



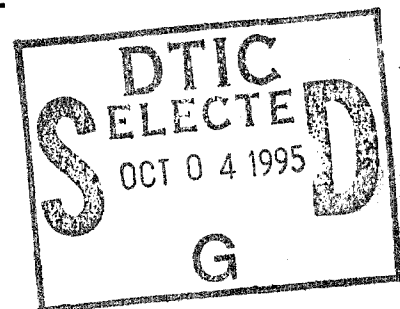
**MATERIAL RECYCLING AND WASTE MINIMIZATION
BY FREEZE CRYSTALLIZATION**

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May 1995



Final Technical Report for Period August 1993 - April 1994

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE May 1995	3. REPORT TYPE AND DATES COVERED Final		
4. TITLE AND SUBTITLE Material Recycling and Waste Minimization by Freeze Crystallization		5. FUNDING NUMBERS F08635-93-C-0108		
6. AUTHOR(S) James A. Heist Ken M. Hunt				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) FTC Acquisition Corporation P.O. Box 40968 3812-B Tarheel Drive Raleigh, NC 27629		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Environics Directorate, Armstrong Laboratory 139 Barnes Drive, Suite 2 Tyndall AFB, FL 32403		10. SPONSORING/MONITORING AGENCY REPORT NUMBER AL/EQ-TR-1994-0022		
11. SUPPLEMENTARY NOTES Prepared for the United States Air Force through the DoD Small Business Innovative Research				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unrestricted - for Public Distribution Contains no proprietary information		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) Freeze crystallization is a generic separation technology that has a number of applications in treating wastes generated in DoD operations. A week spent with engineering support, operations, and environmental compliance groups at an Air Force Logistics Center resulted in the identification of six major waste streams that could be reduced or totally recycled using freeze crystallization. The wastes identified were benzyl alcohol paint stripping wastes; paint thinners and other F-wastes; spent caustic and acid baths; nickel plating rinse waters; electrolytic grinding wastes (D004 thru D040 wastes); and contaminated fuels and calibration fluids. Savings in excess of \$1 million per year could be achieved by recovering, recycling and/or minimizing these wastes. A program is presented that would demonstrate each of these applications with a mobile pilot plant, operating on actual wastes.				
14. SUBJECT TERMS Recycle Liquid Waste (U); Hazardous Wastes (U); RCRA (U); Freeze Crystallization (U); Benzyl Alcohol (U); Vacuum Freeze Crystallization (U); Waste Minimization (U)			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

PREFACE

This report was prepared by FTC Acquisition Corporation, P.O. Box 40968, Raleigh, NC 27629 and the Air Force Civil Engineering Support Agency (AFCEA), Suite 2, 139 Barnes Drive, Tyndall Air Force Base, Florida 32403-5319.

This report presents the results of an examination of the generation of wastes from industrial operations in the Air Force to determine the application of freeze crystallization for direct recycle or recovery of resources. The wastes and their treatment and disposal costs were to be quantified as much as possible, so that a preliminary determination of the relative economics of recovery and reuse could be determined. One of the wastes were chosen for laboratory and demonstration testing to demonstrate the potential for freeze crystallization to recover materials for reuse and recycle.

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1. EXECUTIVE SUMMARY

OBJECTIVES: The goal of this program was to examine the generation of wastes from industrial operations in Air Force and determine if there are wastes that freeze crystallization (FC) can process for direct recycle or where valuable resources can be recovered from the waste. The wastes and their treatment and disposal costs were to be quantified as much as possible, so that a preliminary determination of the relative economics of recovery and reuse could be determined. One of the wastes was to be chosen for laboratory and pilot plant demonstration testing, to demonstrate the potential for FC to recover materials for reuse and recycle. The methods used in this program are described in the Program Description Section of this report.

RESULTS: Six areas of waste generation that produce liquid wastes that can be processed by freeze crystallization were identified in this study. Each produces a RCRA-hazardous waste that is now either treated on-site or sent off-site for treatment and disposal. Nearly 12 million pounds per year of hazardous waste are generated from these six areas at the Oklahoma City Air Logistics Center (OCALC). Over 90% of these materials can be recovered and recycled by the use of FC. Other wastes identified in this study have equal applicability, but are being eliminated from ALC operations. Examples are cadmium plating, plating baths containing cyanide, and perchloroethylene parts cleaning.

USAF ALC APPLICATIONS AND APPLICABILITY TO OTHER NEEDS:

The six applications identified and studied under this Phase I SBIR program included:

1. Benzyl Alcohol Paint Stripping Wash Waters
2. Paint Thinners (F-Wastes)
3. Spent Caustic and Acid Cleaners
4. Nickel Plating Rinse Waters
5. Sodium Nitrate Wastes
6. Fuels and Calibration Fluids

All of these operations are common to DoD industrial operations, and thus have applicability across the spectrum of facilities for all of the services. There are general applications for this technology in related, private sector industries, such as the commercial airline industry, metal plating shops, and general manufacturing.

ECONOMICS: The six areas of waste generation identified in this program represent a cost to the government of over \$2 million per year for waste disposal and chemical replacement alone. All of the wastes could be handled with three (3) identical FC facilities, each processing a maximum of 1000 pounds per hour of waste. Each of these facilities would cost between \$750,000 and \$1 million. Operation and maintenance of the three would cost between \$500,000 and \$750,000 per year, sharing O&M staff. This gives a simple payback period of 2 to just over 3 years.

IMPLEMENTATION: A program described in Section VII will demonstrate these and other applications for FC in the ALC's, with a mobile pilot plant. The pilot plant will have from 5 to 10% of the capacity required of a full-scale facility, and will be able to fully demonstrate recovery of by-products, including producing sufficient quantities for reuse and recycle demonstration and quality control testing. This can be accomplished in a Phase II SBIR program, for which FTCAC is preparing a proposal.

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I. INTRODUCTION

OBJECTIVE

This program was awarded from the 1993 Department of Defense Small Business Innovative Research solicitation, Topic 93-11: Environmental Engineering Research. The subject of this topic was to investigate new technology for waste minimization and reuse. The objective of this program, in response to that Topic, was to investigate the use of Freeze Crystallization for processing, recycling, and in other ways minimizing the generation of wastes from U.S. Air Force industrial activities at its Air Logistics Centers.

BACKGROUND

Freeze crystallization is a classical separation process for purifying chemicals. Its earliest uses predate history, where it was used for obtaining pure water from the sea. The first major application of the technology occurred in the 1940's and 1950's for the separation of xylene isomers to recover p-xylene for polyester manufacturing. In the last half century it has been adapted for a number of generally small-volume, specialty separation applications, where it was the only method that could achieve purity specification.

FTC Acquisition Corporation has been developing this technology for over 10 years for waste management and general separations applications. Freeze crystallization has some significant advantages in product purification capability and low energy consumption that should make it a much more broadly utilized separation process in the world's process industries. This program is an extension of the prior work of FTC in this area, looking specifically at opportunities for waste stream volume reduction and recycling in Air Force Logistics Centers.

SCOPE

The scope of this Phase I SBIR program was to:

- identify applications in Air Logistics Centers (ALC) by visiting an ALC, presenting the technology to individuals there, reviewing waste generating operations, and applying prior experience with the technology to determine which wastes might be processed by freeze crystallization.
- preliminary laboratory tests on an initial identified application.
- evaluation of economic incentives for implementing a recycling and waste minimization program based around this technology.
- recommendation of a Phase II demonstration program, including a pilot plant design.

II. PROGRAM DESCRIPTION

A. SUMMARY

The Phase I program had four major tasks, in addition to reporting:

1. ALC Visit - A week was spent at the Oklahoma City Air Logistics Center (OCALC), discussing possible applications of freeze crystallization (FC) with engineers in the production, industrial waste treatment and environmental departments.
2. Applications Analysis - Operations that generate wastes requiring treatment and/or disposal were identified in the site visit, where quantitative information on the volume of each waste and the costs associated with it were gathered. This information was used to identify opportunities for FC processing. The criteria for inclusion as a possible candidate was either the reduction of generation of a hazardous waste, or more economical processing of either hazardous or nonhazardous streams.
3. Pilot Plant Design - A process design was developed for each of the applications, and a pilot plant designed that should be able to process each of the identified wastes, producing recyclable materials for use in the ALC. In all cases waste is eliminated by the FC process plant, except for small residues or high quality treated water that can be used in other operations in the ALC.
4. Laboratory Testing - The original plan was to obtain a 55 gallon sample of an actual waste from an ALC and process it in a continuous pilot plant in FTC's laboratory. Because of logistics and cost problems in transporting that much hazardous waste, the program was altered to obtain a gallon sample, laboratory procedures were substituted for the pilot plant test, and a synthetic, nonhazardous waste was formulated and used for the larger scale demonstration tests.
5. Reporting - A monthly progress report and final report are required by the contract, and a kick-off meeting with the technical sponsor, Lt. Phillip Brown of the Armstrong Laboratory, Tyndall AFB, was also held.

B. OKLAHOMA CITY AIR LOGISTICS CENTER (OCALC) VISIT

The trip to the OCALC at Tinker AFB, OK took place during the week of August 9, 1993. Captain Darren Gibbs sponsored the visit and arranged for meetings with engineering support and production staff in the various operations that generate liquid wastes at

the ALC, as well as with the Environmental Department at Tinker. The Environmental Department is divided into two groups, dealing with compliance of existing operations and with remediation, respectively. The compliance group provided information on hazardous wastes that must be reported under SARA right-to-know laws, and on projections of those wastes expected to be generated in 1993. Costs for disposal of hazardous wastes are also compiled by this group. The remediation group has an on-going program to identify environmental contamination on the base from past operations, and to remediate those areas that have been contaminated. A large groundwater treatment facility was commissioned in mid-1993 to process contaminated groundwater from a series of extraction wells. A sampling and testing program is underway to identify other contaminated areas on the base.

C. OCALC APPLICATIONS

Applications that were identified that met the waste reduction / economic viability are identified in Section 5 of this report. There are several other wastes that were not considered because they are being replaced or eliminated under other programs. Examples are perchloroethylene parts cleaning, methylene chloride - phenol paint stripping, cadmium plating, and cyanide-chemistry plating. There are also other changes occurring in the ALCs that may impact waste treatment and minimization, or FC economics, such as a major improvement in the plating facilities at the OCALC. As part of the on-site study, facilities for storing wastes were investigated, as a surge capability allows the wastes to be processed at a slower rate over a longer period, rather than at the rate they are generated. Such considerations are discussed in Section 5.

D. PILOT PLANT DESIGN

A preliminary pilot plant design was conducted after meeting with the Technical Officer and establishing the primary design criteria for a field demonstration pilot plant that will be operated at the OCALC, Tinker AFB, OK, and perhaps at other ALCs. The primary criteria are:

- operate on as many streams as possible;
- fit inside a skid that can be easily moved within the ALCs and that will not interfere with normal operations and material flows;
- requires only electricity for operation;
- plant capacity that will give design criteria that can be directly applied to full scale equipment.
- demonstrate material recovery concepts by recovering sufficient quantities for analytical quality control testing and for reuse demonstration.

A vacuum freeze crystallization process was chosen because it can be adapted to all of the identified applications with a few additional pieces of equipment: an absorption cycle for condensing the vapors generated in the crystallizer; a growth column / eutectic separator for growing salt crystals and separating eutectic materials that might

form in some applications; a hydrocyclone (that will be used in place of the eutectic separator in some applications) for removing second liquid phases that form as the primary solvent is removed. The pilot plant will also have wash columns for purifying and recovering the high purity crystals that are formed in the process, and a small, packaged air-cooled condensing unit for providing the refrigeration. A liquid ring vacuum pump will provide the vacuum in the process. The pilot plant will be skid mounted, on two skids that can be bolted together for testing, with each skid mounted on pneumatic wheels to facilitate moving it within the relatively tight confines of the ALCs. The pilot plant will require approximately 20 amps of 240 volt, single phase power.

E. LABORATORY TESTING

All of the waste streams identified as candidates for recovery and reuse processing by freeze crystallization are hazardous wastes, as produced in the ALCs. Previous programs have demonstrated the ability of freeze crystallization to treat metal plating wastes for reuse and recycle.¹ The major waste stream with recycle potential in the ALCs is the rinse water from aircraft paint stripping, where the new benzyl alcohol based strippers are being used. This waste was chosen for continuous pilot plant testing. Quart samples were obtained for characterization testing. This waste is a characteristic hazardous waste because some of the undercoat on the plane is also stripped, and it contains sufficient hexavalent chromium to classify the paint stripping rinse solution as hazardous. The OCALC determined that shipping two drums of this material would require manifesting and all of the requisite controls that go along with shipping hazardous waste. Since there was no budget for this it was decided that testing should be done with a simulated waste, without chrome. A sample of the benzyl alcohol paint stripper was obtained from the supplier and a 2% solution in tap water was mixed to simulate the rinse waters generated in the ALC. Bench scale tests were run with quart samples, and the simulated waste was tested at the bench scale and in the continuous pilot plant.

¹ Heist Engineering, "Development of a Freeze Crystallization Concept as a Pollution Abatement Method for Plating Baths at Naval Aviation Depots," Report No. NAPC-PE-194C. Naval Air Propulsion Command, Trenton, NJ (1990).

III. FREEZE CRYSTALLIZATION TECHNOLOGY

Conventional crystallizers evaporate a solvent to produce the supersaturation needed to crystallize a solute from the solution, as in the production of sugar, a variety of salts, many organic chemicals, and a variety of pharmaceutical products. All of these applications take advantage of the high purification effected when a crystal is produced. However, they sacrifice energy efficiency, as the solvent is often water and they are invariably single effect devices. Freeze crystallization removes heat from the solution, at an operating temperature below the freezing point of the solvent, to remove it as a solid, crystal phase. In waste treatment applications, the ice that is made is often the desired "product", but in many applications, there are contaminants that can be eutectically crystallized, and recovered as a by-product, to help pay for the processing costs.

