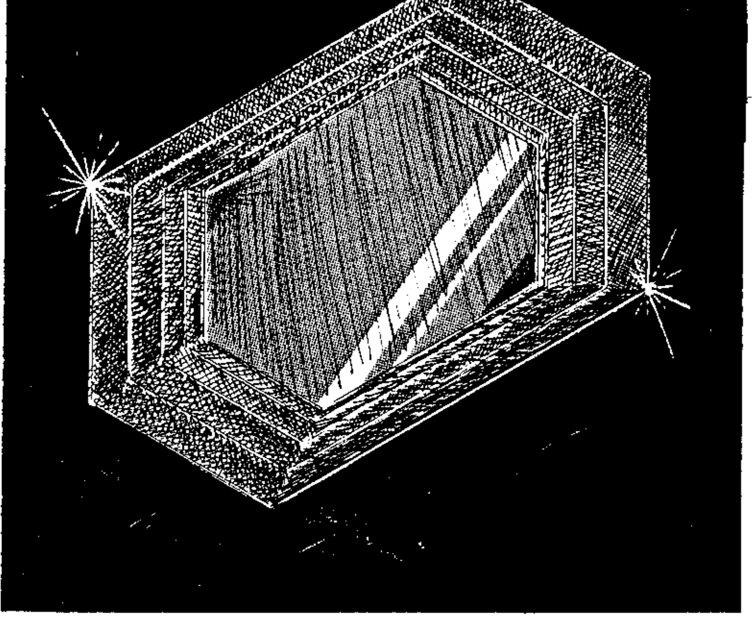

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Freeze crystallization

Fractionation of components of a solution by freeze crystallization can be more energy efficient than are conventional separation processes. This article presents the theory and practice of the process, and ways of performing economic evaluations.

James A. Heist, *Concentration Specialists, Inc.*

☐ Although the vapor-liquid equilibrium is generally employed to separate the components of a solution, use of the solid-liquid equilibrium should also be considered—it may be cheaper. Although freeze crystallization has been used to fractionate solutions in specialized applications, the technique has never been adopted on a large scale.

In some applications, freezing can perform a separation with a 75 to 90% reduction of the energy required by conventional distillation—acetic acid and acrylic acid refining are two examples.

Freeze crystallization also shows significant energy reduction in many applications for which evaporators are commonly employed. Here, the savings are not as spectacular as when replacing distillation, because most large evaporators employ energy-conserving multiple effects. Energy consumption of paper-plant black-liquor evaporators could be reduced by a half by using freezing, as could the energy used in the concentration of citrus juices.

Batch vs. continuous processes

In the past, most chemical process industry freeze separation processes have been batch operations. They have been labor intensive, inefficient (compared with their potential), and limited to low-throughput operations. These shortcomings have been tolerated because the process has been the only one that would work at all.

But, continuous process equipment is now on the market—equipment that makes available more of the inherent capabilities of the technology. Such equipment will be discussed later.

Advantages and disadvantages

Freeze separation is not the answer to every separation problem. Under some circumstances, either capital cost or energy consumption can be excessive.

Freeze separation is a relatively new process; although many of the equipment components are well developed, process and application work with them is still limited. Development work is needed on some of the simplified, less-costly freeze cycles—even some of the cycles that have been proposed and built are not fully developed.

However, experience with new applications in the chemical process industries will indicate where the present processes need improvement. Enough work has been done to warrant consideration of freezing for any separation process.

Some background

The history of modern freeze-separation processes dates only from the early 1950s, when the first continuous equipment was developed. Two very diverse routes were involved.

In the petroleum industry, Phillips Petroleum and then several others developed indirect-contact, scraped-surface heat exchange processes for the separation of xylene isomers. Although these developments were tested in the chemical and food industries, they proved to be too-expensive alternatives. So the xylene application remained the only large-scale user of that type of process.

At the same time, a number of direct-contact freeze separation processes were under development for seawater desalting. This was the first of the separation unit operations that received large-scale development funding from the (now defunct) Office of Saline Water; this funding was indicative of the process's potential for low energy consumption.

These desalting processes operated either at the triple point of water (vacuum freezing using either an absorption cycle or a vapor-compression cycle) or with a secondary refrigerant (both butane and halocarbon refrigerants were used). All of these processes were developed to pilot-plant scales of 10,000 to 100,000 gal/d. The plants were large by most process-application standards, but too small for water-supply applications. The *direct-contact* processes are inherently more efficient than the indirect, but are also (generally) more complex.

Several scraped-surface processes have been commercialized in recent years and have been applied in selected applications where the energy savings can justify this expensive type of heat exchanger. Now in advanced stages of development for industrial applications are freeze processes that use either direct-contact heat transfer, or scraperless exchanger surfaces.

The basis of freeze separation

All freeze separation processes are based on the difference in component concentrations between solid and liquid phases that are in equilibrium. This can be most easily understood by referring to Fig. 1a. As a solution (say, at Point A) is cooled, there will be some temperature at which a solid crystalline phase begins to appear in the liquid phase (Point B).

Usually only one component in the solution crystallizes, and that crystal is pure. This permits operation in a single theoretical stage—as contrasted to the incremental separation and multistage processes needed in vapor-liquid 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.

At the initial freezing temperature, only a small amount of crystal will be formed. As crystals of a component are formed, the concentration of that component remaining in the solution is decreased. This causes the crystallization temperature of the remaining liquid to drop minutely, so that a lower operating temperature is needed to effect further crystallization. Thus, higher conversions to the crystal phase require successively lower temperatures, as shown by the operating line BCD.

In a binary mixture, a point is eventually reached where both components crystallize simultaneously; this is called the eutectic, and is shown as Point D. At the eutectic, the concentrations of the solid and liquid phase remain constant. Removal of more heat converts more of the liquid phase to solid but without any change in temperature.

Individual crystals of the two components are pure. That is, two separate kinds of crystals are formed, rather than one crystal that incorporates the molecules of both components. In some cases, it is possible to fractionate these solid phases. This will be discussed briefly later.

In multicomponent solutions, the occurrence of a dual-precipitation point may not result in constant operating temperature. For example, when freezing the gas-liquor waste streams from coal-conversion processes, three separate solids are formed before a relatively constant operating temperature is achieved. Water and ammonium bicarbonate crystals are formed at progressively lower temperatures; finally, phenol begins to precipitate. In multicomponent solutions, the continued

Freeze-cycle descriptions

[illegible] classified by the [illegible] refrigeration [illegible] process. Although [illegible] processes are [illegible] mechanized [illegible] unique character to the cycle. The freeze processes are divided according to [illegible] mechanism, and subdivided by [illegible] refrigeration cycle.

Indirect-contact cycle. [illegible] heat from the freezing solution through [illegible] transfer surface. [illegible] one in which the refrigerant [illegible] process fluid is used.

☐ Scraped surface. When the [illegible] crystal growth comes through [illegible] crystallization will start on that [illegible] build-up, cutting down heat transfer. The conventional method in freeze processing [illegible] use of scraped surfaces to remove [illegible]

☐ Non-scraped surface. New methods are [illegible] development to eliminate buildup, and [illegible] expensive scraped-surface heat exchangers.

