer, where the impurities are further concentrated, the eutectic temperature could be lowered by this much again.

On this basis a freeze separation process is envisioned that has the following characteristics:

- o Three equally sized freezers, the first two crystallizing only acetic acid, the last one operating at the eutectic of water and acetic acid. The freezer operating temperatures would be:

Stage 1 : 0 to -10°F
Stage 2 : -25 to -35°F
Stage 3 : -40 to -50°F

- o One acetic acid wash column. The crystals from all three stages, are first drained on screens, then reslurried with a warmer, acetic acid rich fluid for slurry feed to the wash column. Since the slurry could represent 40 to 50% of the low quality heat in the freezers, it will be warmed by condensing refrigerant in an indirect heat exchanger. This is both necessary for good wash column operation and advantageous for minimum energy consumption in the refrigeration system.
- o The third stage will have a eutectic separator for separating water and acetic acid crystals. The water crystals may be too small for effective washing in a column, in which case they would be "dewatered" on a screen or in a centrifuge.

TECHNOLOGY TRANSFER

COMPANIES VISITED

- o Celanese Chemical Company
- o FMC Corporation
- o Monsanto Company - St. Louis, MO
- o Monsanto Company - Texas City, TX
- o Publicker Industries
- o Sonoco Products Company
- o Tennessee Eastman
- o Union Carbide - So. Charleston, WV

The listed companies were visited after the preliminary designs of the freeze refining plants had been completed. The economics derived from these designs and the design bases were presented in one segment of the technology transfer seminars. The first segment of the seminars was used to introduce freeze crystallization technology.

In the first segment of the seminars we outlined the present state-of-the-art of freezing technology as a separation process, soliciting comments from the audiences. Topics covered included a review of the various cycles that have been built and operated, a summary of the status of the development of various equipment components, and a discussion of applications in the industry. The more useful information provided from this stage of discussions included:

- o The participants were generally familiar with the process but did not view it as an energy-saving separation technique. This is due mainly to the type of equipment they have used; batch methods have been inherently inefficient because of their design and continuous methods have used large temperature differences in the freezers to minimize capital costs. In many instances energy recovery (from the cold streams) was not practiced.
- o A number of applications that the companies considered better applications than acetic acid were discussed. They included phenol, benzene, acrylic acid derivatives and other light acid refining.

In the second segment of the seminars, where the detailed engineering results and methodology were presented, input from the audiences was solicited. The bases for the economic projections -- conventional process energy use, electricity costs and steam values -- were all discussed. Questions about the design bases of the freezing systems were answered and quality requirements and assumptions were discussed. Information gathered from this included:

- o Steam generation costs used in the economic evaluations were considered low by a factor of about two. Most chemical companies estimate that the total cost of generated steam is \$5 to \$6 per million BTU's.
- o The 316 L. stainless assumed as a material-of-construction in the cost estimates was felt to be more than adequate.
- o Our estimates of present distillation systems were not materially changed; any specific corrections have been incorporated in the analyses in this report.

Finally, the audiences were questioned about the requirements that must be met before they would accept this technology and use it in their operations. The discussions can be summarized by the comments of a technical director for one company; his remark was that if the economics are sufficiently enticing, his engineering department could make the process work and they would incorporate the process into their facility. None of the chemical companies were interested in a joint development/demonstration program. They felt that if the economics justified adoption of the technology that they would develop and use it internally without any further incentive.

Based on the comments from industry and the results developed in this program the following steps are suggested to DOE as a means of speeding the adoption of this very energy efficient technology by the chemical/petrochemical/petroleum industry:

- o Technology Transfer: When information on this process is developed -- either by any segment of DOE, by other government agencies, or when the information is made available by the private sector -- DOE should support its dissemination. This can be done by supporting journal publications, papers at relevant trade shows and technical meetings, and by more Technology Transfer Seminars where the information is taken to the user.
- o Economic Evaluations: It seems that these industries would prefer, almost totally, to perform technical development at their own expense. The decision to progress with the technical development is based solely on economics. Other DOE programs have established the major energy consumption products in these industries. This information could be used to construct a list of applications to be examined for freeze technology. DOE funding for these economics evaluations would then speed the development of economic data needed to justify any technical development.
- o Technical Development: It is unlikely that these industries will rely on DOE for technical development or demonstration of freeze separations in new applications. At the same time the technology is in its infancy for chemical applications. Much basic research and tests with individual components could provide experience that would be universally applicable to any chemical company developing a freeze separation system to make a specific separation. The thermodynamics of this technology are so favorable that DOE should not only support but should solicit programs to extend its use into the chemical industry.

CHAPTER 5

CITRUS JUICE CONCENTRATION INDUSTRY

INDUSTRY PROFILE

In 1973, 1.75 billion pounds of citrus juice concentrate was produced in the United States.¹ For every pound of concentrate produced, approximately 4 pounds of water must be removed from the dilute fresh juice. Presently this water is separated from solution by evaporation.

Concentration of orange juice alone makes up approximately 78 percent of the volume of the citrus concentrate industry.¹ The discussion below is confined, therefore, to this major segment of the industry. Orange juice is concentrated by Thermally Accelerated Short Time Evaporator (TASTE) units. These evaporators are able to concentrate orange juice from 10 degrees Brix (10°Bx) to 65° Bx (°Bx equals weight percent dissolved sugar content). However, orange juice concentrate is sold commercially at 45°Bx. One reason for this is that during evaporation concentration, some of the volatile juice components are driven off and lost. In order to improve taste, single strength (dilute) juice is added back and the resultant mix is therefore blended to 45°Bx prior to packaging.

The TASTE units are 6-effect evaporators utilized to minimize steam consumption. A survey of energy consumption in such evaporators shows that they consume about 260 BTU/pound of water evaporated. This total, as shown in Table 5-1, includes both evaporator steam energy and associated electrical energy for pumping requirements.