A. PHASE THERMODYNAMICS

The first step in understanding the use of freeze crystallization for separating liquid mixtures is to understand the underlying physical thermodynamics. All materials, chemical elements and compounds of the elements, undergo phase transitions from solid to liquid to vapor, at specific temperatures. Also, solid and liquid materials have a certain fraction of their molecules that move in and out of the vapor phase, and in so doing they exert a VAPOR PRESSURE, that is a unique function of temperature. The temperature and pressure at which the solid, liquid and vapor phases are all in equilibrium is called the TRIPLE POINT, and is usually very near the NORMAL FREEZING POINT of the material. The NORMAL BOILING POINT is the temperature at which a material exerts a vapor pressure of 1 atmosphere. The NORMAL FREEZING POINT is the temperature at which a material freezes under one atmosphere of inert gas pressure. The diagram in Figure 1 shows a PHASE DIAGRAM for water, which shows the general phase characteristics common to all materials.

The much more common occurrence, is to have mixtures of elements and compounds. The case of a simple

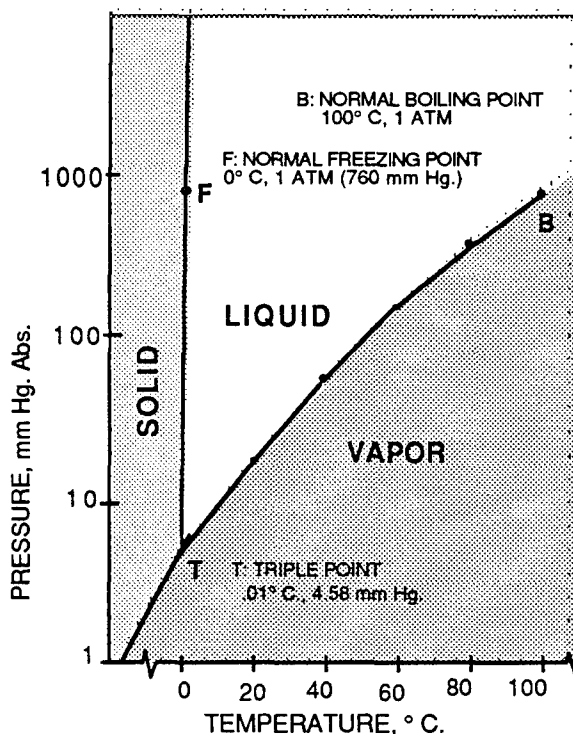
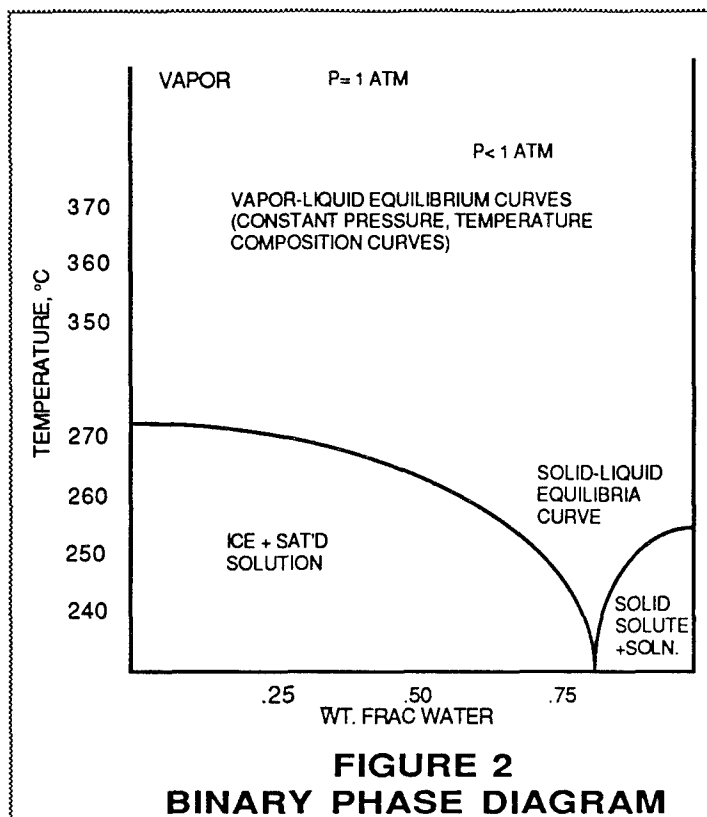


FIGURE 1
PHASE DIAGRAM



binary mixture (2 miscible materials) is shown in Figure 2. Each pure material has its normal boiling point and a normal freezing point represented by their respective 100% compositions. As one of the materials is added to the other the boiling point of the material is elevated and the freezing point is depressed. The vapor above the liquid is a mixture of the two materials. Below the freezing point one or the other of the materials will crystallize into a pure crystal, depending on the composition of the liquid. This is represented by the operating line A-B, with the liquid composition in the region where material 2 is crystallized. As more heat is removed and more and more of material 2 is crystallized, the operating line moves along the

solid-liquid equilibrium line to point C, and then eventually to point E, which is the EUTECTIC COMPOSITION. The word eutectic comes from the Greek *eutektos* meaning easily melted, or more precisely the lowest possible melting point that occurs when metals are alloyed or chemicals are mixed. It is the point at which both materials in the binary solution are crystallizing at the same time. The important point is that in most solutions the crystals that form are pure, and crystals of material 1 form separately from those of material 2. So, if the crystals can be separated by some physical means, it is possible to make pure materials from a solution.

This ability to separate pure components from a solution, in one step, is one of the primary thermodynamic advantages of solidification or crystallization over fractional distillation, where the change in composition between liquid and vapor is used to effect the purification. In fractional distillation, a small increment of purification is achieved in each step, and to achieve the desired purity can require from several to several hundred stages repeating the incremental purification. A crystallization process on the other hand, achieves much higher purities (typically greater than 99.9%) in one stage - there is complete separation of the materials in the pure crystal that is formed. Outside of the metallurgical industry, where mixed crystalline materials are desired and formulated for their physical properties, the occurrence of crystals that incorporate more than one material in the matrix are quite uncommon. Materials that are as similar as isomers (i.e., ortho-, meta-, and para-xylene and ethylbenzene) all form separate crystals when operating at the eutectic points at different solution compositions.

A physical property that has become increasingly important with the increasing cost of energy, is the latent heat involved in phase changes. Typically, the latent heat of fusion is from 10 to 25% of the latent heat of vaporization. This means that it takes 4 to 10 times as much energy to evaporate a pound of material as it does to crystallize by heat removal. For example, at its normal boiling point, it requires 970 BTU's to boil one pound of water, but at its freezing point, only 145 BTU's need to be removed to freeze that same pound.

A final factor in selecting freeze crystallization over conventional evaporators and evaporative crystallizers is the lower solubility of many materials, especially salts in water, at lower temperatures. This can be used to preferentially crystallize one material from a waste stream, so that it can be recovered as a pure by-product. At conventional, elevated temperatures, many organic and inorganic salts, as well as many organics, will remain soluble or miscible in the waste stream, while at the lower operating temperature with freeze crystallization, these materials will crystallize or form a separate liquid phase, which allows their direct recovery.

B. FREEZE CRYSTALLIZATION

The primary steps that are involved in making a separation using a freeze crystallization process are depicted schematically in Figure 3. A typical process flow schematic is shown in Figure 4. Process options include the crystallizer design and the method in which the crystals are separated from one another (if more than one crystal species is formed) and the manner in which they are purified. The CRYSTALLIZER is the device in which heat is removed at the freezing point of the solution, and in so doing causing a portion of the solvent to crystallize. If one or more other materials is at its solubility limit, the conversion of solvent to its crystal form results in an algebraic generation of supersaturation of the solute(s), and their subsequent crystallization as well. There are three basic ways in which heat can be removed:

- 1) Through a heat exchange surface, which requires some variation of a scraped surface to keep the crystals from forming on the heat exchange surface and blocking heat transfer.
- 2) With the addition of secondary refrigerant, usually a CFC, HCFC, or volatile organic materials, with boiling of the (usually immiscible) refrigerant in direct contact with the process fluid. This method generates very large inter facial surface areas, with high heat transfer coefficients, so that the temperature driving force is quite low.
- 3) By pulling a vacuum on the process fluid so that the solvent in the solution acts as the refrigerant by boiling at its triple point. For water this occurs at 32° F and about 4.6 Torr. If the process fluid has components with relative volatility of the same order of magnitude as the solvent, those volatile components can be concentrated in the vapor phase. This cycle can also be the most efficient and simplest to implement.