Direct-contact, secondary-refrigerant [illegible] [illegible] synthetic organic refrigerant (halocarbon) [illegible] volatile hydrocarbon (such as butane) [illegible] liquid, into the process liquid in the freezer. Since the pressure of the system is less than the vapor pressure of the refrigerant, the refrigerant boils up, [illegible] heat from the process liquid, thereby causing crystallization. A mechanical compressor is used to raise the pressure of the refrigerant to a point at which the refrigerant can be condensed by either cooling water or melting crystals.

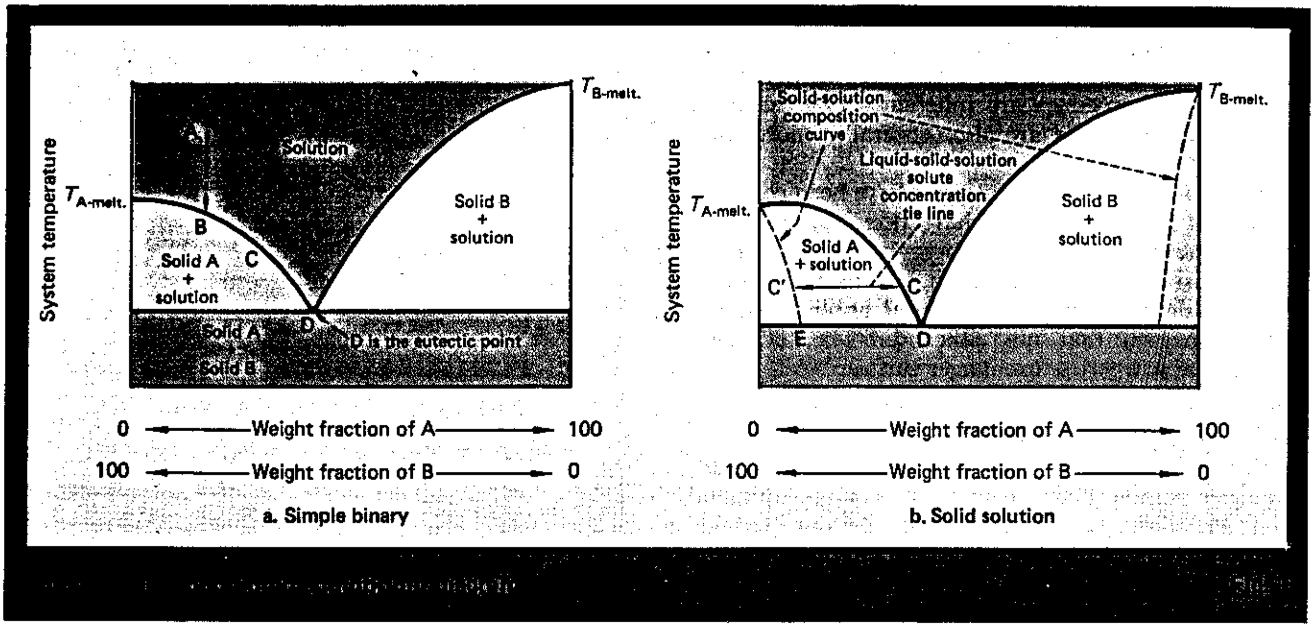
■ Subdivisions of this process are made by [illegible] the refrigerant used, and by the way the [illegible] mixed with the process fluid.

Direct-contact, triple-point processes. The triple point of a substance is that temperature and pressure at which vapor, liquid and solid [illegible] in equilibrium. Removal of 1 lb of vapor from the liquid will [illegible] lower the temperature, but will crystallize [illegible] the remaining solution. The processes [illegible] subdivided according to the method by which [illegible] vapors are removed.

■ Vacuum freeze, vapor-compression. The vapor phase is removed by a mechanical compressor that compresses the vapor sufficiently [illegible] condense either directly on pure crystals or [illegible] heat-transfer surface.

☐ Absorption freeze, vapor-compression. [illegible] process, the vapors are absorbed [illegible] has a vapor pressure below the [illegible] absorbent must be regenerated [illegible] (water removed) [illegible] sufficiently low [illegible] vapor compression [illegible] discharge [illegible] drawing off the absorbed material.

☐ Vacuum freeze, ejector absorption. [illegible] removed by two mechanisms [illegible] and a low-pressure steam ejector [illegible] the ejector is also [illegible] absorbent. The ejector [illegible] to raise the quality of the [illegible] vapor can be condensed.



a. Simple binary

b. Solid solution

concentration of impurities in the liquid phase depresses the freezing point of the eutectic composition by an amount dependent on the concentration of the impurity and the specific contaminant.

In some circumstances, two or more compounds can exist in the same crystal. Such crystals are called solid solutions and are common in metallurgy. (Alloy properties are a result of careful control of the solid solution concentrations.) However, such solutions are very rare in chemical and petroleum applications.

Since the liquid and solid phases in equilibrium with each other contain different concentrations of impurity, the crystal can be purified in a multistage crystallization-melting operation called zone melting [*1,2*]. This is the basis for: the multistage freeze-separation process developed by Union Carbide-Australia; the Brodie Purifier [*3*]; and a device recently announced in Japan by Kureha Chemical Co. This multistage capability results in greater process complexity and equipment expense; higher energy consumption is a tradeoff to minimize the added expense of the scraped-surface heat exchangers.

Components of freeze process systems

A continuous freezing process, such as that shown schematically in Fig. 2, consists of at least the following modules:

A *freezer,* where sufficient heat is removed from the process fluid to crystallize up to 15% of the mass.

A *crystal purifier,* where the crystal is separated from the unfrozen concentrate and washed with a few percent of the melted product to remove any adhering concentrate from the surface of the crystal. The separated concentrate is recycled to the freezer to provide any desired recovery.

A *heat pump* that takes heat out of the freezer and transfers it either to cooling water or to the melting crystal that is removed from the purification section.

A *feed heat-exchanger,* usually employed to precool the feed by using the cold product and concentrate, thus reducing the load on the freezer.

Each of these operations can be performed with different types of equipment. At least six processes, using significantly different equipment, have been devised and built in the size range of 50,000 to 500,000 lb/d of crystal removed. (Only one of these processes has ever been widely used commercially.) A summary of the six processes is included in Table I.

The major pieces of equipment that can be used for each unit operation are summarized in Table II, as is the status of the operation. (Another class of freeze separation processes—the hydrate processes—has been studied for water desalting, but they have limited application in the chemical process industries and are not discussed here.)

Solid-liquid equilibria data

The method of predicting or experimentally determining solid-liquid equilibrium is not important so long as it provides the accuracy needed for the intended use; preliminary analyses require much less precise data than would a final design. But, somehow, the data must be obtained because they are the starting point for any analysis or design of a freeze separation process.