If orange juice were concentrated by the freeze concentration process described herein, it would be less energy intensive than the conventional TASTE units. Reports in the literature² show that orange juice can be concentrated to approximately 30° to 40° Bx. With recent technical developments, we feel that freezing can concentrate the juice to about 50° Bx. The freeze process we envision for this application is an indirect process, eliminating any volatile loss. This allows the producer to concentrate directly from 10° Bx to 45° Bx and then store and package without blending fresh juice. Thus, no juice would be stored at single strength. On the basis of the storage volume needed, freeze concentration is equivalent to present systems.

TABLE 5-1

ORANGE JUICE CONCENTRATION, ENERGY CONSUMPTION AND SAVINGS SUMMARY

	<u>UNIT ENERGY CONSUMPTION (per lb water separated)</u>		
	STEAM (BTU)	ELECTRICAL (kw-hr)	TOTAL (BTU equiv.)
6-EFFECT EVAPORATOR ^a (TASTE UNIT)	260	0.0013	273
FREEZE CONCENTRATION PROCESS ^b	0	0.0114	114
DIFFERENCE			159
U.S. PRODUCTION(1973) 1b of water per year separated from concentrate			6.93×10^9
POTENTIAL YEARLY ENERY SAVINGS BY FREEZING			
BTU/year			1.10×10^{12}
Equivalent barrels of oil/year			197,000

a To 65°Bx; volatile juice components lost, add-back required.

b To 45°Bx only, volatile juice components retained, add-back not required.

c kw-hr converted to BTU at electrical generating station fuel consumption of 10,000 BTU/kw-hr.

On a total energy basis, Table 5-1 shows that freeze concentration would consume less than one half the energy of conventional evaporators. An indirect freezing process using a freon refrigeration system requires only 114 BTU of fuel to generate the electricity required to separate a pound of water. This is the BTU equivalent of the system's electrical energy consumption by compressors and pumps. Based on the difference between the two figures shown, total annual oil savings of 197,000 barrels per year would result from freeze concentration replacing conventional methods.

ECONOMIC SUMMARY

During this project, a freezing process and a TASTE unit were economically compared for concentrating orange juice. Installed capital and energy costs were determined for both processes. The comparison basis, economic parameters, and results are presented in Table 5-2. As noted for the expansion case, wherein freeze concentration capacity would be added on instead of 6-effect evaporation, the pay out period based on annual energy savings for the capital cost difference is about 1.6 years.

It appears that the economic incentive for the implementation of freeze concentration as a replacement unit in the citrus industry is only marginal at this time. This is due in large part to the relatively low number of operating hours per year due to the seasonal nature of the industry. The greater than 50 percent unit energy savings of freezing over evaporation are not as fully realized in 3600 hours of operation as they would be in a chemical plant, for example, operating 8000 hours per year. The pay out period can be expected to decrease for both expansion and replacement cases as:

- o energy costs continue to rise and
- o freezing system capital costs decrease with further development and optimization in the years ahead.

TABLE 5-2

ORANGE JUICE CONCENTRATION ECONOMICS SUMMARY

Basis: 60,000 lb water separated per hour
 3,600 hours per year³
 \$3.50/10⁶ BTU steam cost⁴
 \$0.035/kw-hr electrical energy cost⁵

	<u>6-EFFECT EVAPORATOR^a</u> <u>(TASTE UNIT)</u>	<u>MECHANICAL</u> <u>FREEZING^b</u>
<u>CAPITAL COSTS</u>		
Capital Cost (\$)	710,000	906,000
Incremental Capital Cost of Freezing (\$)	-	196,000
<u>ENERGY COSTS</u>		
Annual Energy Cost (\$/yr)	206,000	86,000
Savings by Freezing (\$/yr)	-	120,000
<u>PAY OUT</u>		
Expansion Case - Incremental Capital Cost Paid Out by Freezing in Energy Savings in	-	1.6 yrs.
Replacement Case - Freezing's Capital Cost Paid Out in Energy Savings in	-	7.6

^a To 65°Bx; volatile juice components lost, add-back required.

^b To 45°Bx only, volatile juice components retained, add-back not required.

FREEZE CONCENTRATION

PROCESS SELECTION

The freeze crystallization system envisioned for orange juice concentration is an indirect contact process employing a mechanical refrigeration cycle. This simply means that the refrigerant does not come in direct contact with the solution being concentrated, but rather the cooling occurs across a heat transfer surface. As noted above, such an indirect process would eliminate volatile component losses.

Two other processes were considered initially but were rejected for the reasons noted below. A secondary refrigerant process, with its problems of separating the secondary refrigerant from the concentrated juice and ice, would be limited further by the interaction between the mixed refrigerant and the juice components. A freezing process employing waste heat for an energy source via an absorption cycle was also considered. Preliminary estimates showed that the low temperature in the freezer (10°F) resulted in a temperature at which the absorbent would require regeneration that was too high for energy efficiency in a single effect regenerator. With multiple effect regeneration in several stages, the cycle became economically unattractive because of the high capital cost.

PROCESS DESCRIPTION

The indirect process, shown schematically in Figure 5-1, cools the feed juice from ambient temperature to approximately 39°F in a plate and frame heat exchanger. The coolants, as shown, are the separated water and the juice concentrate. The feed is then pumped into the freezer, a shell and tube heat exchanger, which operates at approximately 10°F . The feed is partially frozen in the freezer to a 15% slurry of ice in the concentrate. The ice is separated in the wash column, and the concentrate is recycled to the freezer to get an overall high conversion to ice. A portion of the 15% ice slurry is recycled so that it, the concentrate from the wash column and the liquid feed, combine to a resultant freezer feed of $7\frac{1}{2}\%$ crystal concentration.