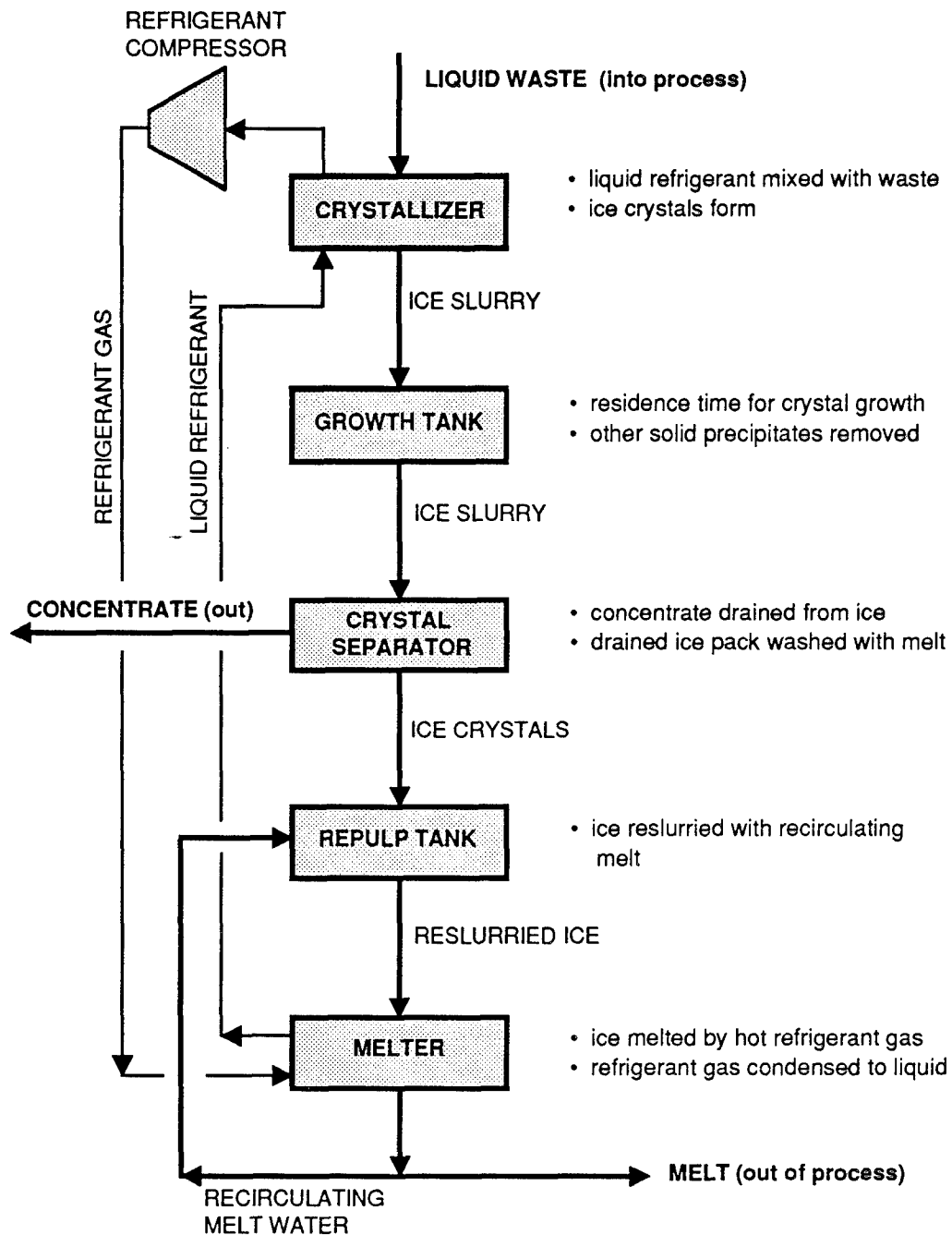


Figure 3
FREEZE PROCESS FLOW CHART

Secondary Refrigerant Freeze Crystallization Process Schematic

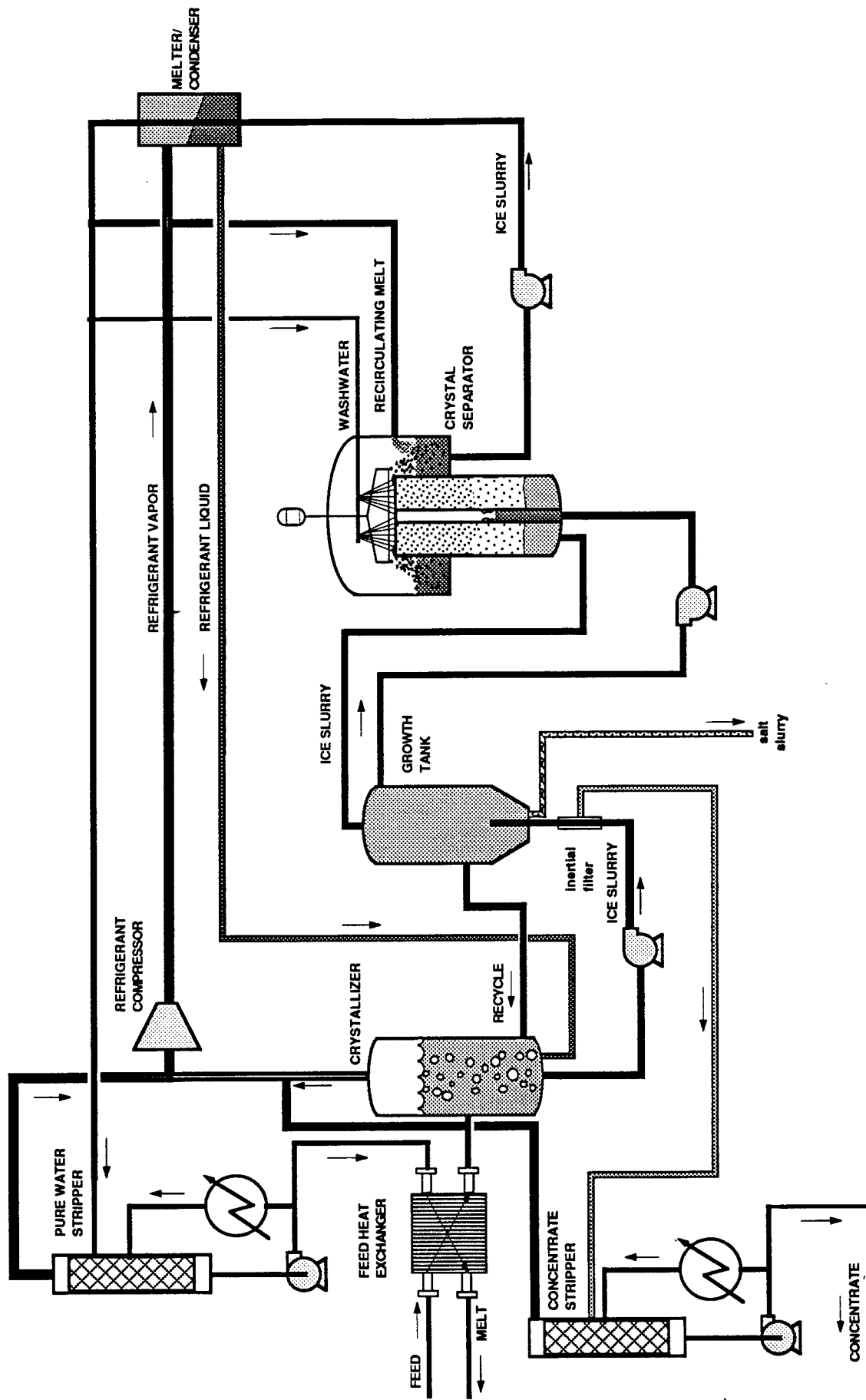


Figure 4

Crystals produced in the crystallizer must be separated from the bulk of the fluid, and washed to remove any residual liquor that is coating the crystal surface. This can be done in filters or centrifuges, but a device that is much more efficient is a WASH COLUMN. A schematic of a wash column is shown in Figure 5. Slurry is pumped in at the bottom of the column, which is conceptually just a vertical vessel with screens mounted peripherally midway up the sides. The liquid flows to and through the screens, but the screen size is chosen to block the flow of crystals. The crystals form a packed bed, which builds down below the screen level. The higher velocity of liquid through the lower crystal bed creates a pressure gradient, which is the force that propels the bed upward, holding the crystals above the screens in place. Note that the crystals are pushed up through the column not by buoyant forces, but by this hydraulic gradient in the lower portion of the crystal packed bed. Wash solvent, which is usually melted crystal, is sprayed over the top of the crystal pack, to counter currently wash the liquor from the crystal surface. This is a very efficient washing device, achieving decontamination factors of 10,000 or greater. This is the equivalent of 10 or more equivalent stages of washing with a filter or centrifuge, and is done with only a fraction of the wash solvent used in conventional wash stations. The purified crystals are scraped from the top of the wash column into either a conveyor or a reslurry tank.

Normally the preferred final product form is as a liquid, so the product crystals are melted in a MELTER, which is typically a shell-and-tube heat exchanger. Where the crystals melt below the temperature of available cooling water, they absorb most of heat that was removed from the crystallizer to make them. In this way, the process refrigeration system becomes a HEAT PUMP. In most instances the heat pump achieves a coefficient of performance of up to 3, further improving the energy efficiency of the process.

Most process fluids and waste streams are complex mixtures that, when processed in a freeze crystallization process at high conversion of the feed to purified product, also crystallize other solutes, or form immiscible liquid phases. These additional phases must be separated from the primary crystal product, and often from one another. The common occurrence is when ice is the primary crystal being produced (from wastewaters or when water is the primary solvent used in the process), and when salt crystals are also being produced. In almost all cases, the ice will be lighter than the process fluid, and the eutectic crystals will be heavier than the fluid. This allows for easy fractionation of ice from salt crystals in a EUTECTIC SEPARATOR that is a simple gravity settling tank. Since salts usually grow at a much slower rate than ice, but if the separator is designed with flow into the bottom, and the salts are heavier than the liquid, a fluidized section in the bottom of the separator becomes a salt CRYSTAL GROWTH COLUMN, where the salt crystals can be grown to the desired size.

Many organic liquids are only slightly soluble in water, and as more ice is removed from a wastewater, the organic forms a second liquid phase. HYDROCYCLONES have been used successfully to remove the organic liquid from wastewater and ice that then flows to the wash column, where the ice is purified and recovered.

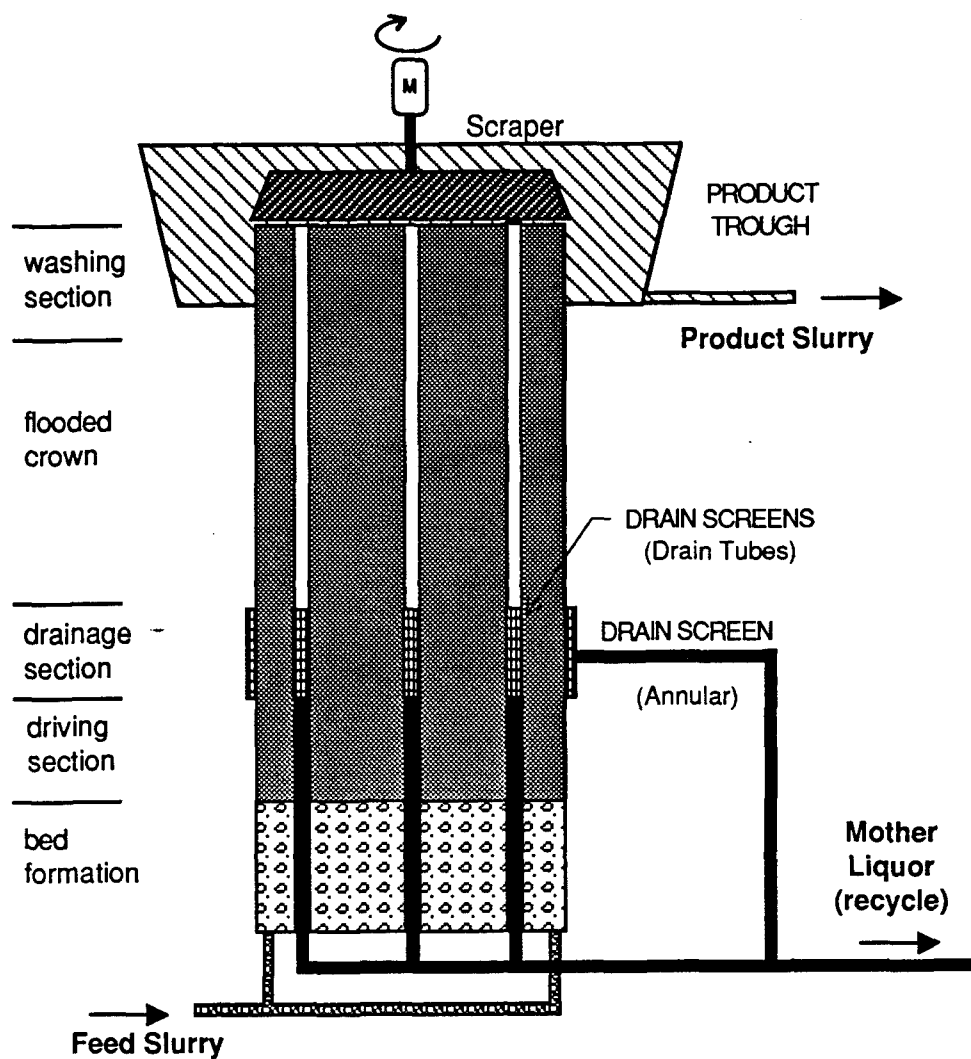


Figure 5
GRAVITY WASH COLUMN
SCHEMATIC DRAWING

IV. APPLICATIONS IN AIR FORCE AIR LOGISTICS CENTERS

A site visit to the Oklahoma City Air Logistics Center (OCALC) at Tinker Air Force Base was made to look for those operations that produce the greatest volume of wastes, or that produce wastes that are the most expensive to treat and / or dispose of. The top 6 application opportunities for freeze crystallization are listed here, roughly in order of their priority for reducing environmental compliance costs. There are a number of other applications, both at OCALC and other air logistics centers (ALC's) that aren't covered here, primarily because they aren't required at OCALC. For instance, OC has essentially eliminated cyanide and cadmium plating. So, while these are viable applications for freeze crystallization, they are either nonexistent at OCALC or they are very small volume generators and not a major economic factor in the operations of that facility. Similarly perchloroethylene cleaning is being phased out. On the other hand, the enforcement against methylene chloride paint stripping has opened up a new opportunity for recovery of its replacement stripper, benzyl alcohol, by freeze crystallization. This is the top priority application on our list. The applications are summarized in Table 1.

The most important information in making a decision about recovering these materials using freeze crystallization is the annual savings possible and the reduction in hazardous material generation, which are estimated as follows:

<u>WASTE</u>	<u>ANNUAL SAVINGS</u>	<u>HAZ WASTE REDUCTION</u>
Paint Stripping Washwater	\$765,500.	4,200,000 #/yr
F-Wastes	\$712,000.	500,000 #/yr
Cleaners, Acid & Caustic	\$62,000.	225,000 #/yr
Nickel Plating Rinsewaters	\$35,000.	1,000,000 #/yr
D- Wastes	\$85,000.	203,000 #/yr
Calibration Fluids & Fuels	<u>\$50,000.</u>	<u>250,000 #/yr</u>
	\$1,704,500.	6,378,000 #/yr

A. AIRCRAFT BODY PAINT STRIPPING RINSE WATERS

The Oklahoma City Air Logistics Center (OCALC) is moving to benzyl alcohol based paint removers, from current methylene chloride - phenol chemistries. Methylene chloride is being phased out to meet Clean Air Act regulations and phenol is a health hazard to workers. The cost of the benzyl alcohol stripper is about \$1200 per drum, and 12 drums are required for most of the craft serviced at OCALC. This is rinsed, along with paint 'chips', into a sewer with about 50,000 gallons of water, into an intermediate sump where the larger paint chips are settled out. Average waste generation is from 6 or 7 aircraft a month, or a little over 10,000 gallons per day, but this is generated in a few hours on each aircraft, in one to three washing - rinsing operations per week.

TABLE 1
APPLICATIONS SUMMARY

Waste Source	Waste Source or Generated From	App. Waste Composition	Waste Generation Rate	Quantity & Cost of Makeup Chemical
1. Paint Stripping Waste-waters	A. Benzyl Alcohol based chemical paint stripping - wash waters.	.8 to 1.2 wt-% stripping chemical in water, with paint 'chips' and small amount of chrome (+6) dissolved from paint.	10,000 to 15,000 gallons per plane; 1 plane per week. (Facility could handle two planes per week)	12 barrels of solvent per plane, sometimes double application \$1000 per barrel. \$624,000 per year.
2. Paint Thinner - F-Waste	A. Paint Equipment Cleanup	Mineral solvents with less than 10% paint solids.	1993 disposal of this F-Waste (RCRA waste) is estimated to be 550,000 lbs.	500,000 #/yr of fresh solvent at \$.35 / lb. \$175,000 per year.
3. Spent Caustic & Acid Cleaners	A. Parts Cleaning & Plating Shop Alkaline Cleaners	5 to 20% NaOH solns, with 1 to 3% silicates in some cases. CO ₃ = levels elevated, & dissolved metals	150,000 pounds per year. Tanks of up to 2000 gallons dumped periodically.	15,000 pounds per year chemical @ \$.50 per pound \$7,500 per year
	B. Plating Shop Acid Cleaning & Metal Preparation	Chromic, phosphoric, nitric, oxalic acid, sodium bisulfite and mixes, 5 to 50% acid.	125,000 pounds per year. From dumping tanks of up to 1000 gallons each	40,000 lbs/yr of various chemicals @ \$.50 to \$2.00 per lb. \$50,000 per year
4. Nickel Plating Rinse-waters	A. Nickel Sulfamate plating - rinsewater	Up to 1000 mg/l Ni+2, depending on water conservation methods	2 gpm per tank, 5 tanks, 200 gallons per hour, 2000 gallons per day.	Application. 17 # Ni per day, requiring makeup of about 70#/day of Ni(NH ₂ SO ₃) ₂ . At \$8.50 / # Ni, 250 days per year: \$36,200 / yr
5. Sodium Nitrate Wastes	A. Rust Inhibitor Tanks disposal	5 to 10% NaNO ₂ and NaNO ₃ solutions	Individual tanks of up to 600 gallons dumped periodically.	Nitrites are oxidized during operation and become ineffective, can't be recycled.
6. Fuels and Calibration Fluids	A. Wet jet fuel and storage tank water condensates B. Shop calibration fluids.	JP-4 and JP-5 fuels, contaminated with water and surfactants (from foam application) Calibration fluid used in testing fuel controls before reinstallation.	250,000 to 500,000 lb per year, total. Some 'accidents' generate 5000 gallons at a time, but usually generated at 1000 to 2000 gallons per day.	These materials are replaced on a 1:1 basis, at a minimum of \$.12 per lb. \$500,000 per year cost.

Benzyl alcohol, and perhaps other additives can be recovered from the rinse waters by freezing. The 'other additives' that are in the stripper formulation include a surfactant to facilitate washing and a thixotropic component to cause the mixture to cling to inclined and vertical surfaces on an aircraft. Ammonia as an active reactant at 2 or 3% has been found effective in removing some otherwise difficult to strip paints and primers. One supplier is developing, and has successfully tested a water-emulsion product, containing up to 50% water, in an attempt to increase the coverage of a given amount of benzyl alcohol.