Experimental procedures

Accurate and reliable knowledge of the phase equilibria for multicomponent solutions requires experimental data that usually do not exist and are difficult to obtain. Several techniques can be used by the engineer to obtain data from actual samples of the material to be processed:

- A *differential scanning calorimeter* can be used to obtain both initial freezing points and heat-capacity/latent-heat data. In some cases, this device can also predict high-recovery operations and eutectic formation.

- A *laboratory ice bath* will predict initial freezing temperatures of a solution—manipulation of the composition of numerous solutions provides data for constructing an equilibrium model for the system throughout the concentrations of interest.
- A freeze-separation *pilot plant* having adequate flexibility can operate over a variety of product-recovery ranges to give data for a particular application.

These methods are cumbersome, time-consuming and expensive. They should be used only when a decision to use a freeze-separation process has already been made, and accurate design data are required. For preliminary evaluations, there are predictive techniques that yield sufficiently accurate data.

Predictive techniques

Predictive techniques vary in their accuracy, and even the best methods lose accuracy around the eutectic point. Rather than going into solid-liquid equilibrium thermodynamics, we will review the various existing predictive techniques and refer the reader to the literature for more-comprehensive treatment.

Theoretical equilibrium—Freezing points of ideal solutions can be predicted from theoretical thermodynamics. In an ideal solution, the solubility of a solid (or the crystallization point of the dissolved material) is independent of the properties of the solvent and is given by the equation [5]:

$$\ln(1/x_2) = \frac{h_{fus}}{RT}\left(1 - \frac{T}{T_t}\right)$$

where x_2 = mol fraction of solute; h_{fus} = molar heat of fusion of the solute; T_t = triple-point temperature of the solute; and T = operating temperature for crystallization to occur at concentration x_2.

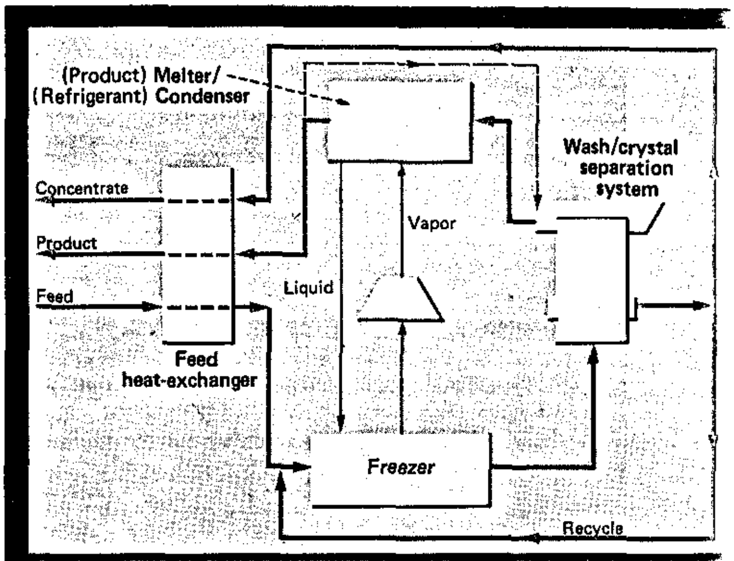
Real binary systems—The ideal equilibrium equation assumes ideal solid and liquid fugacities. In nonideal systems, the liquid fugacity is altered by an experimentally determined activity coefficient, γ, and the equilibrium equation then becomes:

$$\ln(1/\gamma\, x_2) = \frac{h_{fus}}{RT}\left(1 - \frac{T}{T_t}\right)$$

where R = ideal gas low constant.

Activity coefficients in solid-liquid systems are sparse but they do exist for many binary vapor-liquid equilibrium systems. Temperature/activity-coefficient relationships can be projected to the low temperatures associated with solid-liquid equilibria, and used with the above equation to predict binary system behavior.

Real multicomponent systems—The exponential increase in the possible number of multicomponent systems, with increasing numbers of components, requires that binary data be generated and used to predict vapor-liquid equilibria. Various equations have been proposed for combining binary data into multicomponent predictions. Some of the methods are discussed in Refs. [*6,7*]. This approach can also be used for solid-liquid equilibria predictions. Prausnitz and coworkers [*8–10*] have developed a technique using a functional-group-contribution method. This technique, originally developed for vapor-liquid and liquid-liquid equilibria, has recently been expanded to predict solid-liquid equilibrium as well [*11,12*].



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Process considerations

A wide variety of equipment is available to the process engineer as a result of the numerous options for each of the major unit-operations involved in a complete freeze-separation system.

At this stage in the commercialization of freeze-separation processes, no equipment supplier is likely to guarantee (nor is any user likely to purchase) a system without doing some pilot-plant work to demonstrate the abilities of the process.

A general procedure for evaluating new applications is discussed and illustrated later in this article. The procedure will yield total power requirements and capital costs for any prospective application. These are the data from which a process engineer can derive the economic incentive to use a freeze-separation process in place of conventional techniques.

Certain process variables associated with a prospective application can indicate the ability of freeze separation to work in a given situation.

Since reduced power-consumption provides the economic incentive for the process, anything that affects energy requirements is an important factor in the evaluation. The energy needed for a freezing separation is used to remove heat from the process solution. This heat is then pumped to a higher level, by the refrigeration system, so that it can be rejected to either cooling water or one of the process streams (e.g., to melt the crystal). Factors that affect power consumption include:

- Freezing temperature.
- Melting temperature of the pure crystal.
- Cooling-water temperature.
- Heat of fusion of the crystal.
- Heat-capacity ratio (C_p/C_v) of the refrigerant.

Usually, if the freezing temperature is not more than 50°F lower than the crystal melt temperature or cool-

Freezer type	Refrigeration cycle	Crystal separation	Washing	Application	Size, lb/d
Indirect, scraped surface	Closed cycle, fluorocarbon	Wash column	Yes	Xylene separation (other organic isomer separations as well)	50,000
Indirect, scraped surface	Closed cycle, ammonia	Centrifuge	No	Citrus juice concentrate	
Direct-contact, triple-point vapor compression	Triple-point compression	Wash column	Yes	Seawater	750,000
Direct-contact triple-point	Triple-point absorption cycle	Wash column	Yes	Seawater	50,000
Direct-contact, secondary refrigerant	Vapor-compression, fluorocarbon	Wash column	Yes	Seawater	600,000
Direct-contact, secondary refrigerant	Vapor-compression, butane	Wash column	Yes	Seawater	20,000

ing-water temperature, the energy consumption is very low (0.05 kWh/lb of crystal, or less). Temperature differences above 100°F result in large energy consumption (0.10 to 0.25 kWh/lb), and are justifiable only when the conventional process is unusually energy consumptive (2,000 to 5,000 Btu/lb of purified material). The 100,000 gal/d, vacuum-freeze vapor-compression seawater desalting plant, built by Colt Industries for the Office of Saline Water, operated at 45 kWh/1,000 gal, which equals 0.0053 kWh/lb.