The resulting 15% ice concentrate slurry flows from the freezer to a tank providing hydraulic detention time for ice crystal growth. Growth of ice crystals to the proper size range is necessary for the proper functioning of the wash column. The slurry then passes on to the wash column (see description in Appendix) where the concentrate is displaced from the ice by a portion of the melt. The ice scraped from the surface of the wash column is reslurried by recirculating melted ice to the wash column's slurry trough.

FREEZE CONCENTRATION OF ORANGE JUICE
FIGURE 5-1

This slurry is then melted in tube side of the indirect melt heat exchanger. The still cold melt water and concentrate streams are conducted to the feed heat exchanger as explained above.

The heat is removed from the freezer by isothermal spray film evaporation of the refrigerant (Freon 22, chlorodifluoromethane) on the shell side of the exchanger. The refrigerant is then compressed to 73.3 psia where 78 percent of these vapors are condenses at 40°F on the shell side of the indirect melter. The remaining 22 percent uncondensed vapors are compressed to 211.9 psia where they condense at 100°F against cooling water entering at 80°F and leaving at 95°F in the heat rejection loop of the refrigeration system. The refrigerant condensates from the heat rejection condenser and melter then return to an accumulator, and then recycle back into the freezer.

Engineering Package

This section contains a summary in tabular form of the process design for the orange juice freeze concentration system:

- o Table 5-3 - Major Equipment List
- o Table 5-4 - Pump List
- o Table 5-5 - Line Index
- o Table 5-6 - Heat Transfer Summary

CAPITAL COST ESTIMATES

Table 5-7 presents the breakdown of the installed capital cost estimates for the freeze concentration system. The estimate for a 6-effect evaporation is shown for comparison. The freezing system estimate is based on the preliminary design previously described. The evaporator estimate was supplied by a juice processor. *

TECHNOLOGY TRANSFER

As part of the evaluation of the citrus juice application, we had conversations with the personnel of several companies to discuss technology transfer. These companies included:

- o Alcoma Corp.
- o Coco-Cola Foods Division
- o Lykes-Pasco Packing Co.

TABLE 5-3

MAJOR EQUIPMENT LISTORANGE JUICE CONCENTRATION

<u>Equipment Description</u>	<u>Surface Area (ft²)</u>	<u>Equipment Description</u>	<u>Surface Area (ft²)</u>
1. Serial No. 1000 Feed Heat Exchanger, Qty. 1 Plate and Frame Material: 304SS 244 Plates 2.5' Height 6' Length	1309	5. Serial No. 5000 Heat Rejection Condenser, Qty. 1 Material: Carbon Steel Shell and Tube (horizontal) Operating Pressure (400 psia) Shell I.D. 24" Tube O.D. 1" 1½" Tri-Pitch N=245 L=20'	1404
2. Serial No. 2000 Freezer, Qty. 14 Shell and Tube Exchanger (2-4) Shell I.D. 16"+6" Entrainment Tube O.D. 1" 1.25" Tri-Pitch L=20 ft. N=96 Material: 304SS (shell & tube)	6913	6. Serial No. 6000 Main Compressor, Qty. 1 Centrifugal with Motor Drives Inlet Pressure: 38.7 psia Outlet Pressure: 83.2 psia	<u>Horsepower</u> 584
3. Serial No. 3000 Melter, Qty. 1 Shell and Tube Exchanger (horizontal) Material: Carbon Steel with Epoxy Coating for Shell Side and tube side Pressure Capacity (400 psia) Shell I.D.=45" Tube O.D.=1" 1½" Tri-Pitch L=20 N=1000	4548	7. Serial No. 7000 Heat Rejection Compressor, Qty. 1 Centrifugal with Motor Drives Inlet Pressure: 83.21 psia Outlet Pressure: 210.6 psia	181
4. Series No. 4000 Crystal Tank, Qty. 1 Material: Carbon Steel 10' ID 15' Height Insulation 2" Polyurethane	<u>Volume</u> 1201 ft ³	8. Serial No. 8000 Wash Column, Qty. 1 Material: Fiberglass 8.4' I.D. 17' Height Cylindrical Screen 1' Height at Midsection Internals: Piping, & Metal Scraper with Motor	<u>Volume</u> 942.1 ft ³

TABLE 5-4

PUMP LISTORANGE JUICE CONCENTRATION

<u>PUMP NO.</u>	<u>DESCRIPTION</u>	<u>CAPACITY (#/hr)</u>	<u>HEAD (ft)</u>	<u>HP</u>
1	Feed to Feed Heat Exchanger	75,000	23.1	2.19
2	Recycle of Concentrate	1,425,000	28.85	37.75
3	Recycle of Crystal with Concentrate	4,275,000	24.0	86.36
4	Recycle of Ice Slurry Leaving Melter	1,200,000	20.0	22.03
5	Recycle of Refrigerant	100,000	15.0	1.90
TOTAL				<hr/> 150.23

TABLE 5-5

PIPING SYSTEMORANGE JUICE CONCENTRATIONLINE INDEX FOR JUICE AND WATER SUBSYSTEM

<u>Line No.</u>	<u>Description</u>	<u>Material</u>	<u>Size (in)</u>	<u>Mat'l in Line</u>
1000	Feed to Freezer	304 SS	3	10% DS Sugar, 90% H ₂ O
1010	Feed to Crystal Tank	304 SS	24	10% Ice, 50% DS Sugar, 40% H ₂ O
1020	Ice and Concentrate Recycle	304 SS	20	14% Ice, 50% DS Sugar, 36% H ₂ O
1030	Concentrate Recycle	304 SS	12	50% DS Sugar, 50% H ₂ O
1040	Feed to Wash Column	304 SS	14	4% Ice, 50% DS Sugar, 46% H ₂ O
1050	Feed to Feed Exchanger	304 SS	3	10% DS Sugar, 90% H ₂ O
1060	Brine from Wash Column	304 SS	1½	50% DS Sugar, 50% H ₂ O
1070	Water from Melter	304 SS	3	100% H ₂ O