In laboratory experiments the thixotropic agent acted like an insoluble glue and settled to the bottom of the mixing tanks. Even after intense agitation that seemed to have emulsified this material, within a few hours it had again collected into globules on the bottom of the tank. The benzyl alcohol forms a separate liquid layer that is 20% denser than water, and can be either settled out or removed from recirculating ice slurry in a 3 phase hydrocyclone. The ammonia and other volatiles can be condensed separately in an overhead condensate, and added back to the benzyl alcohol. To assure that they meet MIL specs, the benzyl alcohol / mixture would have to be stored and analyzed, and reconstituted as necessary.

The rinse water is removed as high-purity ice, and melted, and can be recycled for subsequent washing, rather than discharged through the industrial waste treatment plant. The benzyl alcohol from stripping one plane adds over 8500 pounds of BOD load to the waste treatment plant, which can be essentially eliminated by recycling all of the waste in this manner. A small amount of hexavalent chrome is leached from the undercoat, and this will build up in a concentrated liquid stream, that will have to be periodically discharged and treated in the industrial waste treatment facility. The last step in depainting is an alkaline wash, Mil-C-87936, which will also end up in the sump, and needs to be examined for its effect on benzyl alcohol recovery.

The samples of rinse water obtained from the OCALC contained less than 1% benzyl alcohol, well under the 3 to 4% that should be soluble at rinse water temperatures. An option to minimize waste volumes would be to have a two stage rinse, 'counter-current' rinse, the first with water from the basin under the rinse area, and the second with clean water recycled from this basin by a freeze crystallization plant. This would cut the volume of waste to be treated by half or more, and could allow the current paint stripping area to double its capacity without generating any additional 'net' waste.

Benzyl alcohol value	\$14,400 per plane @ 50 planes/yr	=	\$720,000
BOD Load Reduction	\$ 850 per plane	=	42,500
Volume to be Treated	10,000 to 11,000 gallons per day, 4 to 6 days per month		
Haz Waste Reduction	4,200,000 pounds per year		
Freeze Cycle	Flash Vacuum Freeze Crystallization		

B. F-WASTES - PAINT THINNER

This solvent is used to clean up equipment after painting air-craft, engine assemblies and aircraft components, requiring at the OCALC that about 550,000 pounds per year of liquids be disposed of as hazardous waste. These are F-wastes and cost \$.84 per pound to dispose of, under contract in 1993. The aircraft paint shops plan to put in one or more solvent recovery stills, but freeze crystallization is an alternative that will have less emissions and could recover more solvent as at the lower temperatures there would be less tar-forming reactivity in the solvent. The paint solids that are left behind in current tanks, are put in barrels and disposed of at \$1.92 per pound. The paint solids left in the solvent recovery units will also have to be disposed of in the same manner, but should represent no more than 10% of the weight now disposed of. Direct recycle of the solvent may not be possible without checking that quality meets MIL spec standards first.

Disposal Costs	\$462,000
Solvent Value	\$250,000
Volume to be Treated	550,000 pounds per year
Haz Waste Reduction	500,000 pounds per year
Freeze Cycle	Vacuum Stripper w/ agitated bottom

C. SPENT CAUSTIC AND ACID BATHS

Most of this seems to be generated from cleaning operations, primarily in the propulsion command. The industrial waste pretreatment system can't handle the loads, and thus the wastes are either bulked or drummed and shipped off-site for treatment. The alkaline wastes are primarily caustic based proprietary compounds, while the acids are primarily nitric and sulfuric acids used for pickling, cleaning, or surface pretreatment. Water is absorbed from the atmosphere and produced as a by-product of the cleaning operations, and metallic and other impurities build up in the solution until it is unsuitable for further use. Nitric acid disposal is a sufficiently difficult problem for the DoD that Battelle Pacific NW Labs has been given a contract to develop a recycle method. We will work with Battelle to help them assess this technical option against other alternatives they are evaluating.

The approach with freeze crystallization is to precipitate impurities (much less soluble at lower temperatures), and concentrate the acid/alkaline values by removing water. This should be able to reduce disposal volumes by 80 to 90%. Assume a 10% residual NaOH or acid content in all wastes.

Volume

Bulk: 205,000 #/yr- 120,000 #/yr alkaline & 85,000 #/yr nitric acid

Drummed: 60,000 #/yr- 35,000 #/yr alkaline & 25,000 #/yr unknown acids

Disposal Costs - Bulk @ \$.18 / # = \$36,900 / yr

Drummed @ \$.56 / # = \$33,600 / yr

Chemical Value Alkaline @ 10% of 155,000 #/yr & \$.25 per lb. = \$3,875

Acid @ 10% of 110,000 #/yr & \$.25 per lb.= \$2,750

Assumed savings by recovery / recycle @ 80% \$61,700

Volume to be treated - 265,000 pounds per year

Haz Waste Reduction - 225,000 pounds per year

Freeze Cycle - vacuum freeze; perhaps will require hydrate process to get higher final product concentration

D. NICKEL PLATING RINSE WATERS

Most nickel plating at the Oklahoma City Air Logistics Center (ALC) is from sulfamate baths. All nickel rinses in the past were collected and processed through a cation exchange resin, to capture the nickel. The nickel was then released with a HCl regenerant, giving a nickel chloride concentrate for recycle to Watts nickel baths. There is more nickel chloride produced this way than can be consumed, and the excess is disposed of as a waste. The sulfamate is a much more expensive nickel source, and the current treatment system is being abandoned because of mechanical deterioration, so there is a double incentive for developing a more efficient process that will recycle both the nickel and the sulfamate.

Volume - highly variable, estimated at 500 gallons per day, 250 days per year

Treatment Costs - unknown for old ion exchange process

Disposal Costs - \$.18 per pound for liquids &
\$1.50 per pound for drummed sludges.

Replacement Costs - \$25. per # Ni in nickel sulfamate solutions.

Recovered Chemical - 1000 pounds Nickel Sulfamate per year
(400 # Ni per year)

Recovered Chemical Value \$10,000 per year

Reduced Disposal Costs \$25,000 per year

Avoided Capital Costs \$500,000 (ion exchange treatment system)

Haz Waste Reduction - 1 million pounds per year

Freeze Cycle - Vacuum Freeze Crystallization

E. D004 thru D040 Toxic Wastes

This waste is reported to be mainly NaNO_3 wastes from 'electrolytic grinding' operations. Over 200,000 pounds per year of this liquid, and 114,000 pounds per year of sludges are expected to be generated in 1993, based on prior year operations. Disposal costs of the liquids are \$.42 per pound. This is a quite wide range of wastes, and no one in the production operations knew where this might be coming from. The prioritization of this waste is based on this preliminary information, but needs further investigation. The sludges, if this is from electrolytic grinding, are probably metal sludges that will continue to require disposal or being sent off-site for recovery.

Volume -	203,000 pounds per year liquids
Off-site Disposal Costs -	\$85,260.
Replacement costs -	unknown
Hazardous Waste Reduction	203,000 pounds per year
Freeze Cycle -	Vacuum freeze crystallization, or secondary refrigerant at higher recovery

F. MIL C-7024 CALIBRATION FLUID, D001 DRUMMED FUELS & WET / CONTAMINATED FUELS

The only of these that has been quantified is the D001 drummed fuels, that are collected when tanks are drained before maintenance. Projections are for about 54,000 pounds of this material to be generated in 1993 at the OCALC. Periodically fuel becomes contaminated with water, fire fighting foam, or other materials and is disposed of. And a fuel like material is used to calibrate fuel control instruments before they are reinstalled in aircraft. No one has compiled the total volumes, and they do vary greatly, but the general feeling was that the total annual quantity is somewhere between 250,000 and 500,000 #/yr. A new term-sell agreement will send much of this material to a recycler at no net cost to the government for disposal, but some materials do cost for disposal. And all of these materials have a replacement value of a minimum of \$.15 per pound.

Volume -	250,000 pounds per year
Off-site Disposal Costs -	minimal
Replacement costs -	\$50,000
Hazardous Waste Reduction	250,000 pounds per year
Freeze Cycle -	Vacuum freeze crystallization, sometimes using the process only as a vacuum stripper, without any freeze crystallization.

G. GROUNDWATER PUMP & TREAT

A 200 gallon per minute pump-and-treat system has been installed to treat an expanding groundwater plume. It has air stripping, chrome reduction, and hydroxide precipitation. Off gases are treated in activated carbon beds to remove VOC's and the carbon is regenerated by steam distillation, generated from an electric boiler. The base is undergoing remediation investigations that are expected to result in additional pump and treat systems. Some of these will be aimed at recovering the non-aqueous phases from the formation, as well as the source of heavy metal contamination. Restrictions on air stripping emissions by the new Clean Air Act Amendments could increase the costs of this treatment train by a factor of 2 or 3.

Freeze Cycle - Vacuum freezing, possibly operating in some cases as a vacuum stripper. This will recover the materials for recycle that are now being lost.

V. LABORATORY TEST PROGRAM

Bench top tests were run on quart samples of paint stripping rinse water taken after settling in the collection basin, that were sent by the OCALC. The washwaters become contaminated with up to 50 mg/l of total chrome (about half of which is hexavalent), and thus are a characteristic hazardous waste. The costs of controlling, manifesting and shipping a hazardous waste were not in the budget, and no sponsor was found, so tests on the continuous pilot plant were run with simulated wastes. Lab tests were run on the quart samples of actual wastes that were sent, and are reported here. Bench top tests with such small samples are generally much less effective in demonstrating separation capabilities. Test methods were run as outlined in Appendix 2, with exceptions as noted here.

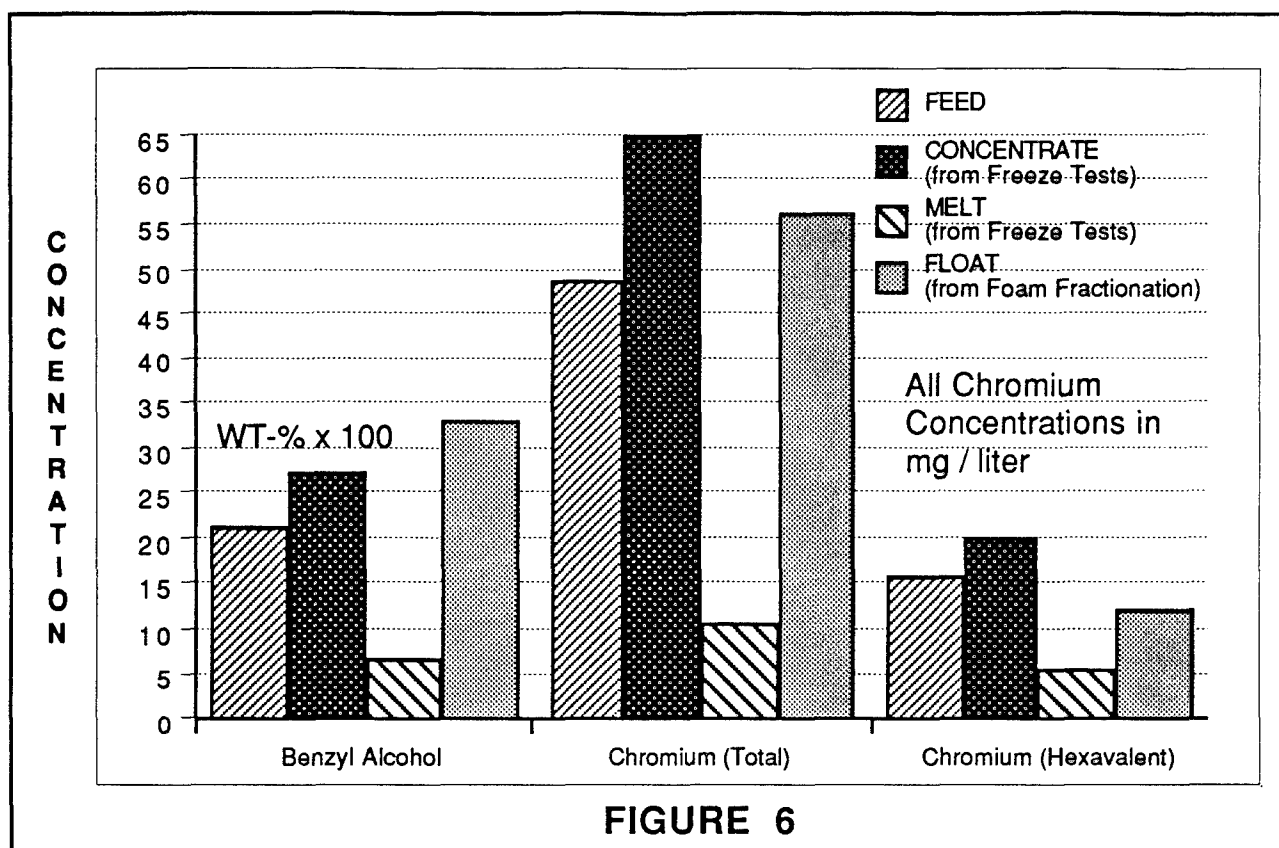
A. RESULTS

Freeze crystallization produced ice that was separated and melted demonstrating a decontamination factor of 3 to just over 4, for all measured constituents (benzyl alcohol, total chrome and hexavalent chrome). This is about the same level of separation from the ice fraction that is typically observed in these small scale tests, and are indicative of being able to achieve a 1000 to 10,000 decontamination factor in full scale equipment. The decontamination factor is defined as:

$$\frac{[\text{Concentration of Contaminant in Feed}]}{[\text{Concentration of Contaminant in Product}]}$$

Analytical reports from an outside testing laboratory are included as Appendix 4 to this report. The results are presented graphically in Figure 6. Concentrations of benzyl alcohol, total chromium and hexavalent chromium are shown for the feed stream, a recovered stream of melted ice, and for the final concentrate left at the end of the tests. The figure also shows an analysis for a foam fraction that was recovered from the crystallizer, which was generated when nitrogen gas was injected into the waste to cool it. More will be said about foam fractionation at the end of this section, but the results here show that the foam was slightly enriched in the benzyl alcohol and total chrome, but slightly depleted in the hexavalent chrome. This would indicate that a foam fractionation process would make a partial separation between the trivalent and hexavalent chrome species, but that the effect would probably not be large enough to be an effective separation process.