A multicomponent eutectic (several crystals forming simultaneously) or the occurrence of a solid solution can require a multistage freezing process. In the case of the solid solution, a Brodie Purifier type of device can provide the multistage operation needed for fractionation. For eutectic operations, pilot-plant work has shown that the two crystals can be effectively separated if one is lighter than the process liquid, and the other heavier.

Gravity separations of two crystals can be made quite effectively, if the crystal growth conditions are controlled and the specific gravities differ by 5% or more.

Freezer/heat-pump systems

The only freeze-separation processes that have been demonstrated on large-scale equipment for non-seawater applications use indirect scraped-surface freezers. The scraped-surface heat exchanger adds significantly to the cost of the freezing process. Indirect freezers that do not require scraped surfaces have been the subject of past research. Development of this concept is now going on in several companies.

Triple-point freezers, using both compressors and absorption cycles, have been demonstrated in seawater pilot plants. The freezing apparatus is well developed, but the refrigeration cycles present major problems in certain applications. With a vapor-compression cycle, the volumes to be handled at the triple-point are relatively large, and the adiabatic head requirements often dictate a multistage compressor. Fans, centrifugals and blowers are the only compressors that meet the process requirements, but they all have limited adiabatic-heat capabilities.

The absorption cycle will work only if all volatile materials are absorbed. If a nonabsorbable volatile material is present in the process fluid, it will build up in the vapor space and inhibit the mass transfer between the process fluid and the absorbent.

Secondary-refrigerant freezers overcome many of the problems of the triple-point process. The refrigerant can be selected to yield any desired pressure at the freezing conditions. A smaller compressor (lower inlet volume) results, but the compressor savings must be weighed against the added complexity introduced by the refrigerant.

Refrigerants are always soluble (to some degree) in the process fluids, so both the product and concentrate must be stripped. Usually, this added complexity is justified only in larger plants, where the economy of scale favors the simple and low-cost design of the direct-contact freezer.

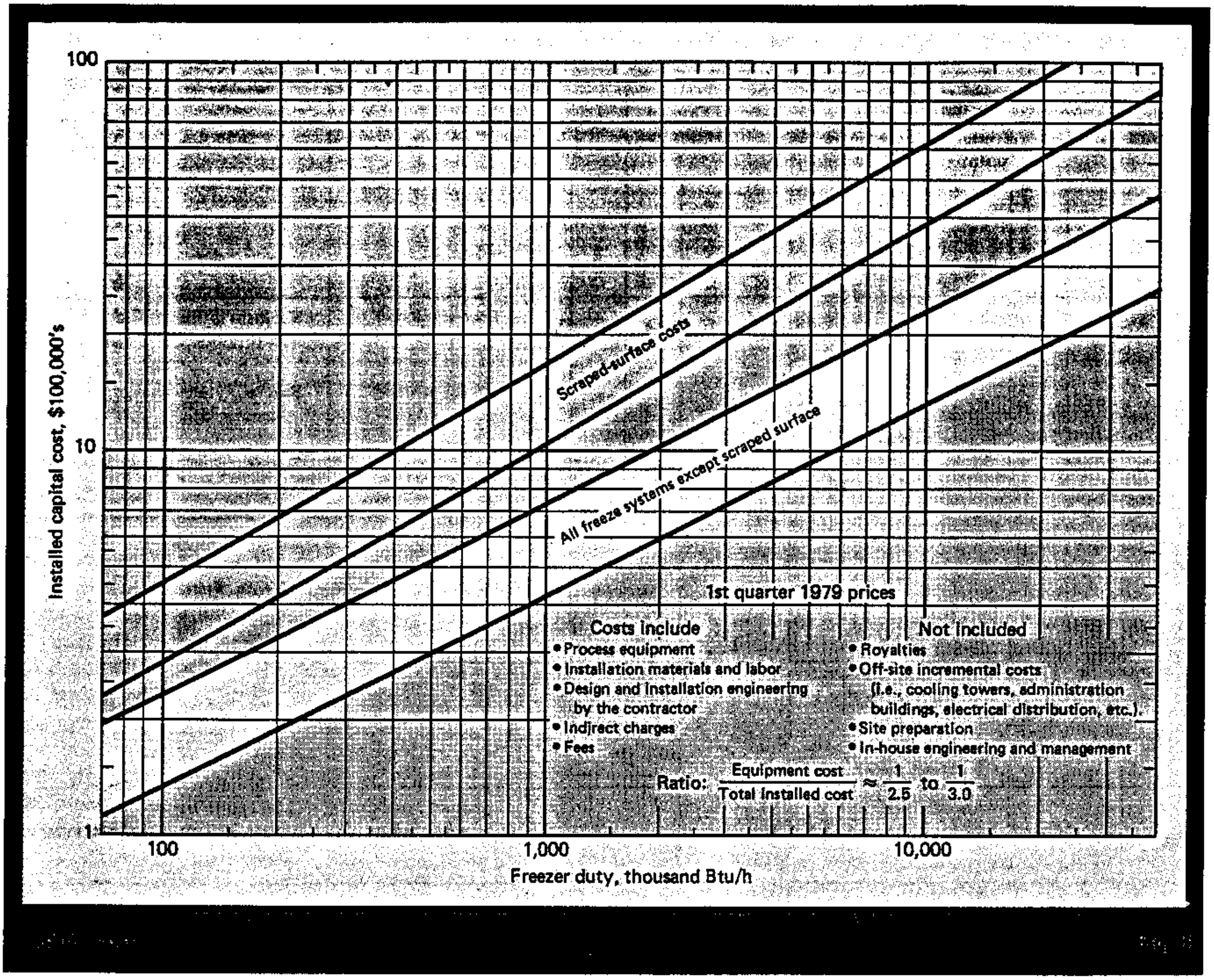
Crystal separation/purification

The *wash column* has proven a very effective device for both separating the crystals produced in the freezer and purifying them. For a slurry to remain pumpable, the upper limit on crystal content cannot be over 15 to 20%, so the column has to remove a great deal of liquid. To

Freezers/refrigerators								Crystal separation		Melting			
Indirect contact		Triple-point			Secondary refrigerant								
Scraped surface	Non-scraped surface	Vapor compression	Steam ejector	Absorption	Butane	R-114	R-C318	Centrifuge	Wash column	Direct	Indirect	Process name	Status
✓									✓		✓	Brodie purifier Phillips crystallizer Kureha crystal purifier	Six installations worldwide, all on organic separations Several xylene separation installations Two installations on organics
✓								✓			✓	*Orange juice*	*Tested on* >10,000-lb/d equipment during mid-1960s. Fruit-solids losses in centrifuge. Project abandoned
		✓							✓	✓		Vacuum freeze, vapor-compression	100,000-gal/d plant for Office of Saline Water (OSW) in late 1960s by Colt Industries
			✓	✓					✓	✓		Vacuum freeze, ejector-absorption	6,000-gal/d bench-scale plant built for OSW in late 1960s by *Colt Industries*
				✓					✓		✓	Absorption freeze, vapor-compression	25,000-gal/d seawater pilot plant now being built for Office of Water Research and Technology (OWRT) by Concentration Specialists
					✓				✓		✓	Immiscible refrigerant freezing process	10,000-gal/d seawater bench-scale unit built for process development by U.K. Atomic Energy Authority
					✓				✓	✓		Secondary refrigerant freezing process	15,000-gal/d seawater plant built for OSW in late 1960s by Carrier Corp.
						✓			✓		✓	Crystallex	75,000-gal/d seawater plant built for OSW in early 1970s
							✓		✓		✓	Direct-freeze separation process	Bench-scale tests for OSW in mid-1960s by Avco

work effectively, the column should receive a stream of relatively uniform and large (>150 μm) crystals. The wash column is unable to separate two different crystals unless one of them is more dense than the process fluid, or unless it is so small (<25 μm) that it can be washed out.