LINE INDEX FOR REFRIGERATION SUBSYSTEM

<u>Line No.</u>	<u>Description</u>	<u>Material</u>	<u>Size (in)</u>	<u>Mat'l in Line</u>
2000	Recycle Refrigerant	Coated Steel	8	Freon 22 Liquid
2010	Inlet to Compressor (1)	Coated Steel	12	Freon 22 Vapor
2020	Outlet to Compressor (1)	Coated Steel	8	Freon 22 Vapor
2030	Inlet to Compressor (2)	Coated Steel	3	Freon 22 Vapor
2040	Inlet to Condenser	Coated Steel	3	Freon 22 Vapor
2050	Outlet to Condenser	Coated Steel	1½	Freon 22 Liquid
2060	Inlet to Freezer	Coated Steel	1	Freon 22 Liquid

TABLE 5-6

HEAT TRANSFER SUMMARYORANGE JUICE CONCENTRATION

Shell & Tube Exchangers	Heat Load BTU/hr	Individual Coefficients (BTU/ft ² hr°F)				Overall Coefficients U _o BTU/ft ² hr°F
		h _o	h _i	h _w	h _f	
Freezer	10.024 x 10 ⁶	302	762	1620	685	145
Melter	9.249 x 10 ⁶	270	444	1620	10,000	142
Condenser	2.492 x 10 ⁶	262	706	1620		164

Plate & Frame Feed Exchanger	Heat Load BTU/hr	Individual Coefficients (BTU/ft ² hr°F)					Overall Coefficients U _o BTU/ft ² hr°F
		h _{fj}	h _c	h _p	h _w	h _{ff}	
a) Feed-Melt	2.4 x 10 ⁶	728.9	-	833.3	2824	10,000	330
b) Feed-Concentrate	0.594 x 10 ⁶	728.9	118.5	-	2824	2,000	93.8

Nomenclature for Heat Transfer Coefficients

h_o outside of tubes
 h_i inside of tubes
 h_w tube wall or plate
 h_f fouling factor
 h_{fj} feed juice
 h_c concentrate
 h_p separated water
 h_{ff} fouling factor for plates

TABLE 5-7

INSTALLED EQUIPMENT COSTSORANGE JUICE CONCENTRATION

BASIS: 60,000 lb water separated/hr

FREEZING

<u>Item No.</u>	<u>Component</u>	<u>Installed Cost</u>
1	Feed Heat Exchanger	\$ 30,000
2	Freezer	107,300
3	Melter	48,600
4	Crystal Tank	54,200
5	Heat Rejection Condenser	14,300
6a	Main Compressor	272,200
6b	Pump & Compressor Driver	71,300
7a	Heat Rejection Compressor	64,800
7b	Pump & Compressor Driver	9,700
8	Wash Column	150,000
9a	Pump No. 1	5,900
b	Pump No. 2	22,400
c	Pump No. 3	33,500
d	Pupm No. 4	16,400
e	Pump No. 5	5,300
TOTAL		\$905,900

EVAPORATION

1	Six-effect Evaporator with Condenser	\$710,000 ⁶
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Concentration of orange juice by freeze concentration is not new. It was tried in the 1960's but was unable to compete economically with evaporation. This was mainly due to the scraped surface heat exchangers and centrifuges used for freezers and ice crystal separators, respectively. Capital and energy costs for the system employing this type of equipment are higher than for the system now proposed.⁷

Neither device is used in the process we propose for this application. A large recycle rate through a standard shell and tube heat exchanger to enhance heat transfer replaces the scraped surface exchanger, and a crystal growth tank and gravity wash column separates the ice crystals from solution in place of the centrifuge.

A major problem with the old freezing process was separating the ice crystals from the concentrate. The crystals produced in a scraped surface device are agglomerates that entrain concentrate with the ice matrix. Our process uses a crystallization tank which produces crystals in the 200 to 300 micron size range; this is optimal for their separation in a gravity wash column.

The methods noted above, which we propose to use, are relatively new and, therefore, require research and development to establish optimum design parameters and operating conditions. We feel that difficulties might arise with the increasing fluid viscosities at higher juice concentrations. Rates of nucleation and crystal growth have to be determined, as do the basic physical properties of orange juice at low temperatures and various concentrations (for example - heat capacity and thermal conductivity).

The only way that freezing is going to become a commercial reality is to first solve the problems that we expect, and identify any new problems on a small scale. Once this is accomplished, a demonstration unit should be built.

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CONCENTRATION

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APPENDIX A

FREEZE CRYSTALLIZATION SYSTEMS

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FREEZE CRYSTALLIZATION SYSTEMS

FREEZING PROCESSES

The investigation of freezing processes as a means of extracting pure water from a solution and/or concentrating a solution by such extraction has been actively pursued since the mid 1950's by the U.S. Department of Interior, Office of Saline Water (OSW), predecessor office to what is now the Office of Water Research and Technology (OWRT), and several industrial concerns. Several forms of freezing processes have evolved.^{1,2} All of the processes are based on the fact that when a crystal is formed from a solution, the crystal is pure solvent, excluding all impurities contained in the original solution. These processes have several inherent advantages that have given them potential economic attractiveness:

1. Low Energy Consumption
2. Low Corrosion Rates
3. No Pretreatment for Scale Prevention Required
4. Applicability to a Wide Variety of Solutions

Low energy consumption results from the use of a heat pump cycle to transfer the heat and the practicality of small temperature differences in the various parts of the cycles. The low energy consumption does not relate to the fact that the latent heat of fusion for ice is 1/7 that of the latent heat of evaporation.² However, this 1/7 ratio does reflect the ratio of heat to be transferred in the freezing processes vs evaporation processes and thus permits savings in heat transfer surfaces and the use of lower temperature differences.