The analytical results show that the benzyl alcohol was concentrated to about .27 wt-% in the freeze crystallization tests. At the end of the tests, after the liquids had been drained and samples taken, a residue of viscous organic materials was found on the surfaces of the apparatus, and collected in some low areas. The observed concentration in the concentrate sample was probably the solubility limit of benzyl alcohol in these wastes at the freezing point, and the second liquid phase of benzyl alcohol and perhaps other organics from the stripping chemical did not stay preferably

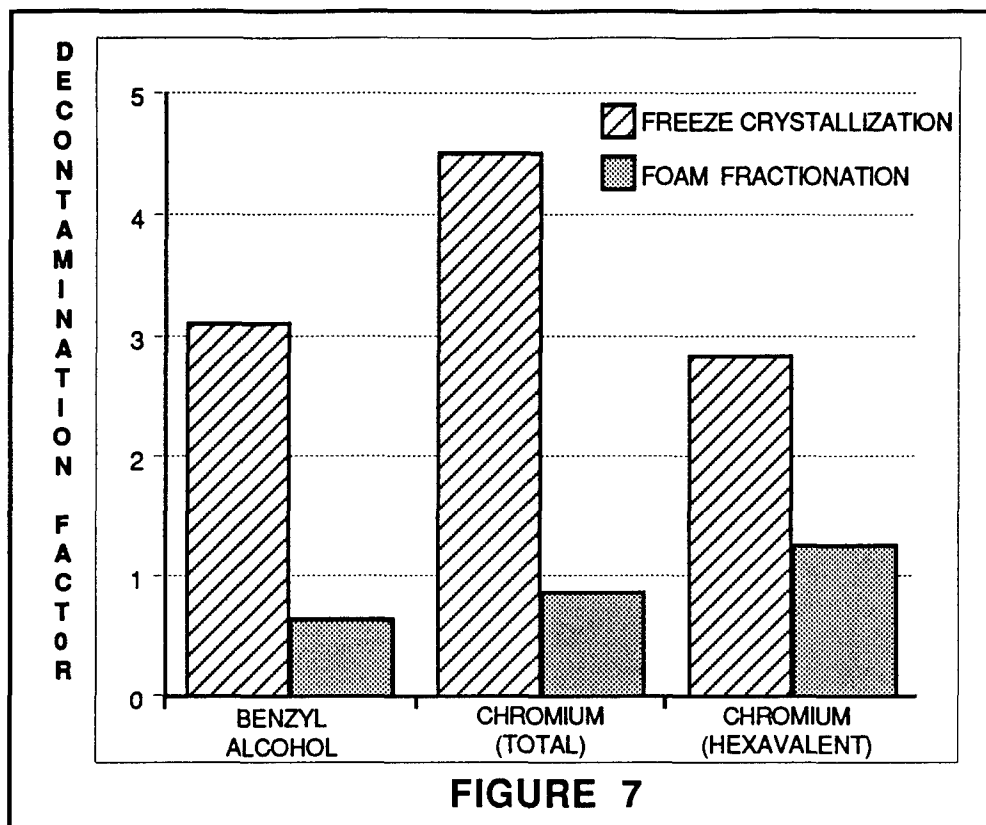


with the ice. The ability to separate the organic phase from the ice is a critical part in recovering it for reuse in paint stripping by a freeze crystallization process. The separation of contaminants from the ice is similarly important, and one way of looking for problems of removing contaminants from ice is by looking at the relative degree of reduction of each contaminant. This is done in Figure 7, showing decontamination factors of the both the simulated freeze crystallization process, and the foam fractionation process, for each of the three contaminants. The relatively equal degree of removal of contaminant from the ice indicates that it will be possible to remove all of these materials very effectively, so that the water may be reused.

Initial freezing point, viscosity, and phase observations were determined on the quart samples of OCALC waste. The freezing point was just a few tenths of a degree below 32° F on the waste as received, it had a significant yellow tint, and was almost void of any suspended solids. The viscosity was measured with a Cannon-Fenske Kinematic viscometer tube. The viscosity of the waste was within the accuracy of the method, the same as that of tap water, or about 1 centiStoke.

B. SYNTHETIC WASTE TESTS

A 2 wt-% stripping chemical in water was mixed to simulate the wash waters from the OCALC wash racks. Sufficient stripper was obtained from the supplier, El Dorado Chemical Co, San Antonio, TX.) to make 100 gallons of this simulated waste. An initial test was run to determine the physical characteristics as compared to the waste



obtained from OCALC. The thixotropic material in the stripper formulation is nearly insoluble in water, as determined by trying to dissolve it at a .2 wt-% concentration in water. With a high level of agitation it was possible to emulsify the water and thixotropic component of the stripper but within a few minutes it would settle out and gradually coalesce once again into a few distinct balls, on the bottom of the flash. This material is probably building up in the bottom of the settling basin at the wash rack, or is being taken out with the paint chips that are washed from the aircraft surface.

The initial tests with cryogenic nitrogen as the refrigerant (this was the crystallizer configuration being used in the continuous pilot plant at the time) resulted in excessive foaming, with foam being blown from the crystallizer. Further testing was done with reduced refrigeration flow to control foam production, but as the temperature approached the freezing point, foaming became much more prominent again, and when nitrogen flow was further reduced to control foaming, the flow was so low that there was no net refrigeration effect, and the sample temperature began to gradually rise again. At this point, samples of actual waste were tested with cold nitrogen gas to simulate a dissolved air flotation, or foam fractionation, process. Foam was produced by bubbling nitrogen into a 2000 ml beaker, and the foam was allowed to overflow into a collection pan. When the foam had collapsed, the liquid sample was collected and sent for analysis along with the other samples. The results are discussed above along with the results of the freeze crystallization tests. In summary, foam fractionation was found to slightly concentrate the benzyl alcohol (and presumably surfactants used in the formulation to enhance washing from the aircraft), and the hexavalent chrome, in

the 'float' or foam fraction. Trivalent chrome was slightly less concentrated in the float. There was not enough separation to indicate that this would be a particularly good process for recovery of the paint stripping chemicals, but might be enhanced with surfactant addition.

C. FOAMING IN FREEZE CRYSTALLIZATION PROCESSES

Foaming is not an uncommon problem in applications of freeze crystallization technology. It can be handled in most instances with the addition of modest amounts of anti foam chemical. In this application, where the 'contaminants' in the waste are a valuable product that is to be reused, the addition of this chemical could significantly affect its performance in paint stripping, and therefore is preferably avoided. Prior work developing a vacuum freeze crystallization process has shown that a falling film vacuum crystallizer can avoid much of the foam generation with a number of different wastes. While there were no tests done with such a device in this program, it should be pursued in a follow-on program.

D. GAS CHROMATOGRAPHY ANALYTICAL RESULTS

Chromatograms of each of the treated waste samples, using EPA Method 8015, are included in Appendix 4. Water and benzyl alcohol are the only identifiable peaks in these chromatograms, and were used to quantify the separation of benzyl alcohol by the freeze tests. However, the chromatograms do provide some additional insight into the fate of, and the source of, various impurities in these wastes. Figure 8 compares peak heights for each of the 22 separate identifiable peaks. All of these peaks are seen in the concentrated waste (containing the concentrated benzyl alcohol in solution). Some of them disappear from the 'float' sample, and relatively few of them (5 of the 20 non-water and non-benzyl alcohol components) are in the melted ice fraction. This indicates that the freeze process was very effective in eliminating the impurities introduced in paint stripping from the ice fraction.

Comparing the wastes to the 'synthetic waste' sample shows that only three of the 20 components other than benzyl alcohol in the wastes, come from the benzyl alcohol stripping chemical. The other peaks are generated from the chemical paint stripping, and are probably oligomers of the various paints and undercoats on the plane at the time. The solvent action would be expected to break off segments of the paint polymers of varying sizes and molecular weights, and probably are the primary sources of the other 16 or 17 peaks.

What can't be determined at this time, and that will require additional testing, is whether these 'by-products' of the stripping process will remain in the aqueous phase, or be absorbed into the benzyl alcohol phase and thus be recycled back to the stripping operation. If it builds up in the benzyl alcohol, the effect on long term stripping effectiveness will have to be determined.

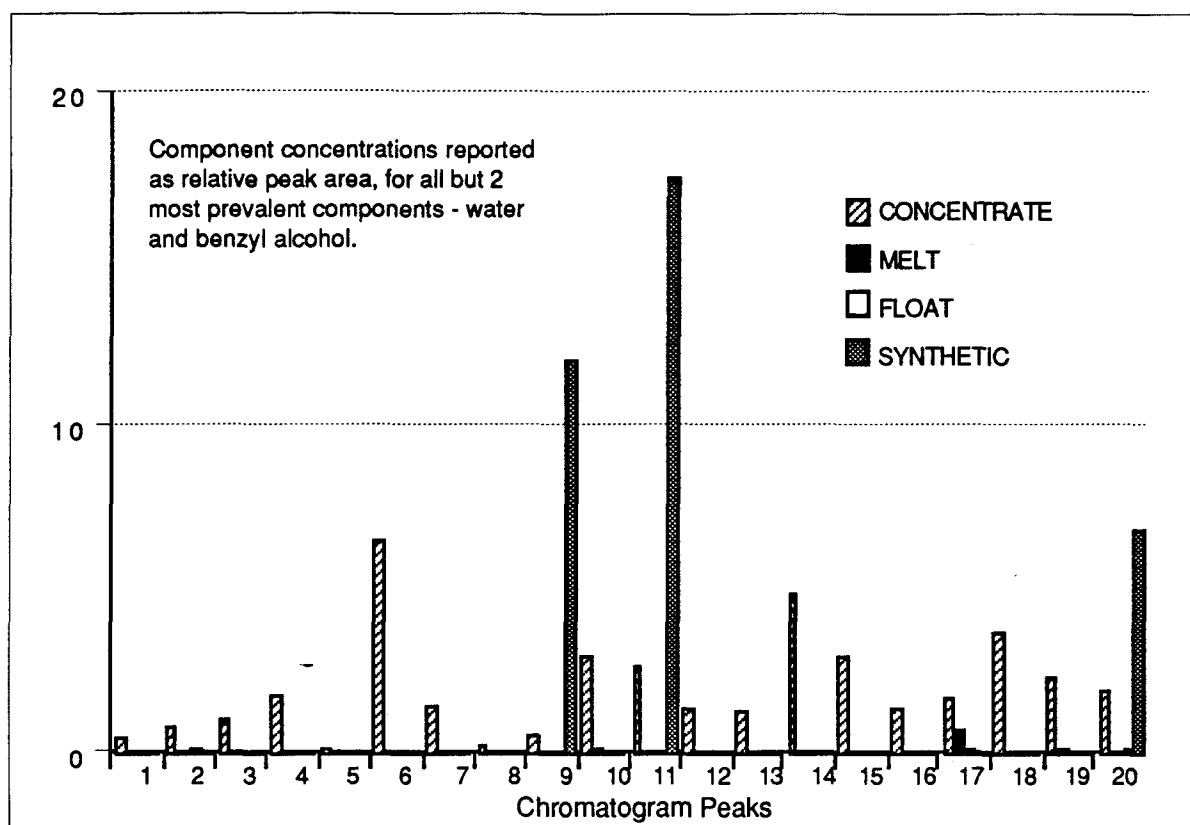


FIGURE 8

VI. PILOT PLANT DESIGN & COST ESTIMATE

A. DESIGN CRITERIA

Before a freeze crystallization process can be designed, built and used to recover industrial wastes from ALC activities, each application must be demonstrated adequately to justify the capital expenditure for the freeze crystallization equipment. This will require a field demonstration, not only for process viability demonstration purposes, but also to develop design information for full-scale equipment, and to produce sufficient recovered materials for reuse testing. Reuse testing will have to be coordinated with the commands in the ALC, recovering sufficient materials from the wastes to perform either controlled laboratory or full-scale tests using the reclaimed materials in place of the virgin chemicals that are now used.

The need for a field demonstration pilot plant was clearly demonstrated by the cost and controls required in transporting waste samples off-site from an ALC. Since nearly all of the identified applications involve controlled RCRA wastes, and full demonstration of recovery and reuse of materials from the wastes might require treating several hundred to over a thousand gallons of waste in some instances, it was obvious that it would be more cost effective to build a field demonstration pilot plant, rather than use the continuous pilot plant in FTC Acquisition Corporation's test facility.

The design guidelines for this pilot plant evolved out of project meetings with the OCALC (Oklahoma City Air Logistics Center) and the Technical Project Officer, and from a tour of the OCALC. The highest requirements of the Air Force for a freeze crystallization recovery process are ease of operation and process reliability. Both of these are met if there is a common process that can be easily understood by operating personnel, highly automated, and having a single process that, with few modifications, meets the needs of all applications for recovery of materials from the wastes. A vacuum freeze crystallization process was identified as meeting these requirements. The crystallizer and ice wash column that are the core of any freeze crystallization process are supplemented with other unit operations to meet the total separations and purification requirements of each application. This ancillary equipment will change between applications, as illustrated in Table 2, which lists the process requirements for each of the six major applications identified in Section IV of this report..