Centrifuges have been used for crystal separation in some xylene fractionation systems, and in a developmental program on citrus-juice concentration. A centrifuge can remove most of the brine from the crystal mass, but it lacks the wash column's abilities to counterwash the crystals with melted product. In the citrus application, this drawback led to excessive loss of fruit solids.



Filtration has proven less effective for crystal separation. It also cannot be used for washing the crystals. And, the screens or filter-cloths have a history of "freezing up" (brine freezing in the openings of the weave).

For separating eutectic crystals, it may be necessary to use the centrifuge, followed by reslurrying of the crystals in a wash column. When one crystal is heavier than the solution and the other is lighter, the separation can be made hydraulically; when they are both lighter (or heavier), this cannot be done. Scroll centrifuges can make fractional separations based on relatively small differences in specific gravities—as demonstrated when the precipitates from lime softening operations are separated for purging impurities from the calcium salts before recalcination.

Melter/condenser

As explained earlier, much of the refrigerant vapor can be condensed at low temperatures by melting the crystal products. The device for doing this can be either a direct-contact or shell-and-tube one. Direct-contact condensers are used only with direct-contact freezers; in an indirect cycle, the refrigerant remains isolated, to simplify the refrigeration system and ensure reliability.

Under some circumstances, an indirect melter-condenser may be mandatory—i.e., when product purity is essential, or refrigerant losses due to solubility are excessive.

Solid-liquid equilibria analyses

For preliminary analyses, crude estimates can be made in a number of ways. A binary solution is the simplest system to work with, and it can often be assumed in the preliminary work. The International Critical Tables [*13*] have data in various sections, often expressed as freezing point depressions, that approximate more-complex solutions.

Theoretical calculation of the temperature-solubility relationship can be used in organic solutions to predict both temperatures and eutectic compositions—this relationship becomes less accurate as the difference in molecules increases. Solution properties of electrolytes in water can be predicted by the colligative properties; the necessary details are available in most physical chemistry texts.

If your company has the computer program FLOWTRAN, or a similar simulations program with physical property generation, it can be used to provide the needed data.

Before final design or any major commitment is made, laboratory analyses with real (not simulated) solutions should always be made.

Process definition

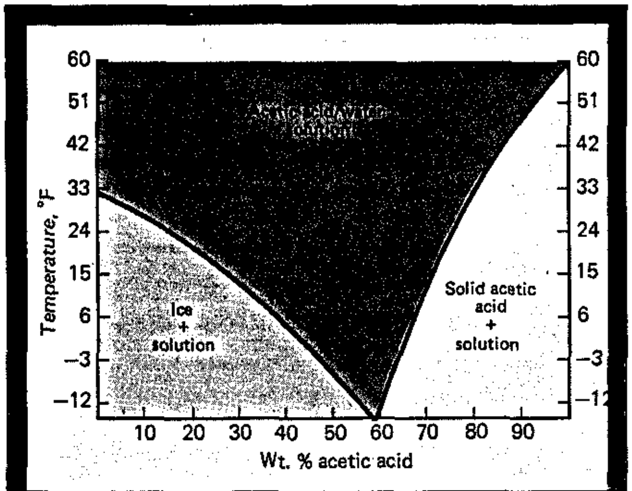
Once the temperature/composition relationship has been defined, a process can be formulated to make the separation. Here are a few generalizations to note:

- First, determine the total recovery; if sufficient recovery can be achieved before a eutectic is reached, the system will be much simpler. Eutectic separations are best done in a separate stage dedicated to that purpose. Separation of the two crystals must be accomplished so that the product-rich stream can be recycled for purification, and the other material purged from the system. This separation can be nearly ideal—as occurs when the specific gravities of the crystals are above and below that of the solution—or as low as only a few percent upgrading of the product concentration.
- If the final crystallization stage is more than 40°F lower than the initial freezing point, a second stage that is designed to carry half of the freezing heat load is usually economically justified by virtue of energy reduction. In small systems (<500,000-Btu/h freezer heat load), a single-stage process is most economical.
- Three-stage systems are seldom justified on energy savings alone, unless the system is very large (>25-million-Btu/h freezer heat load). If a second eutectic point is reached, and it is desirable to separate the second and third crystals from each other, then a third stage should be added, so as to produce as much as possible of the second crystal (in Stage 2) independently of the third (produced only in Stage 3).
- At this point in the evaluation, it is not necessary to stipulate the freeze cycle beyond differentiating between scraped-surface and nonscraped-surface types. The scraped-surface cycle can be substantially more expensive than the others.
- If a solid solution occurs, one of the multistage fractional-crystallization processes must be used, unless the solid solution concentration of impurities is low enough not to cause a problem.

Mass and energy balances

Once the number of stages and the operating conditions in these stages have been defined, a total mass balance can be constructed around the system. Process heat loads on the freezers can be calculated from the heat of fusion of the crystallized material, together with the sensible heat load in cooling the process fluid between the inlet and discharge temperatures of that stage. In calculating the heat load, the following assumptions can be used for simplification:

- The full feed stream is cooled to the discharge temperature, and then the crystal is precipitated at the low temperature.
- Pumps and mechanical agitators add energy, ultimately in the form of heat. Full-shaft horsepowers are converted ideally at 3,413 Btu per kWh, or 2,545 Btu/(hp)(h). In small, multistage systems (i.e., <100,000 Btu/h), add 25% to the freezer heat load for mechanical heat additions. For large multistage systems (>500,000 Btu/h total process heat load), add 15%, and for large single-stage systems, 10%.



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- Ambient heat loads also have to be removed by the refrigeration system, and are seen by the system as process heat load. This is usually about 10% of this load.
- Take the sum of these three heat loads to estimate the capital cost of the system, by using Fig. 3. No further process or design calculations are necessary for a preliminary evaluation. For intermediate levels of sophistication, the individual components must be designed. Operating and maintenance costs can be estimated from the energy balance carried out as above.