Corrosion is said to double for each 10°F temperature rise. With much of the processes operating at or below 32°F, freezing has much lower corrosion rates than any evaporative process and thus lower cost materials of construction can be used. For sea water applications, the use of steel vessels, aluminum heat transfer surfaces and pvc piping has been well demonstrated in several pilot plants. The use of materials more exotic than 316 stainless are seldom required for corrosive chemical solutions, even in those that require the use of titanium, alloy 20, or hastalloy for evaporative processes.

Pretreatment of the feed for scale control is not required. For the direct contact processes, since there is no heat transfer surface where the concentration occurs there is no surface to

scale. The indirect contact processes use scraped surface heat exchangers and thus minimize scaling. For these solutions that contain low solubility salts, such as calcium sulfate, the resulting precipitates leave the process with the brine. Salts of higher solubility materials, such as sodium sulfate, must be separated from the ice prior to washing the ice if high purity melt is required.

Freezing processes are applicable to an extremely wide variety of solutions. Both organic and inorganic solutions can be treated. The solution need not be aqueous; several chemicals are now recovered by freezing them from an organic based solution. The processes insensitivity to fouling and scaling make it applicable where other concentration methods cannot be used or require prohibitively expensive pretreatment. The process is equally adaptable to process concentration, waste treatment or desalination applications.

GENERAL PROCESS DESCRIPTION

For all processes, a general process description can be applied, (Figure 1). The feed water passes through a heat exchanger and is cooled to within a few degrees of its freezing point by the melt and concentrate streams leaving the process. The feed enters a freezer where heat is removed, thus forming ice crystals. The resulting ice-concentrate slurry flows out of the freezer to a wash column (see next paragraph) where the concentrate is displaced from the ice by a portion of the melt. The ice is transferred to a melter where the heat removed in the freezer, after being elevated in temperature by a compressor or absorption refrigeration cycle, is reapplied to the ice to accomplish the melting. Because of work input by pumps and compressors and lack of perfect closure of the heat exchangers, there is more heat available in the melter than can be absorbed by melting the ice, and therefore, a heat rejection system is required to elevate this quantity of heat to a high enough temperature so that it can be rejected to an ambient sink.

The ice crystals that are formed in the freezer are pure, but are coated with concentrate. In order to remove this concentrate a device known as a countercurrent wash column is used. The wash column is a cylindrical vessel with screens, either in the walls of the column or in interior drainage tubes, at approximately the mid-point of the column. The ice-concentrate mixture is pumped into the bottom of the column and the concentrate flows out of the screens. The ice forms into a pourous plug, with a consistency much like a snowball. The continuing flow of concentrate through the ice plug propels it upward through the column. Meanwhile, a portion of the melted ice is sprinkled on top of the ice pack. This forms a nearly stationary layer in the upper portion of the column through which the ice passes and which displaces the concentrate. About 2% of the melt is lost in this process to provide a slight downward flow of melt to counteract the slight dispersion of concentrate at the concentrate-melt interface.

FIGURE 1
GENERAL PROCESS SCHEMATIC

PROCESS VARIATIONS

Several forms of freezing processes are currently being, or have been investigated to take advantage of freezing's benefits. They can be classified by several features which distinguish the various processes:

1. Direct or Indirect Contact Freezing

Direct Contact processes have been the most widely investigated and most likely to be used in large applications (above 50,000 GPD). Direct Contact means that the refrigerant being used to cool the fluid is mixed with the fluid being concentrated. The advantage of this type of process is that since there is no heat transfer surface where the concentration occurs there is no scaling (i.e., build-up of low soluble salts on the heat transfer surface) and the heat transfer coefficients are high which means very low energy consumption. The refrigerant may either be the fluid itself, usually water vapor, or a secondary fluid such as butane or a flouorocarbon refrigerant. Hence, the definition of a subclassification:

- (a) Vacuum process denoting those using the fluid being used as a refrigerant, or
- (b) Secondary refrigerant for those in which a separate refrigerant is added.

Indirect Contact freezing processes are those in which the removal of heat from the fluid being processed occurs through a heat transfer surface. The use of a surface increases the resistance to heat transfer and thus the energy requirements, although not sufficiently to eliminate this type of process from consideration. The surface adds cost to the process which is somewhat compensated for by the elimination of some components in an indirect contact process, compared to a direct contact process. In most forms, the use of a surface requires that a scraped surface heat exchanger be used which is a mechanical complexity. Some versions have eliminated this by washing and melting the ice in situ on the heat transfer surface. Another alternative that has been used to a limited extent is to limit the temperature differences, highly polish the heat transfer surfaces and operate at high velocities so that freezing on the walls is minimized. This approach still requires a scraper of sorts, although it is only used as a safeguard to prevent occasional ice attachments to the walls. Indirect contact is currently used for small applications -- up to 2-3,000 GPD and are likely to be developed for applications up to at least 10,000 GPD.

In general, vacuum freezing processes have higher heat transfer coefficients -- thus lower energy, while requiring somewhat larger equipment because of the very high specific volumes of water vapor. Secondary refrigerant processes are claimed to be more scalable to large sizes because the compressors are smaller and thus larger plants can be built with a single compressor. Because of the equipment necessary to recover the secondary refrigerant, the process is more complex and perhaps therefore more costly than vacuum processes. These differences are very small, however, and both secondary and vacuum processes are viable.