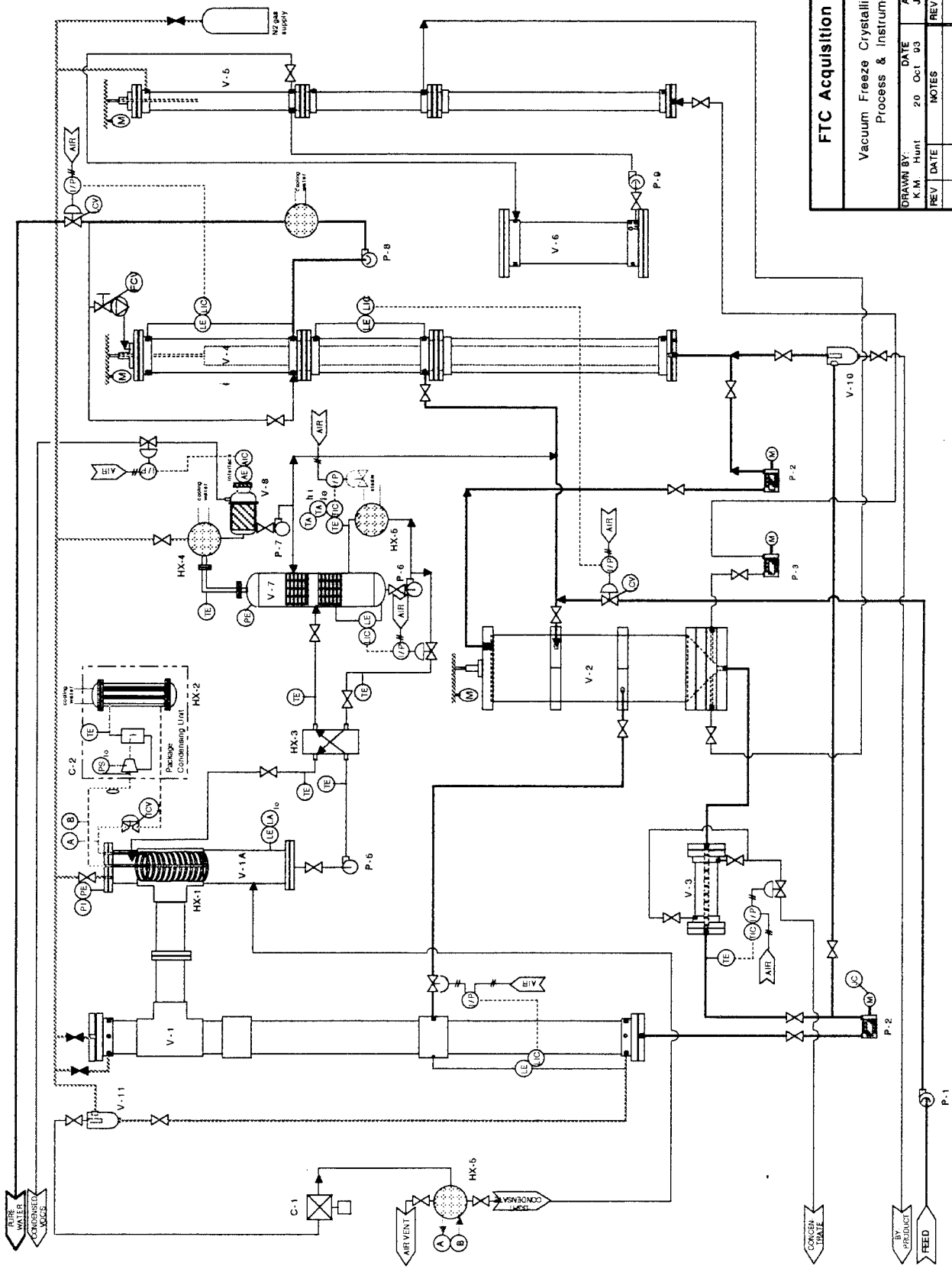
A demonstration pilot plant should include all of the ancillary unit operation equipment to be able to process any of the identified wastes. This means that in any given application there will be some components of the pilot plant that are not being used, and will be isolated from the operating part of the plant either by closed-valves or by removing sections of piping. A Process & Instrument Diagram (P&ID) was developed that meets these capabilities, and is shown in Figure 9.

TABLE 2
PROCESS REQUIREMENTS

WASTE	Crystallizer	Condenser/ Absorber	Eutectic Separator	Wash Column(s)	Intermediate &/or Product Storage
1. Paint Stripping Waste-waters	Primarily aqueous waste; water below its triple point; foaming character require special design, or antifoam chemical feed.	Below water triple point, so either a desubliming condenser or an absorption cycle.	Organics remain fluid, but insoluble and viscous... can probably remove in hydrocyclone.	Used to purify water for reuse in paint stripping operation.	Sump under paint stripping area used to hold wastes during 4 or 5 days they are being processed. 15,000 gallon clean water storage.
2. Paint Thinner - F-Waste	Cold solvent boils above triple point; paint solids agglomerate and harden, water forms ice.	Simple refrigerated condenser, since solvent vapors are above their triple point.	Tacky Paint solids may cause problem in hydrocyclone... may require gravity settling, or screen.	Not required.	Drum storage of raw wastes and recovered solvent. Drum disposal of paint residuals.
3. Spent Caustic & Acid Cleaners	Water triple point is depressed by acids and bases in waste; impurities precipitate; 50% water removal as ice	Water activity is depressed by the acid and caustic, so requires absorber loop to get pressures below 2 mm Hg absolute	Caustic baths will precipitate some carbonate salts; acid baths may produce some heavy metal salts... remove & partially dewater in hydrocyclone, grow for recovery in eutectic separator.	Used to purify the ice removed from the used / diluted acid and caustic cleaning solutions. Minimizes the loss of residual cleaner, and gives water that meets discharge standards or can be reused.	Wastes stored and transported in bulk, or processed from their current process tanks. Water discharged or stored for reuse, residual sludges stored in drums for disposal service.
4. Nickel Plating Rinse-waters	Simple water balance application; slight depression of water triple point; may be some impurities that precipitate.	Water slightly below its triple point, therefore a desubliming condenser or an absorber loop.	Little in the way of impurities... use hydrocyclone to remove them.	Used to purify ice that is removed from the wastes, so that it meets quality standards for reuse as a rinse water.	Either adapt current rinse tanks to contain material between runs, or store in new bulk storage tank. Water recovered is either discharged or stored for reuse; chemicals recovered are recycled to bath.
5. Sodium Nitrate Wastes	Eutectic crystallization, with significant depression of water triple point	Water activity is depressed by the high salt content, so requires absorber loop to get the low vapor pressure (<2 mm)	NaNO ₃ crystals need to grow for easy recovery & decontamination... need growth column / eutectic separator.	Used to purify ice removed from the waste; also may need a separate column for purifying the salt crystals that are recovered.	Waste transported in bulk or processed directly from tank. Water discharged or stored; salts stored in drums for reuse / resale.
6. Fuels & Calibration Fluids	VOC's operating significantly above triple point; water crystallizing by direct contact with cold VOCs	More volatile fuel components are the direct contact refrigerant, and can be condensed against a cold surface on the condensing coil.	Water solids (ice) is 'heavy' component (density greater than that of the fuel) and can be removed in hydrocyclone; when melted will form a separate layer.	Not required.	Wastes stored in bulk between recycling runs; treated product stored in drums for reuse.

MAJOR EQUIPMENT LIST

- V-1 Crystallizer
- V-1a Vapor Condenser
- V-2 Electric Separator / Growth Column
- V-3 Internal Filter
- V-4 Ice Wash Column
- V-5 Salt Wash Column
- V-6 Salt Product Tank
- V-7 Absorbent Regeneration Column
- V-8 Absorbent Decanter
- V-9 Hydrocyclone
- V-10 Separator
- V-11 Separator
- P-1 Feed Pump
- P-2 Slurry Pump
- P-3 Ice Column Pump
- P-4 Salt Column Pump
- P-5 Condensate Pump
- P-6 Regeneration Column Bottoms Pump
- P-7 Regeneration Column Wash Water Pump
- P-8 Salt Product Pump
- P-9 Salt Product Pump
- P-10 Cooling Water Pump
- C-1 Compressor / Vacuum Pump
- C-2 Refrigeration Compressor
- HX-1 Main Condenser
- HX-2 Refrigeration Condenser
- HX-3 Absorbent Interchanger
- HX-4 Regeneration Column Condenser
- HX-5 Regeneration Column Reboiler
- HX-6 Mellor
- HX-7 Non-condensables Condenser



FTC Acquisition Corporation

Vacuum Freeze Crystallization Pilot Plant Process & Instrument Diagram

DRAWN BY:		DATE		APPROVED BY:		DATE	
K.M. Hunt		20 Oct 93		J.A. Heist		30 Oct 93	
REV	DATE	NOTES	REV	DATE	NOTES		

Figure 9

Other design criteria arrived at in these discussions are summarized in Table 3. Since the full scale facility requirements are for not more than 1000 pounds per hour of waste processed, the capacity of the pilot plant should be not less than 10 nor greater than 100 pounds per hour. The final determination of the pilot plant capacity will depend to some degree on the availability and capacity of pilot plant equipment that will be determined in the detailed design activity of a Phase 2 program, but a preliminary size of 20 pounds per hour was selected.

The pilot plant will need to be as compact as possible, and easily movable between locations in an ALC. At the OCALC all of the industrial facilities other than paint stripping are located indoors, but there is generally good access to the cleaning and plating operations through the walls of the building. Most of the parts racks, aircraft in different states of disassembly and reassembly, and material is pulled on hard-wheeled carts, by small tow tractors. The hard wheels are suitable for indoor moves, but outdoor movement along the periphery of the building will require pneumatic tires. The corridors within the OCALC are all at least 10 feet wide and have a minimum of 14 feet clearance overhead. The pilot plant equipment can be mounted in a 4' x 8' skid, mounted on pneumatic tires, and any vessels that exceed available clearances can be mounted in place on the skid for each test. A second mobile skid containing a feed tank, a product water storage tank, and a final product tank may also be required for tests where interim storage is not available. Any sludges or residues will be collected in plastic barrels or hoppers during the tests.

The pilot plant will be designed to eliminate the need for all utilities other than electricity. Cooling will be provided by air-cooled heat exchangers, and heating where required will be by electric resistance heating. Any water needed to fill the plant for start-up will be supplied by a temporary garden hose or from a storage tank on the pilot plant. Instrument air will be supplied by a small, on-board air compressor and refrigerated dryer.

Materials of construction in the pilot plant have not been finalized. It is always preferable to have visibility into pilot equipment during operations, to see what is physically happening, but glass is generally not a good material selection for equipment that is going to be moved frequently. Acrylic, clear PVC and some clear olefin materials are available in the sizes needed for vessel fabrication, but compatibility with benzyl alcohol and some of the solvents that might be tested could be a problem with plastic fabrication. At this point, it would appear that the best combination of conservative design with pilot plant utility and flexibility is to fabricate the vessels and buy off-the-shelf pumps and other process equipment made of 316L stainless steel, to use stainless steel tubing for major lines that won't have to be changed very frequently, and to use a teflon type material for tubing and piping where flexibility and easy modification is needed.

TABLE 3

DESIGN CRITERIA

CAPACITY

50 pounds per hour crystallized water
@ 50 to 90% recovery

FEED CAPABILITY

Capable of processing any of the six
candidate wastes from ALC's
with minimum re-piping and no
assembly of additional unit operations.

EUTECTIC OPERATION CAPABILITY

- Growth tank capable of providing
5 hour crystal growth time.
- • Hydrocyclone for separation of 'sludges'
and small crystals from ice.
- Eutectic Separation capable of
50 pounds per hour of ice

SECOND LIQUID PHASE CAPABILITY

- Separation of "heavier than water"
organic phases from
ice and from mother liquors
(3 phase separation capability)

CRYSTAL PURIFICATION

- Wash Columns for both Ice and Eutectic Salts

UTILITIES

- Self Contained except for electricity, 240 v 3 Ø
- On-board air compressor and dryer for instrument air
 - Electric Heating and Air Cooling

MOBILITY

- Skid Mounted on pneumatic tires
- Overall skid dimensions not to exceed
4'w x 10' long x 16' tall

MATERIALS OF CONTRUCTION

Vessels and Process Equipment of 316L Stainless
Pipe / Tubing of 316L or fluorocarbon pipe or tubing

B. PILOT PLANT DESCRIPTION

This pilot plant will use a falling film, vacuum flash freeze crystallization process that has been developed and tested under previous programs in FTC Acquisition Corporation's laboratory. Foaming is greatly reduced by evaporating liquid from a rapidly regenerating surface, rather than from deep in a pool. A spray of recirculated liquid falling within the crystallizer also mechanically breaks the foam that is produced. The residence time in the falling film is only about 30 seconds or less, so the time needed to grow ice crystals is provided by the pool in the bottom of the crystallizer and the residence time in the bottom of the eutectic separator / growth tank, if it is being used.

The eutectic separator / growth tank is physically as depicted in the P&ID. It has a conical bottom where the salt crystals, being heavier than the process fluid in all cases studied in this program, will form a fluidized bed, with the largest crystals in the bottom of the apex of the cone, and progressively smaller crystals in the upper part of the cone and in the bottom of the straight-wall cylindrical section. A collection ring in the bottom of the cylinder collects the concentrated process liquor, along with the smallest of the salt crystals, for recycle to the crystallizer, where additional solvent is removed to create additional supersaturation. Between the bottom collection ring and the upper ring, the ice floats through a generally quiescent zone, and most of the impurities are displaced from the crystal surfaces. An ice slurry is taken off of the top of the separator and pumped to the ice wash column. Drained liquid from the crystals, along with excess wash water, is recycled to the separator through the upper ring.

The pilot plant will also have a hydrocyclone for applications where salt crystals can be removed without the need for significant purification, and where heavy liquid organic phases are formed and need to be removed from the ice slurry. In a centrifugal liquid flow that is created in a cyclone, the ice, since it is lighter than the liquid, is forced to the center, and flows upward through the inner collection tube out of the top of the hydrocyclone. Heavy liquids and solid phases are removed through the bottom cone of the hydrocyclone.

Wash columns are included in the design for both ice purification, and for salt purification, if that should be a desired goal of any of the defined applications or of other applications identified in the future.

The refrigeration for the pilot plant is provided by an air-cooled, package condensing unit that is normally used in split air-conditioning systems in homes. The units are well developed, off the shelf, inexpensive, and relatively efficient. This is piped to a condensing coil in the top of the condensing section of the crystallizer, and flow of refrigerant is controlled by a superheat-control expansion valve.