Component sizing

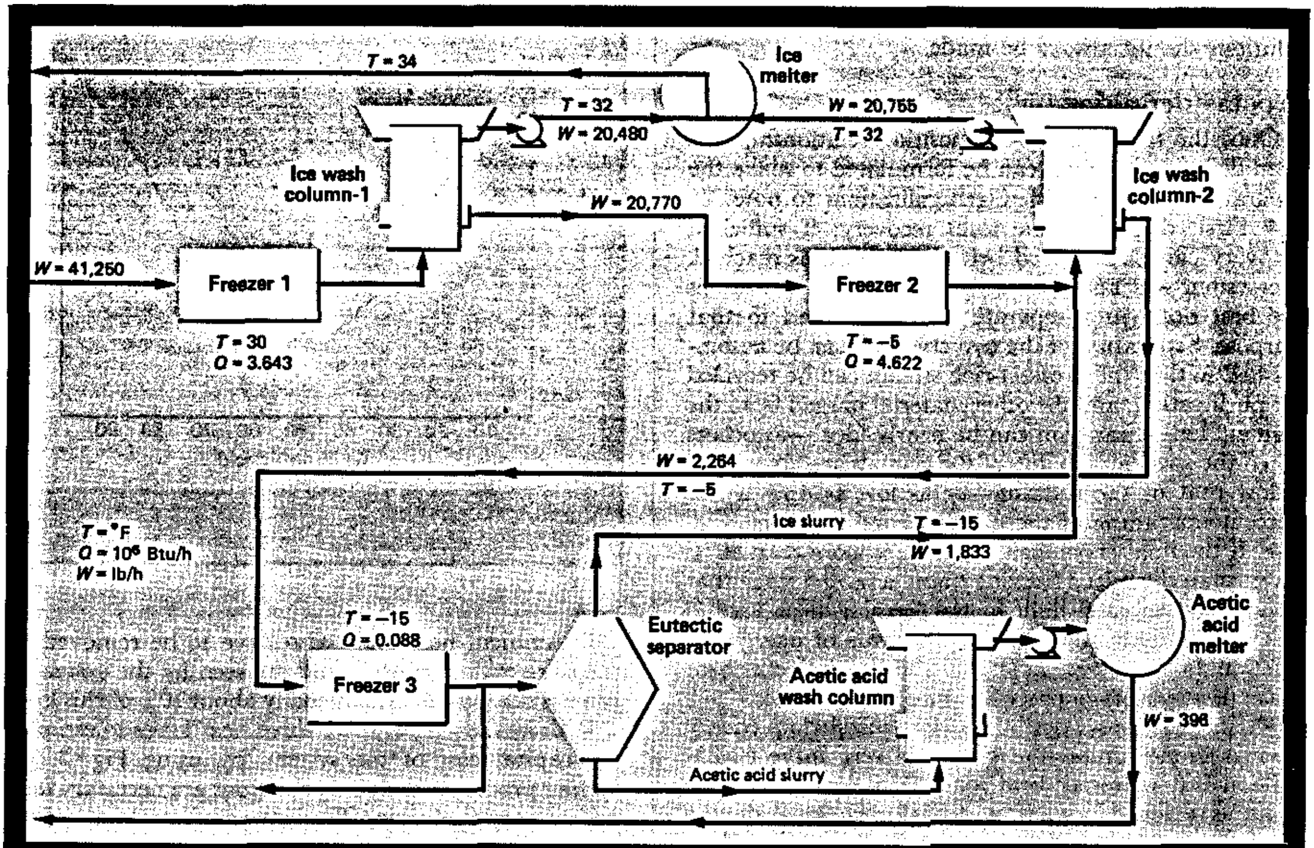
The individual pieces of process equipment can be sized by using criteria available in the literature, by getting performance estimates from equipment suppliers, or by applying performance data from similar equipment with which the engineer is familiar.

Cost estimates

Crude capital costs can be estimated by using Fig. 3. In a multistage process, the heat load on each stage should be estimated, and the cost per stage then estimated and totalled to give the system cost. These costs are on an installed basis and include: equipment, installation materials and labor, engineering (by the contractor only), and indirect charges. Not included are: offsite incremental costs (e.g., electrical distribution, cooling towers, boilers), site preparation, in-house engineering, management or administrative costs, and royalties.

The direct-contact processes and the nonscraped-surface indirect-contact processes have capital costs that are relatively the same, and have therefore been lumped together in one band on the cost curve. The costs of the scraped-surface system reflect systems that have been designed for energy conservation rather than economic optimization. Local conditions and energy costs will affect these capital costs.

The driving forces (ΔT's) used in determining the costs have generally been 10 to 20°F; depending on process variables, cost minimums can require ΔT's of 40°F or more. Since scraped-surface devices are the



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biggest costs in those systems, that design philosophy can reduce capital costs significantly.

The major operations and maintenance costs are for energy and operating/maintenance personnel. Maintenance costs for crystallization systems are the best basis for this estimate, if the user has experience in that area.

Otherwise, a value of 6 to 9% of the capital cost can be used to estimate the yearly maintenance budget. The process requires only one operator per shift if a manpower pool for maintenance assistance is available. The process is usually heavily instrumented, and large plants should have an instrument mechanic assigned full time (one shift per day).

Energy costs can be estimated from the energy balance. Refrigeration-system power requirements will depend on the operating temperatures and the ΔT's assumed. (See the following example for details on this calculation. Note that, in the example, the refrigeration system is a cascade arrangement to minimize energy consumption.)