2. Method of Refrigeration

Three methods of providing refrigeration for freeze crystallization systems have been proposed -- mechanical compressors, ejectors, and absorption cycles.

- (a) Mechanical Compressors - Most processes have utilized mechanical compressors. In indirect processes, they have been quite conventional and not caused any problems. All direct contact processes have had some problems with compressors due to carryover of brine through the compressors. These problems are solvable, but each process development has required considerable effort to get this program under control. The Vacuum Freezing - Vapor Compression process required development of a special low cost high volume compressor and was eventually successful.
- (b) Ejectors - One vacuum process uses an ejector. This is used to eliminate the need to build extremely large compressors for large vacuum processes. Although inefficient by itself, it has been combined with an absorption refrigeration cycle to a moderately efficient process.
- (c) Absorption Processes - Use of an absorption cycle has been limited to vacuum processes. An absorption cycle eliminates the need to develop large volume compressors. Absorption cycles are less mechanically complex than vapor compression cycles. Use of an absorption cycle can eliminate a compressor in the rejection section of the process also, further reducing the cycle complexity. Efficiency of absorption cycles can be made quite high merely by adding effects to the absorber generator. The energy advantages gained in this manner must be traded off against the cost and complexity of added heat transfer surfaces.

3. Method of Melting

Direct and indirect melting is possible with most processes. Direct melting has been used in most direct contact freezing processes. It is the least expensive method both in terms of energy and capital. Two types have been used with equal effectiveness. Dumped bed melters in which ice is merely scraped into a volume, are a little less complex, not requiring fluidization of the ice at the top of the wash column. Packed tower columns in which a slurry of ice is cascaded over a packing, have been used successfully and are more scalable to larger size plants.

Indirect melters are those in which an ice slurry is passed through a heat exchanger and the refrigerant is condensed on the other side of the heat transfer surface. This type of melter is required when the fluid being processed contains volatiles which are not wanted in the resulting melt. Because it requires a heat transfer surface, it adds both energy and capital costs to the processes. Since heat transfer coefficients are lower for secondary refrigerant processes, the penalty is larger for them. All indirect freezing processes also use indirect contact melters.

2. Absorption Process

This process is the least mechanically complex process, not requiring a refrigerant compressor in the main cycle, but rather using an absorbent to transfer the heat from the low temperatures to ambient (Figure 3). Lithium Bromide and Sodium Hydroxide have been used as absorbents. The water vapor which evaporates in the freezer is absorbed in the absorber, heating and diluting the absorbent. The absorbent is kept cool with cooling water and recirculated through the generator where it is concentrated to its original strength before returning to the absorber. The vapor from the generator is used to melt the ice. Heat rejection is accomplished by a refrigerant cycle which condenses the excess water vapor produced in the regenerator. Lack of a main compressor is the main advantage of this cycle. With multiple effect regeneration of the absorbent the power can be quite low, but at the cost of a greater complexity. However, with a single effect regenerator, the process is not very efficient.

FIGURE 3
ABSORPTION FREEZING

PROCESS DESCRIPTIONS

Brief process descriptions are given for six of the freezing processes.

1. Indirect Freezing

This is the simplest freezing process and the only process currently being used commercially. Conventional refrigeration equipment is used and the only nonconventional device is the wash column (Figure 2). Feed goes directly to a scraped surface heat exchanger where the ice is formed. The refrigerant evaporated in the shell of the freezer is condensed in the shell of an indirect melter. The heat rejection is accomplished by compressing the excess refrigerant in the melter to above ambient so that it can be condensed on cooling water. The disadvantage of the process is that the scraped surface heat exchangers are very expensive and therefore the capital cost is high. In order to compensate for the freezer cost the temperature difference used in the freezer is high, thus increasing the energy costs. However, in small (less than 20,000 GPD) applications, this type of process is likely to continue to be the most economical freezing process due to its relative simplicity.

FIGURE 2
INDIRECT CONTACT FREEZING

3. Vacuum-Freezing Vapor-Compression Process (VFVC)

This process ^{4,5} has the least elements and most closely resembles the general case. As shown in Figure 4, water vapor is evaporated in the crystallizer, compressed and condensed in the melter. The heat removal system consists of a refrigerated heat transfer surface, located in the melter, on which the excess vapor is condensed. Because of the large volumes of vapor that would have to be handled in the air purge if the air in the feed were not removed, a deaerator is required. The primary advantage of this system is its relative simplicity. Disadvantages are its large size and low efficiency, both caused by the large volumes of low pressure vapor which must be handled, i.e., the crystallizer operates at a pressure of about 0.08 psia where water vapor has a specific volume of 4,600 cubic feet per pound. This has led to the development of special high volume compressors for small plants and limits module size to 250-500,000 GPD. The special compressor also makes this process unsuitable for many high concentration applications.

FIGURE 4
VACUUM FREEZING VAPOR COMPRESSION PROCESS

4. Secondary Refrigerant Process

This process ^{6,7,8} overcomes the disadvantages of low pressure- by introducing an immiscible refrigerant into the system, rather than using water vapor as a refrigerant (Figure 5).

Several refrigerants have been used including butane and R-114. The volume of vapor that has to be handled is about 1/100 that of water vapor. Because of the higher pressure operation it is economical to purge the air dissolved in the feed in the air purge system and eliminate the deaerator. Also, because of the higher pressures it is economical to compress the excess refrigerant vapor in the melter to a pressure high enough so that it will condense on cooling water. This eliminates the energy loss associated with condensing the excess water vapor on a refrigerated surface as in the vacuum freezing process. The primary disadvantage of the process is that additional equipment must be added to strip the refrigerant from effluent streams.