Pumping requirements in pilot plant operations are best met with positive displacement pumps with DC, variable speed drives. Progressive cavity, peristaltic,

TABLE 4
Pilot Plant Equipment

V-1	Crystallizer	12" Nominal x 10' tall Low-foam internals	P-3	Ice Column Pump	Peristaltic Pump, .25 to 2. gpm 50 feet head
V-1A	Crystallizer Condenser	1.5 ton coil, finned surfaces Aluminum construction	P-4	Salt Column Pump	Peristaltic Pump, .25 to 2 gpm 50 feet head
V-2	Eutectic Separator / Growth Column	15" cylinder dia. x 36" high 3:1 Cone slope, semi-elliptical head, internal pin stirrer	P-5	Condensate Pump	Progressive Cavity, .1 to 1. gpm 50 feet head
V-3	Inertial Filter	1" diameter slotted tube in 3" pipe shell	P-6	Regeneration Column Recirculation Pump	Progressive Cavity, 1 to 5 gpm 50 feet head
V-4	Ice Wash Column	6" ID nominal column Drain collection tank annulus Melt repulp trough annulus 10 rpm scraper w/ wash arms	P-7	Regeneration Column Overheads Pump	Progressive Cavity, .5 to 2 gpm 50 feet head
V-5	Salt Wash Column	2" ID nominal column Drain & Melt Annuli 10 rpm scraper	P-8	Melt Pump	Centrifugal Pump, 1 to 3 gpm 15' head maximum
V-6	Salt Product Tank	12" diameter nominal x 36" tall PVC, PP or PE construction	P-9	Salt Product Pump	Centrifugal Pump, 1 to 3 gpm 15' head maximum
V-7	Absorbent Regener- ation Column	6" dia x 10 ' tall, 2 ea x 2' packed sections 3' deep sump & 2' open at top	HX-1	Main Condenser	Coil, 1.5 ton capacity Aluminum, finned tube
V-8	Absorber Decanter	4" flanged horizontal vessel Sight-glass heads	HX-2	Refrigeration Condenser	Part of package condensing unit (standard AC package)
V-10	Hydrocyclone	5 gpm maximum feed rate	HX-3	Absorbent Interchanger	Plate & Frame, aluminum 5000 BTU / hr, 10° LMTD
V-11	Vapor Line Cyclone	minimum opening 3/16": PE, PP or fiberglass suitable	HX-4	Regeneration Column Condenser	Coil, finned tube, aluminum 15,000 BTU / hr capacity
P-1	Feed Pump	Diaphragm, .25 to 5 #/min (2 to 35 gallons per hour) 10 psig maximum head	HX-5	Regeneration Column Reboiler	Electric Emersion Heater, 5 kw on temperature control with solid state relay
P-2	Slurry Pump	Lobe Pump, 1 to 5 gpm 35 feet head	HX-6	Melter	Electric Emersion Heater, 2 kw on temperature control with solid state relay
			HX-7	Non-Condensibles Condenser	Coil, aluminum, finned surface 2,500 BTU / hr capacity

flexible impeller and lobe pumps are all available in this size range, are all positive displacement with varying degrees of slippage, and all in about the same price range. To the greatest degree possible, selection of pumps and spares should allow interchange-ability between the types of pumps in each service in the pilot plant. The use of positive displacement pumps with calibration curves is also an inexpensive means of determining flow rates in a process without investing in expensive flow meters.

Instrumentation needs have been kept as minimal as possible. Temperatures will be obtained through high-accuracy thermocouples with ice point calibration. Up to 20 points will be accessed by each of two multi-point selector switches. Two of the thermocouples will provide input to control loops. Vessel levels will be measured with differential pressure (dP) instruments in 5 places, and three of these will provide input to controllers. The 2 temperature and 3 level controllers will be self-tuning PID controllers. In the pilot plant the absorbent regeneration column reflux will be controlled manually, as will bleed of any heavy or light organic liquid phase.

Major process vessels and equipment are summarized in Table 4. Sizing in this table is based on a plant capacity of 50 pounds per hour of crystallized water at an absorbent liquid temperature of 25° F. Ambient heat leaks into the process vessels and from mechanical heat input is assumed to be equal to 100% of the process load in this application, for a total refrigeration heat load of 15,000 BTU per hour.

VII. IMPLEMENTATION PROGRAM

FTC Acquisition Corporation recommends an implementation program consisting of a Phase II SBIR program, followed by installation of one or more plants at the OCALC for processing one or more of the wastes identified in this report. The Phase II program will consist of 3 major activities:

1. Further laboratory development and demonstration, particularly of the low-foaming vacuum freeze crystallizer, and testing it on simulated paint stripping wastes to determine that foam generation can be controlled.
2. Detailed design, procurement and fabrication of a transportable pilot plant that will be moved to the OCALC and tested on one or more waste streams.
3. Field Tests at the OCALC.

An implementation program should also include Technology Transfer within DoD, other government agencies and private industry. The applications for metal finishing wastes and aircraft paint stripping can be used directly by the commercial airline industry, the aerospace industry, and general manufacturing. The U.S. Army has been looking for alternatives to dichlorobenzene for stripping CARC paints and undercoats from helicopter magnesium airframes. Work done at Tooele Army Depot and the Corpus Christi Army Depot are being documented by a team at Battelle Columbus.

A fourth component of this program should be the active Technology Transfer of not only the activity here, but such things as the use of benzyl alcohol based paint strippers and minimization of cyanide and cadmium plating, that is being developed at OCALC. This can be done by presentations at technical conferences, such as AIChE and ACS meetings, and by direct communications with other government facilities. FTC will take a lead in these technology transfer activities in Phase II, and work with the Technical Project Officer at Tyndall AFB, as well as with other U.S. Air Force personnel in the various ALC's in this activity.

VIII. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

Several conclusions about freeze crystallization, in general, about opportunities for material recovery and recycling in DoD industrial facilities, and about the integration of the capabilities of the freeze crystallization process into these DoD opportunities, can be made as a result of the study completed under Phase I of this SBIR grant:

1. The Air Logistics Centers (ALCs) in the United States Air Force (USAF) present a number of opportunities for material recycling and waste minimization using freeze crystallization. At one ALC - The Oklahoma City ALC (OCALC) at Tinker AFB - opportunities were identified that will save over \$2 million per year, and reduce the generation of toxic wastes by over 10 million pounds per year. This can be done with three freeze crystallization (FC) plants, each costing between \$600,000 and \$1 million and costing less than \$200,000 per year to operate.
2. A vacuum freeze crystallization process can probably be designed that will work universally on all of the applications identified in the ALCs. The crystallizer and refrigeration equipment will be the same for all applications, as will the ice purification column. Equipment for separating the other materials for recycle - the paint stripping chemicals, the impurities from the cleaning baths, etc - could require one of several different devices. A demonstration pilot plant should include the flexibility of having all of these devices, but the production units would require only the device needed for the specific application.
3. The optimum capacity for freeze crystallization plants (FC plants) in ALCs is 1000 pounds per hour (#/hr) or less (3000 gallons of water recover via crystallization per day), or less.
4. In most cases one plant can service multiple applications, since waste generation is intermittent. The applications that will require a dedicated FC plant are recovery of benzyl alcohol paint stripping chemicals, and recovery and recycle of chemicals and rinse water in nickel plating.
5. Wastes from paint stripping and nickel plating can be totally recycled for extended periods. Periodically a small amount of waste will have to be bled off to remove the build up of contaminants that will occur in both paint stripping and nickel plating operations. The water crystallized from both can be used for washing/rinsing operations. The paint stripping chemicals and nickel plating salts can be recycled directly to their respective operations.

6. Acid and caustic cleaning solutions, nitrite/nitrate surface preparation baths, cleaning solvents, calibration fluid, and contaminated fuels, are all dumped periodically and can be treated in batches when sufficient quantities accumulate in the storage containers that exist at the ALC's.
7. Contaminated groundwater is processed at the OCALC in a vacuum stripper with carbon adsorption to remove VOCs from the air after the stripping tower. The carbon is regenerated with steam, and the vapors from the regenerator are condensed and sent out as a hazardous waste for incineration. There is also a very low level of contamination from heavy metals, so the air stripped effluent is polished with reduction (of chrome) and hydroxide precipitation of the heavy metals. The economics do not appear to warrant processing of the groundwater in a VFC plant, because of the relatively low levels of contamination. However, it does appear that vacuum stripping will be more cost effective than air stripping for expansion of the groundwater facilities at OCALC, and probably at other DoD facilities as well. Vacuum stripping is used in freeze crystallization plants to deaerate feed to the process and to strip refrigerant from the effluent to less than 10 ppb. It has technical and economic advantages over air stripping when very low effluent concentrations are required and/or with decreasing volatility of the VOCs.

B. RECOMMENDATIONS

The major recommendation from this Phase I work is that a Phase II should be implemented that would produce a field pilot plant for demonstrating the use of FC technology as outlined in this report, with the tests on that pilot plant providing the design data needed for commercial equipment. Elements of the Phase II program that are needed to insure successful operation of the field pilot plant, include:

1. Crystallizer Development - all of the applications can be processed with a vacuum freeze crystallization process, but several of the applications have a foaming characteristic. Foaming is normally handled by the addition of chemicals to reduce the surface tension between the interacting, foaming chemicals (usually water and a surfactant, only in fuels it can be between different organics). Where the material is to be recycled it is best to avoid the addition of anti-foaming chemicals. FTC Acquisition Corporation has had some success with a new crystallizer concept, which will be further developed and demonstrated in the early months of a Phase II program.
2. A pilot plant was designed in this Phase I contract, that will be built and tested in Phase II, to demonstrate in the field the ability of a Vacuum Freeze Crystallization (VFC) process to process the various wastes at the OCALC for reuse and recycle.

3. Implementation of VFC in the ALC's will produce cost savings and reduce the generation of toxic wastes needing treatment, discharge and destruction. Field tests of the pilot plant need to be coordinated with the production departments at the ALC so that samples of recovered materials can be tested to assure they will meet quality control requirements, and not impact the operations of the ALC.
4. Environmental compliance personnel need to be involved in implementing this technology, since it is treating streams that are now considered wastes, many of them hazardous. Treatment of hazardous wastes requires permitting the site as a treatment facility, and obtaining a Part B permit. The VFC plants will, in actual fact, be part of the production facility, recycling materials used in the production process, and it will only be the residues from the VFC plants that will be wastes. This philosophy needs to be incorporated in the environmental compliance and reporting functions at the ALC.
5. The pilot plant has been designed so that it can also operate as a vacuum stripper. Tests on pump-and-treat groundwaters at the OCALC should be scheduled, as this eliminates the need for vacuum absorbers on the air stream used in air strippers, and can be implemented and operated more economically than the systems that are currently used there. The demonstration of vacuum stripping can lower the capital and operating costs for future pump-and-treat systems, that will be needed for additional capacity at the OCALC and other U.S. Air Force / DoD facilities in the future.

[illegible]

TASK NO: 2 **TASK TITLE:** Needs Identification

OBJECTIVES & DELIVERABLES

1. Visit engineering, environmental, and operations staff at Tinker AFB, OK to identify operations that generate industrial wastes that either present a disposal problem or that represent a potential by-product recovery / waste reuse and/or recycle opportunity.
2. List these potential applications and work with TPO and Tinker AFB staff to develop a prioritization of these applications.

WORK DESCRIPTION, RESOURCES, METHODS, ETC

1. Conduct interviews with designated personnel at Tinker AFB by phone, prior to visit. Arrange visit to view industrial operations, including but not limited to: paint stripping; parts cleaning; electroplating operations; painting; vehicle maintenance; fuel storage and transfer; current waste treatment operations; and any remediation sites.
2. Assemble data on quantities, flow rates, and chemical compositions of wastes from the various above areas and operations.
3. Identify candidates that present the greatest technical challenge to the Air Force in terms of ability to treat with conventional technology, project operating capabilities with freeze crystallization of each of these streams, and prioritize the applications in terms of greatest needs and projected capabilities of freeze crystallization to meet the needs of the Air Force.

MILESTONES:

- Tinker AFB Visit 2nd month
- Applications Priority List Draft 2nd month

SCHEDULE:

Start - Month 2 Finish - Month 2

[illegible]

Job NO.: 31 JOB TITLE: Material Recycling & Waste Minimization by FC
TASK NO: 3 TASK TITLE: Laboratory Testing

[illegible]

TASK NO: 4 **TASK TITLE:** Engineering and Cost Support

OBJECTIVES & DELIVERABLES

1. Predict costs for processing candidate waste streams and process fluids at US Air Force Air Logistics Centers, and for treating wastes at remediation sites.
2. Develop a design and preliminary costs estimate for pilot plant for Phase 2 SBIR support.

WORK DESCRIPTION, RESOURCES, METHODS, ETC

1. Preliminary cost information on various applications will be developed using computer programs based on historical data on plant capital and operating costs, adapted to the conditions of each application. The costs reflect the specific freeze plant configuration needed for individual applications, and are adaptable between secondary refrigerant and vacuum freeze systems.
2. The Phase 2 pilot plant will be designed with input from the Project Technical Officer. First, the objectives of the pilot plant, its test location(s), flexibility to treat different wastes, capacity and refrigeration cycle will be determined. Other design criteria relating to details of materials of construction, applicable codes, etc, will be defined in this process of defining design criteria.
3. Preliminary engineering design of the pilot plant will include developing heat and mass balances, selecting equipment, and designing vessels, layouts and piping and instrument details.
4. A preliminary budget will be developed for the pilot plant, using verbal quotes from vendors and fabricators, and estimating assembly and engineering costs.

MILESTONES:

- | | |
|------------------------------|-------------------------------|
| • Estimate application costs | Start month 2, finish month 3 |
| • Establish design criteria | Start month 2, finish month 4 |
| • Preliminary design | Start month 3, finish month 5 |
| • Phase 2 Pilot Plant Budget | Start month 4, finish month 5 |

SCHEDULE:

Finish - Month 5

[illegible]

TEST PLAN

for

U.S. Air Force, SBIR 93-11
MATERIAL RECYCLING & WASTE MINIMIZATION
BY FREEZE CRYSTALLIZATION
TYNDALL AFB
Lt. Phillip W. Brown
Program Technical Officer

OCTOBER 1993

SUMMARY

This Test Plan describes the methods and predicts the results that are expected in running bench top and continuous pilot plant tests on the following samples:

- Washwaters from aircraft paint stripping with benzyl alcohol strippers.