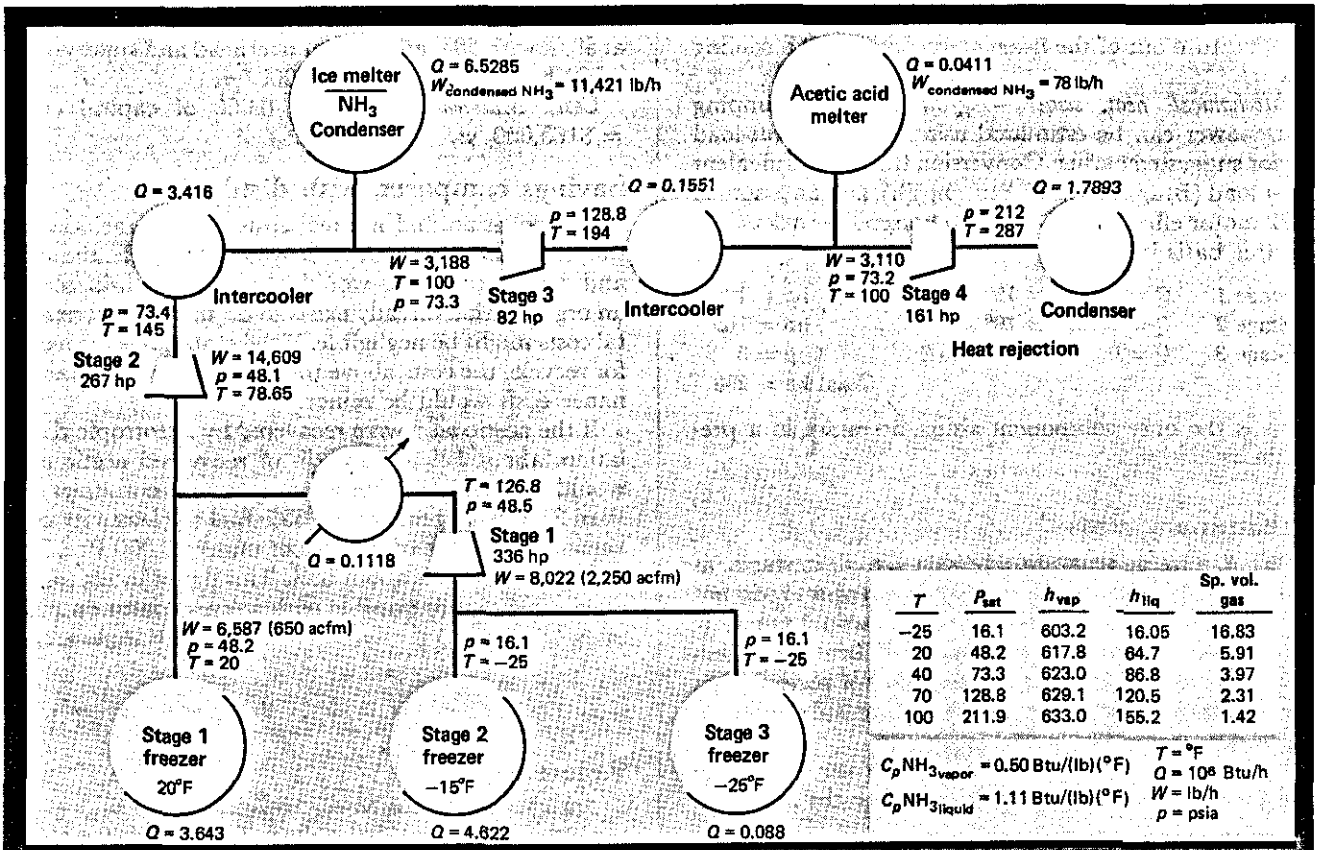
Cooling-water requirements are needed for compressor intercoolers and the final refrigerant condenser that is used to reject heat from the system. (All ambient heat loads, mechanical additions, inefficiencies, and exothermic concentration effects must be rejected from the system by compressing the refrigerant to a high enough temperature to transfer that heat to cooling water.)

Sample calculation

Application

In the chemical process industries, weak aqueous acetic acid streams are typical of many wastes. They are

Physical data											Heat loads, Btu/h X10^{-6}				
	Water				Acetic acid				Operating temperatures		Sensible		Latent		
Stage	In, lb/h	Crystallized, lb/h	C_p	λ_{fus}	In, lb/h	Crystallized, lb/h	C_p	λ_{fus}	T_{in}	T_{out}	Water	HAc	Water	HAc	Total
1	41,250	20,480	1.0	144	416	–	0.52	–	30	28	0.0825	0.0004	2.9491	–	3.0356
2	20,770	20,480	1.0	144	416	–	0.52	–	28	–15	0.8931	0.0093	2.9491	–	3.8515
3	290	275	1.0	144	416	396	0.52	84	–15	–16	0.0003	0.0002	0.0396	0.0333	0.0734



T	P_{sat}	h_{vap}	h_{liq}	Sp. vol. gas
–25	16.1	603.2	16.05	16.83
20	48.2	617.8	64.7	5.91
40	73.3	623.0	86.8	3.97
70	128.8	629.1	120.5	2.31
100	211.9	633.0	155.2	1.42

$C_p NH_{3_{vapor}}$ = 0.50 Btu/(lb)(°F)
$C_p NH_{3_{liquid}}$ = 1.11 Btu/(lb)(°F)

T = °F
Q = 10^6 Btu/h
W = lb/h
p = psia

Freeze separation process for recovery and refining of weak aqueous acetic acid streams **Fig. 6**

produced from such operations as fiber spinning and partial-oxidation processes.

Freeze separation is uniquely able to recover the organic components in these wastes, by crystallizing and separating ice. In the case of acetic acid, no other process is capable of economic recovery.

Recovery of the acid has an added advantage because it would otherwise incur high waste-treatment costs.

These waste streams typically have 1 to 5% organics. In some cases, the organic fraction is predominantly acetic acid. In partial-oxidation wastes, the stream is usually predominantly acetic, with two or three other acids present at 10 to 20% of the weight of acetic acid. For this example, we will consider a stream containing 1% of acetic acid only.

Solid-liquid equilibria

The water/acetic-acid binary is well studied, and data are available in the literature—these are summarized in Fig. 4. Note that the eutectic point is at 59% acetic acid and −16°F. If the stream contains no (or few) impurities, all of the acid can be recovered.

Process definition

The basis for this calculation is: 1 million lb/d of feed (or approximately 83 gal/min); 1% acetic acid; 95% recovery of the acid.

Since the initial freezing point is 30°F, and the eutectic point is at −16°F, the dehydration step will be done in two stages, with a third stage operating at the eutectic to crystallize acetic acid and water simultaneously. The two crystals can be separated very effectively by gravity. The ice (sp. gr. = 0.92) floats in the solution (sp. gr. = 1.03), while the acetic acid crystals (sp. gr. = 1.05) settle to the bottom. The first two stages are designed for equal ice removal. The process schematic is shown in Fig. 5, and the energy balance in Table III.

The refrigeration system is cascaded, as shown in Fig. 6. For simplicity, we will assume an indirect process with an ammonia refrigeration cycle. The 20% added heat load for pumps and ambient loading is included in the values shown next to each freezer.

If capital costs are all that is required, this information is sufficient for estimating. However, a complete evaluation requires some estimate of the operating costs as well. Major operating costs are: power, manpower and maintenance. Power estimates require some equipment sizing.

Component sizing

Compressors—Heat loads and operating conditions in the compressors are shown in Fig. 6. The suction pressures of the first two compressor stages correspond to the saturated temperatures of the freezers. The suction and discharge pressures for Stages 3 and 4 correspond to the pressures at which the refrigerant will condense in the ice and acetic acid melters—in this case, condensing at 40°F when melting ice (32°F), and at 70°F when melting acetic acid (61°F). Note that the suction temperature to Stages 3 and 4 are both 100°F, which is the temperature out of the intercoolers (using 80°F cooling water).

Mechanical heat sources—Agitation and pumping horsepower can be estimated using the 10% heat-load factor suggested earlier. Conversion from the equivalent heat load (Btu/h) is 2,545 Btu/(hp)(h), and an assumed 0.92 motor efficiency. The pump horsepower calculated on this basis is:

Stage 1	$Q = 0.3036 \times 10^6$ Btu/h	hp = 130
Stage 2	$Q = 0.3852 \times 10^6$ Btu/h	hp = 165
Stage 3	$Q = 0.0073 \times 10^6$ Btu/h	hp = 3
		Total hp = 298

This is the only component sizing necessary in a preliminary design.

Preliminary costs

When a freeze separation process is built in stages, as in this application, all of the economies-of-scale do not apply. However, a refrigeration system would normally be built in stages with intercoolers. Combined wash columns would achieve good economy of scale so that the economic advantage of size would still apply to some degree.