FIGURE 5
SECONDARY REFRIGERANT PROCESS

5. Vacuum-Freezing Ejector Absorption Process (VFEA)

This process attempts to overcome the size limitations and efficiency disadvantage of the mechanical compressors in the vacuum-freezing vapor-compression (VFVC) by combining an ejector and absorption system (Figure 6). An ejector powered by a portion of the steam produced in the regenerator replaces the main (mechanical) compressor used in the VFVC process. The absorption system and condenser also replaces the mechanical refrigeration system. The system is more complex than the previous systems described. However, it is less mechanical in that both the primary and heat removal compressors have been eliminated.

The system still retains the physical size disadvantage associated with low pressure operation. The use of steam as the primary source of energy is an advantage in locations where low cost steam is readily available, however, if steam generation equipment must be installed the additional capital equipment makes this process expensive and more complex, as well as requiring more energy than most of the other freezing processes.

FIGURE 6
VACUUM FREEZING EJECTOR ABSORPTION PROCESS

6. Absorption Freezing - Vapor Compression* (AFVC)

The AFVC process has been proposed based on the premise of having a highly efficient freezing process which requires little development, that can be easily scaled up, and is free from the compressor problems that have plagued other processes. This has been accomplished by using an absorption process with closed cycle refrigerant vapor compression for regeneration of the absorbent.

As shown in Figure 7, the feed enters the freezer after passing through a deaerator and heat exchanger. The water vapor which evaporates in the freezer is absorbed in the absorber. Cooling of the absorber is accomplished through a closed cycle refrigeration system which rejects its heat to the generator. The ice, after passing through the wash column is melted by the vapor released in the generator. This can either be direct or indirect, depending on the process requirements. Heat rejection is accomplished by cooling the absorbent which operates above ambient temperature.

The process eliminates the large compressors or ejectors required with the VFVC and VFEA process and substitutes a small conventional refrigeration compressor. Damage to the compressor due to entrainment is eliminated by using the refrigerant in a closed cycle, also eliminating the environmental concerns associated with secondary refrigerant processes. All of the process components have been previously demonstrated so that process development is minimized.

FIGURE 7
ABSORPTION FREEZING VAPOR COMPRESSION PROCESS

*Concentration Specialists, Inc. is currently filing for a patent on the AFVC process.

PROCESS COMPARISONS

The next two figures represent Concentration Specialists, Inc. economic and feature comparison of the various freezing processes.

Figure 8 compares the power consumption of the various freezing processes, vapor compression evaporators, and multiple effect evaporators. Sea water conversion was chosen for comparison because most of the economic studies made for freezing processes were for this application. Column 1 is the amount of electricity used by each process for producing 1,000 gallons of potable water. Column 2 is a direct conversion of electrical use into BTU's of electrical energy per pound of potable water produced. For those processes using steam, usage is indicated in Column 3 as BTU's of steam per pound of potable water converted. Column 4 converts energy consumption into actual fuel usage including inefficiencies in power generation and steam generation. Units are BTU's of fuel used per pound of product water. Column 5 shows energy costs for 330 days operation per year at \$.04 per Kilowatt hour and \$4.00 per 10^6 BTU's of steam.

Figure 9 is Concentration Specialists, Inc. subjective comparison of the various processes based on our extensive past experience.

P R O C E S S C O M P A R I S O N

100,000 GPD 3.5 Sea H₂O 50% Conversion

PROCESS	<u>KW/K Gal.</u>	<u>BTU-Elec. lb. of Water</u>	<u>BTU Steam lb. of Water</u>	<u>BTU Fuel lb. of Water</u>	<u>Energy Cost \$/Yr.</u>
Absorption Freezing-Vapor Compression (AFVC) (Direct Melting)	43	17	-	51	\$56,800
Absorption Freezing-Vapor Compression (AFVC) (Indirect Melting)	48	20	-	55	59,400
Vacuum Freezing - Vapor Compression	45	18	-	49	59,400
Secondary Refrigerant (Direct Melting)	50	20	-	55	66,000
Secondary Refrigerant (Indirect Melting)	60	25	-	66	79,200
Vacuum Freezing-Ejector Absorption	14	6	71	104	132,000
Absorption (1 Effect Regeneration)	14	6	166	223	263,000
Vapor Compression	70	29	-	76	92,400
3 Effect Evaporator	6	2	400	507	566,000
6 Effect Evaporator	9	4	200	274	313,000
12 Effect Evaporator	12	5	100	138	168,000

(1) Energy Cost Taken as 4¢/KW Hr. & \$4 per 10⁶ BTU Steam

FREEZING PROCESS COMPARISON

	VFVC	VFEA	Secondary Refrigerant	Absorption	Indirect	AFVC
COMPLEXITY	2	3	3	1	1	2
POWER CONSUMPTION FOR SEA WATER DESALTING	1	3	2	3	3	1
ENERGY SOURCE	Elec.	Steam	Elec.	Steam	Elec.	Elec.
ABILITY TO ACCOMPLISH HIGH CONCENTRATIONS	3*	3*	1	1	1	1
POWER CONSUMPTION FOR INDUSTRIAL WASTE	2	3	2	3	3	1
COMPRESSION SYSTEM COMPLEXITY	3	3	2	N/A	1	1
COMPRESSOR ENTRAINMENT	3	2	3	N/A	1	1
HAS PROCESS BEEN DEMONSTRATED	Yes	No	Yes	Yes	Comm'l.	No

SPECIAL PROBLEMS

VFVC -	Very special compressor, limited in size.
VFEA -	Requires large ejectors.
2nd Ref. -	Refrigerant separation and related problems.
Absorption -	Complexity becomes great if efficiency is increased.
Indirect -	Power consumption and ice on heat transfer surfaces limit to small plants.
AFVC -	Undemonstrated.