As a conservative measure of capital costs, each stage should be priced separately. Here, using the heat load on each freezer, and the capital cost chart (Fig. 3), the cost of each stage is:

Stage	High estimate, $	Low estimate, $	Average, $
1	1,500,000	900,000	1,200,000
2	1,700,000	1,000,000	1,350,000
3	210,000	125,000	170,000
		Total	2,720,000

Equipment costs for this system would be $700,000 to $1 million. Note that the midpoint costs from the band in Fig. 3 were used; the band represents a +35/-15% range that results from the uncertainty of the application and process details at this point.

All of these data are meaningless unless they can be converted into costs and benefits. Methods for an absolute analysis vary between companies, but the basic data are easily developed at this point.

Benefits—Acetic acid value at $0.24/lb. 9,500 lb/d × 365 d/yr × 0.94 time onstream × 0.24/lb = $780,000/yr.

Biological treatment credit—1.067 lb COD/lb acetic × 0.6 lb BOD/lb COD × 10,000 lb acetic/d × 365 d/yr × 0.94 onstream × $0.12/lb BOD = $265,000/yr. (Note, COD = chemical oxygen demand, BOD = biochemical oxygen demand.)

If a biological treatment system is already installed, only the operating portion of this $0.12/lb BOD would be saved. Biological treatment costs are divided approximately equally between amortization and operating costs.

Costs: Power—Refrigeration, 850 hp; pumps, 200 hp; total, 1,050 hp. 1,050 hp × 0.7457 kW/hp × 24 h/d × 365 d/yr × 0.94 onstream × $0.03/kWh = $195,000/yr.

Costs: Manpower—Assume one man assigned full time at $8/h with 50% add-ons for overhead and supervision. 8,760 h/yr × $12/h = $105,000/yr.

Costs: Maintenance—Assume 0.060 of capital costs = $165,000/yr.

Savings compared with distillation

Amortization and indirect costs are not included in this analysis. If the acid is recovered for resale, the sales and distribution costs would have to be considered. If an organization already exists to do this, the incremental costs might be negligible. If the material is recovered for recycle, the costs above these operating and maintenance costs would be minor.

If the acetic acid were recovered by azeotropic distillation, about 125,000 Btu/lb of recovered acetic acid would be required. The freezing system consumes less than 2 kWh/lb product. At 35% fuel-to-electricity conversion, this is the equivalent of under 20,000 Btu. The energy reduction is about 85%. This figure indicates the energy reductions possible with freeze-separation processes. ***R. V. Hughson, Editor***

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HEIST ENGINEERING CORPORATION

HAZARDOUS WASTE MANAGEMENT APPLICATIONS
USING FREEZE CRYSTALLIZATION PROCESSES

Freeze crystallization is proving to be a versitile and economical process for treating liquid - both aqueous and organic - hazardous wastes. The variety of applications is outlined below and detailed in the attachments. The generic abilities of the process are addressed in the following paragraphs. We hope that with this information an understanding of the process will be conveyed that will enable you to identify applications within your organization for which freeze crystallization might be appropriate.

A variety of hazardous waste applications (facilities, locations or effluents that are governed by the RCRA and/or CERCLA legislation) have been examined for which freeze crystallization has been shown to have technical and/or economic superiority over alternative treatment processes. Among these applications are:

- Treatment-Storage-Disposal (TSD) Facility lagoons have a mixed aqueous waste from which freeze crystallization can extract effluent quality water and produce a concentrate and sludge that can be economically stabilized and/or incinerated.

- Metal Finishing Industries produce a variety of wastes that can be individually concentrated by freezing, producing an effluent of superior quality to that from conventional treatment processes. Often the concentrates can be recycled within the metal finishing operations, reducing purchases for expendibles within the process and eliminating sludges and spent activated carbon.

- Pickle Liquor is a 5 to 10% sulfuric or hydrochloric acid solution that contains from 5 to 10% dissolved iron. It is used to clean steel before forming operations and often before metal finishing. Freeze crystallization concentrates the waste acids so that they can be reused in the cleaning operation. The dissolved iron is precipitated at the low temperatures, and recovered as a by-product from the freeze process.

- Incineration Enhancement is an attractive application for the process because of the increased capacity and reduced energy consumption of the incinerator. In typical applications the freeze crystallization process removes from 75 to 95% of the water from the waste, and the concentrate is sufficiently concentrated in organics to eliminate the need for additional firing in at least the primary incinerator chamber.

- Incinerator Scrubber Blowdown contains the residues of the combustion operation. This stream is usually a highly concentrated brine of either calcium or sodium chloride. The freeze crystallization process is used to recover solid salts that become by-products rather than wastes for disposal.

- Solvent Recovery is enhanced by freeze crystallization when compared to current evaporative processes. Typical spent solvents are mixtures of a variety of solvents and the residues that they are used to remove. Current evaporative processes are unable to fractionate the solvents, so the recycled product has less value. The current processes are also unable to recover the more volatile solvents such as methylene chloride, which result in emissions that are becoming increasingly unacceptable. Freeze crystallization recovers the volatile materials and fractionates the aromatic solvents from the chlorinated and Stoddard solvent types.

- Groundwater Treatment is attractive where contaminantation is from organic and ionic sources. As the concentration and variety of contaminants increase conventional treatment becomes increasingly expensive, if able to provide sufficient cleanup, and freeze crystallization becomes a more viable alternative.

- Resource Recovery is often technically feasible only with the freeze crystallization process. An example is an ammunition plant, where a variety of wastewater streams are generated. Of all treatment/destruction technologies examined, freeze crystallization was the most economical, actually providing a net return because of recovered product and reactants. Acetic acid recovery from a variety of industrial wastes is similarly only economically possible with this process.

HEIST ENGINEERING CORPORATION

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Gary [illegible]

14 November 1986

Mr. Roger Schecter
North Carolina Dept of Natural Resources
Pollution Prevention Program
P.O. Box 27687
Raleigh, NC 27611

Subject: Heist Engineering Freeze Crystallization Process
Literature Transmittal & Applications Discussion

Dear Roger:

Thank you for describing your program to me and taking the time to discuss our technology. I am enclosing information on the process and various wastewater and hazardous waste remediation activities that we are currently investigating with clients. After you've had time to look over this information I would like to schedule a meeting either in our offices or yours as follow-up.

The freeze process has two characteristics that make it ideal for resource recovery of wastewaters and remediation of hazardous wastes:

- Phase equilibria can be tailored to preferentially segregate components and remove them either for direct recycle or to remove them from concentrated liquids to be recycled. Since our process uses direct contact refrigeration it can operate in saturated conditions where materials are crystallizing without fouling heat transfer surfaces.

- The process is relatively insensitive to the wastewater composition coming to it. It adjusts automatically to changes and can accomodate wide fluctuations in flow and quality.

Thank you for your consideration and your help in identifying people in this state who have a need for this type of technology.

Very truly yours,

James A Heist

James A. Heist, P.E.
Vice President

Encl: ChemEng, HazMaCon, Economics, Applications
CC: NC071; route; Client: NCDNR