* Unsuitable in many cases

- 1 Best or Least
- 2 Moderate
- 3 Worst or Most

FIGURE 9

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APPENDIX B

DREW

Forest Chemicals Laboratory

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(904) 268-3177

October 12, 1978

FROM John Drew

FOR Mr. Paul Swydan

DFC No. 122

VISCOSITY OF BLACK LIQUOR

Purpose

The purpose of this trial was to determine the viscosities of various black liquor concentrations at various low Fahrenheit temperatures. A freezing point, if obtainable, was to be determined for each concentration of black liquor tested.

Equipment Used

For these particular viscosities a National Instrument Model VT-02 (high range) Viscosimeter was used. This viscosimeter was standardized with a known substance (SAG-470) at 2,000 cps. Standard deep freezes were used to take the liquors to freezing. An ice and acetone bath was used to maintain cold temperatures while viscosities were taken.

Liquors Used

Black liquors were obtained from two pulp mills: St. Regis, Jacksonville, Florida; and Alton Box Corp, Jacksonville, Florida. The St. Regis liquors were taken at 44% solids, 24% solids, and 15% solids and represent typical mill concentrations. The Alton Box liquors were taken at 35% solids, 32% solids, 26% solids, and 18% solids. For a more representative set of test samples, these liquors were reduced or increased to 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, and 55%. Both sets of samples came from similar digester feeds consisting mainly of slash pine with a small percent of hardwood, which is basically representative of a Southeast kraft mill.

Procedures and Methods

After dilution or reduction of each liquor to the proper concentration, three aliquots of 150 mls each were drawn and placed in a deep freeze. After maximum low temperature was reached, they were removed and placed in an ice and acetone bath. The temperature was increased slowly and viscosity readings were taken at 10°, 20°, 30°, 40°, 50°, and 80°F.

To determine an exact freezing point, each sample was held at the suspected temperature for some time. Liquors were then allowed to come to room temperature and another viscosity reading was taken. A percent solids was determined on each liquor sample using PCA Method No. 11, modified for black liquor. Each viscosimeter reading was recorded and then averaged for application on a graph.

Results

Table I contains both the averages and freezing points (where applicable) for each of the Alton Box liquor concentrations tested. Table II contains the same results for St. Regis liquor samples. Viscosity graph number 1 plots the data points for St. Regis liquor samples and Viscosity graph number 2 plots the Alton Box samples.

Conclusions

There is a significant variation in black liquor viscosities between pulp mills. Although the same wood furnish is used, other variables such as sulfite content and lignin content, affect the viscosities and freezing points of the liquors produced. Rather than obtaining an exact freezing point for a particular liquor concentration, it would be more feasible to determine a range. Within the two sets of samples we tested, those with 15% solids had a freezing range of 22°F to 28°F and those containing 25% solids froze from 15°F to 21°F.

At concentrations of 40% solids and above, the liquor became thick and gelled but would not crystalize. At these concentrations liquor evidently is amorphous and a freezing point cannot be determined.

Summary

Black liquor can be frozen at concentrations up to 35% solids. At concentrations above 40% solids the liquor thickens but does not freeze (verified to 8°F). Thus each pulp mill should be tested individually due to the many variables.

Don Andrews

da

attach: Table I, Table II, Graph 1, Graph 2

TABLE I

Alton Box Liquors

<u>% Solids</u>	<u>Temp. °F</u>	<u>Viscosity-CPS</u>	<u>% Solids</u>	<u>Temp. °F</u>	<u>Viscosity-CPS</u>
50	80	200,000	25	80	< 30
	50	> 400,000		50	< 30
	40	> 400,000		40	< 30
	30	> 400,000		35	35
	20	> 400,000		30	40
			21	Freezing Pt.	
40	80	100	20	80	< 30
	50	15,000		50	< 30
	40	55,000		40	< 30
	30	> 400,000		30	< 30
	20	> 400,000		25	Freezing Pt.
	10	> 400,000			
35	80	30	15	80	< 30
	50	260		50	< 30
	40	700		40	< 30
	30	950		28	Freezing Pt.
	20	1200			
	12	Freezing Pt.			
30	80	20			
	50	55			
	40	130			
	30	200			
	20	310			
	17	Freezing Pt.			

TABLE II

St. Regis Liquors

<u>% Solids</u>	<u>Temp. °F</u>	<u>Viscosity-CPS</u>
55	50	48,000
	40	85,000
	30	145,000
	20	350,000
<hr/>		
25	50	15
	40	20
	30	35
	20	40
	15	Freezing Pt.
<hr/>		
15	50	<30
	40	<30
	30	<30
	22	Freezing Pt.

SEMI-LOG
KELVIN

SEMI-LOGARITHMIC 4 CYCLES x 60 DIVISIONS
KELVIN
CENTIPOISES
46 5890

VISCOSITY #1

VISCOSITY OF ST. REGIS LIQUORS
GRAPH NO. 1

RED - 25% Solids

BLACK - 55% Solids

VISCOSITY #2

APPENDIX C

RESUME

PATRICK J. HURLEY

EDUCATION: B.S.Ch.E., Gonzaga University, Spokane, WA, 1961

EXPERIENCE: United States Navy, four years. Employed with Weyerhaeuser Co. for ten years. Five years in Technical Department of Longview Wash Pulp Mill. Five years in Corporate Engineering and Research and Development. Manager of Process Energy Design Group of Corp. Engineering for the two years prior to leaving Weyerhaeuser Co. Authorized a report published by the Institute of Paper Chemistry on Pulp Mill Recovery System (1978). Participated in DOE funded Thermal Energy Storage Project at Boeing Co. (1978). For past three years have operated as a consultant to Pulp and Paper Industry on a variety of energy related projects.