Test apparatus, detailed operating instructions, expected results, analytical support requirements, data reduction methods, and specific goals of these tests, are detailed in the sections following this summary, dealing with specific tests on specific streams.

The specific objectives of the test(s) described here include:

- Applications Identification - The testing that will be done as part of this program will help identify and prioritize opportunities for this technology in Air Logistics Centers in the U.S. Air Force. Bench top testing will help define operating conditions and highlight any potential difficulties with individual applications. A Continuous Pilot Plant Test will demonstrate the capability of freeze crystallization (FC) on one stream - Benzyl Alcohol paint stripping wash waters.
- Solid-Liquid Equilibrium - All tests provide freezing point data as a function of solution chemistry, and thus provide points or small increments of knowledge about the phase behavior of the individual solution. These tests will also determine if the benzyl alcohol forms a separate organic phase that can be recovered and reused in paint stripping operations at the ALCs.
- Purification Capability - In general, bench-top tests only succeed in reducing impurity levels in crystals by a factor of 2:1 to 10:1, because it is impossible to remove all of the (impure) mother liquor from the crystal surface. It is more important, therefore, to look at trends in removal of each contaminant, since if any are removed less efficiently in these tests it indicates that they are part of the crystal being formed (a solid solution) or are a separate crystal (a eutectic) that must be physically separated from the desired product crystals. The anticipated purities of

the melted ice that will constitute a successful test here are:

<u>Constituent</u>	<u>Initial Concentration</u>	<u>Final Concentration</u>
hexavalent chrome	unknown	50% or less of original
total chrome	unknown	50% or less of original
benzyl alcohol	.5 to 1%	50% or less of original
other organics	unknown	50% or less of original

- **Product / By-Product Recovery** - The goal of these tests is to simulate a full-scale plant that can recover all of the water for reuse in washing paint and stripper from aircraft, and all of the dissolved benzyl alcohol and associated additives for direct application on other aircraft surfaces..
- **Crystal Habit & Crystallization Kinetics** - These tests will provide specific information on crystal growth kinetics as needed to design crystallizer residence times for a portable field pilot plant.
- **Heat and Mass Balance Information** - A DSC scan produces adiabatic data on the sensible and latent heat of the solution as a function of temperature, showing the net cooling that is required to achieve incremental degrees of recovery. Pilot plants are generally not sufficiently well instrumented or calibrated to give accurate projections of ambient heat gains, nor are pilot plants generally fully representative of the full scale plant. Only in dedicated and specialty pilot plants can this data be produced by testing. These tests will provide phase data needed to define the operating conditions in a continuous freeze crystallization process operating on benzyl alcohol stripping wastewaters. The mass balance will be dictated primarily by the initial composition of the wastewater and the anticipated separations into separate product streams. The energy balances of field pilot and full-scale plants can be accurately predicted from operating temperatures and mass balance information.
- **Process & Component Design Data** - Bench treatability tests provide little useful design data, limited only to freezing points and some basic physical property data, such as viscosity, densities, (limited) phase equilibrium data, and general observations on how the process works. Continuous pilot plant tests begin to provide detailed design data for the crystallizer, wash column, other major process vessels, and define the pumping requirements, as well as define any special process capabilities needed for the application.

TEST PLAN
U.S. AIR FORCE SBIR 93-11
BENZYL ALCOHOL STRIPPER RECOVERY

BENCH TOP TREATABILITY TESTS

1. Goals and Anticipated Results

- **Phase Equilibria:** Each test gives data about freezing points and the existence or lack thereof of eutectic conditions at one solution composition. Since only about 20% of the solution is crystallized in these tests before the crystal mass becomes indiscernible, there is no significant change in solution composition. Therefore, to build a more complete picture of the phase equilibria of the system, tests with different compositions must be run. Tests will be run with actual wastes taken from the sump under the wash racks at the OCALC (Oklahoma City Air Logistics Center), Tinker AFB, OK. Additional tests will be run with wastes simulated by mixing stripper (El Dorado Chemical Product SR-125A Polysulfide Remover) with water, at concentrations up to 2% by weight).

- **Crystal Habit & Crystallization Kinetics:** These tests are generally run with very large and uncontrolled subcooling, resulting in excessive nucleation and short crystal growth periods, so the crystals remain very small, and little can be discerned about crystal habits or growth rates on the various faces of the crystal.

- **Physical Properties:** These tests will at partially define a number of physical properties of the solution, including density, crystal density, solution viscosity, freezing point, and the occurrence of additional phases in the waste as it is being processed.

- **Purification Abilities:** These tests do not produce the reduction in impurities that are seen in continuous freeze crystallization, or that is inherent in the purity of crystals that grow from melts or from solution. The product to be pure must have all impure solution washed from the crystal surface by pure melted product, which can't be done because of the typically small amount of crystal formed and its small crystal size. Bench top tests typically produce a product with a reduction in impurities of 30 to 50%. When the crystallizing temperature is at or above room temperature, and the mother liquor has a low viscosity and surface tension, the reduction in impurities can go as high as 90 to 99%, but only in those specialized circumstances. A reduction of 50% or more of the specific contaminants in the melt will demonstrate a separation capability that will justify further demonstration in continuous pilot plant equipment.

It is more important in these tests to compare the reduction of individual impurities, as this will show whether there might be a solid solution (one or more of the impurities in the solution is soluble in the crystal that is being formed) or a eutectic condition (where more than one component in the solution is crystallizing at the same time). If either of these conditions occur, the concentration of the impurity in the desired crystal product often increases or has minimal reduction. Here we will be looking more for the onset of a second liquid phase, representing the separation of

recoverable benzyl alcohol.

- **Solvent/Solute Recovery:** Individual tests provide little data on ultimate recovery of any constituent in a process stream. Since the paint solids will for the most part be insoluble and separated from the liquid wastes, the benzyl alcohol and water should be totally recyclable, requiring only infrequent bleeding to purge impurities from the system. Determination of how much purging will be needed will require processing large volumes of waste, and probably won't be determinable at least until field pilot plant tests.

- **Continuous Facility Design Data:** These tests are too limited in scope to provide any significant design data, beyond general process capabilities.

2. Test Apparatus & Description of Tests

The major components needed for these tests include the following:

- a dewar or other insulated flask that can hold a cold liquid bath, to dip the sample into.
- Glass bottles with sample, with sufficient head room to allow for any expansion when the solution crystallizes; typically from 15 to 1 liter in size. Use an appropriate stopper with either an expansion thermometer or an electronic thermometer through the stopper.
- An acrylic tube from 1.25 inches in diameter (3.25) cm in diameter, plugged at the bottom with a porous plate, that allows liquid flow but stops small crystals.
- A cold source, which for these tests needs to only generate a temperature of -3° C (26° F), which will be done with ice in a salt brine. Tests will also be attempted by direct contact with cold N2 gas (-360° F at the point it is generated.)
- A calibrated thermometer, scales, and calibrated Cannon-Fenske viscometer tubes.

3. Methodology

- **Test Methods & Data Points - Indirect freezing**

1. Prepare cold bath
2. Place desired volume of sample in a glass bottle
3. Insert the bottle in the cold bath, slowly stirring with tongs.
4. Remove the bottle from the bath every 3 to 4 minutes to inspect for freezing and to measure the liquid temperature.
5. When crystallization begins, observe crystal habit and approximate size, and record any subcooling that was observed.

NOTE: If subcooling exceeds 20° C below the expected initial freezing point, try to induce nucleation with more agitation, by tapping on the glass, or by seeding.

6. When the crystal density becomes so thick that the flow becomes thixotropic,

it is time to stop cooling and pour the slurry into the drain tube.

7. Fill the drain tube with slurry, and measure the volume of filtrate with time; measure the height of the resulting crystal bed when the liquid has drained, and if less than 8" high, refill the tube with slurry and measure the resultant volumes over time. Measure the final crystal bed height, and observe any 'meniscus' effects of undrained liquid in the crystals. Remove a sample of the filtrate for analysis.
8. Blow a small volumetric rate of air through the crystals, from the top, with the air temperature above the melting temperature of the crystals, which will melt the crystals. Collect separately the melted crystal that drains, and segregate especially the last of the melt for analysis.

- Test Methods & Data Points - Indirect freezing

1. Place sample in a globe or pear shaped separatory funnel, up to about 1/3 of the height of the funnel. (In a 1 liter flask this will hold about 200 to 250 ml of sample).
2. Connect a flexible hose to the vapor connection on a liquid nitrogen cylinder. If the cylinder doesn't have a needle valve, connect one to the valve on the cylinder, and the flexible hose to the needle valve.
3. Blow cold nitrogen vapor through the line until it becomes evidently cold by a build up of frost (condensed, water from the air) on it. At this point, decrease the flow of gas to almost nothing and insert it into the liquid in the flask. Increase the flow of gas again until boiling becomes so violent that some liquid is entrained in the gas flow out of the top of the funnel. Decrease the gas flow by 1/4 to 1/2 turn on the needle valve, so that there is no carryover of liquid.
4. Continue blowing gas until the liquid freezes and the amount of ice becomes such that the gas flow can no longer keep the slurry homogenized. At this point shut off the gas flow, measure the temperature, and drain the liquid through the drain column, following steps 7 and 8 above.

- Data Reduction

- Observe and record the initial freezing point, which will be approximately the temperature that is seen just after nucleation begins.
- Measure the velocity of the drain fluid through the bed of crystals (which is approximately the rise rate of crystals in a wash column).
- Remove cold sample from the drained liquid and measure its viscosity in a calibrated viscometer that has been kept at approximately the freezing temperature of the liquid. Note: If the viscometer is colder than the freezing point, it will freeze up when sample is added, so keep the viscometer slightly above the freezing point, preferable in a cold bath, and measure and record the temperature of the bath.

- Analytical

- Analyze for chrome (total and hexavalent), and benzyl alcohol.

4. Health & Safety

- General Notes & Precautions

- Ventilation: the refrigeration sources generate gas that can cause suffocation, and thus should be used only in a well ventilated area.
- The cold sources present a hazard of local area frost bite, and direct contact with skin or other body parts should be avoided by wearing heavy gloves, long sleeve shirts/coats and full face shields while working with the fluids.
- Make sure that a first aid kit, a fire extinguisher, a wash station and absorbent material is on hand before beginning any test. Review precautions in the appropriate Material Safety Data Sheets (MSDS's).
- Hexavalent chrome is a suspected carcinogen. When handling the sample of waste from the OCALC, do so with rubber gloves, and wear goggles or a face shield while testing. Take care not to spill any sample or otherwise contaminate equipment, or ingest the sample in any way, or allow sample to remain on exposed skin surfaces. If sample does come in contact with skin, wash thoroughly with soap and water. If it comes in contact with eyes, flush thoroughly with cold water and eye wash.

- Emergencies

- Always be sure that a dry chemical or foam-type fire extinguisher is nearby when starting any test with a flammable material.
- Absorbent materials sufficient for containing the full volume of liquid used in the test should be at hand before starting any test.
- In the event of an emergency, shut off all power to the test unit, stop the test and secure the sample.

- MSDS Sheets

There are no data sheets specifically for the OCALC waste. Sheets for hexavalent chrome and for the benzyl alcohol stripper are attached at the end of this test plan.

CONTINUOUS PILOT PLANT TESTS

1. Goals and Anticipated Results

- **Phase Equilibria:** A series of tests in the continuous pilot plant (CPP) gives a fairly complete picture of the solid-liquid equilibria of a specific solution, at conditions ranging from the initial conditions to those after 80 to 90% or greater of the material in the solution has been crystallized. If eutectic conditions appear, these tests and the CPP are designed to allow the second crystal to grow, get separated from the primary crystal species, and then be removed and washed to high purity, just as does the primary crystal. These tests will be more limited in scope, and will attempt to show that benzyl alcohol forms in a separate phase that can be separated from the wastewater, and that pure water can be produced from the wash waters for reuse on the planes.

- **Crystal Habit & Crystallization Kinetics:** By testing at different solution compositions, with varying residence times and driving forces, crystallization kinetics can be fairly well defined. There is an inverse relationship between the size of the crystallizer and the size of the wash column, and in general the larger the crystal size the purer the melted product will be. Ice crystals tend to grow quite rapidly with very little subcooling (driving force), typically at 20 to 50 micrometers per minute. Only ice is expected to crystallize in these tests, as the solution temperature will still be above the freezing point of the benzyl alcohol phase that forms.

- **Physical Properties:** These properties will be determined in the laboratory tests, described above.

- **Purification Abilities:** The goals vis-a-vis purification of these tests will be to demonstrate melted ice purity and determine if the additives (to benzyl alcohol, in the stripper) will partition with the benzyl alcohol in the second liquid phase.

- **Solvent/Solute Recovery:** Tests in the continuous pilot plant (CPP) allow recovery of 80 to 95+% of the material from the feed, depending on the amount of feed processed, and the configuration of the pilot plant. The maximum recovery is limited by the volume of liquid in the process at the end of the test, and the fraction of crystal that is left in that liquid. The major process components and the associated volume of liquid in each at the end of the test (including ancillary piping, pumps, etc) is approximately as follows:

<u>Component</u>	<u>App Volume. (gal)</u>
Crystallizer	3 gallons
Eutectic Separator	22 gallons
Growth Tank	22 gallons
Wash Column	8 gallons

Thus, in tests that don't require the eutectic separator or a growth tank, which this application does not, 80% recovery can be achieved with 55 gallons of feed and 90% with 2 - 55 gallon drums. Higher recovery demonstration requires 'spiking' the test material with excess impurities or processing larger volumes. Recovery at 80% of the feed should be more than adequate to demonstrate the occurrence of the benzyl alcohol feed.

- Continuous Facility Design Data: These tests provide detailed design data on all major components of the plant, and give performance data over a wide variety of operating conditions. Specifically, the tests encompass the capabilities and limitations summarized in the table, "Test Capability & Limitation Summary".

2. Test Apparatus & Description of Tests

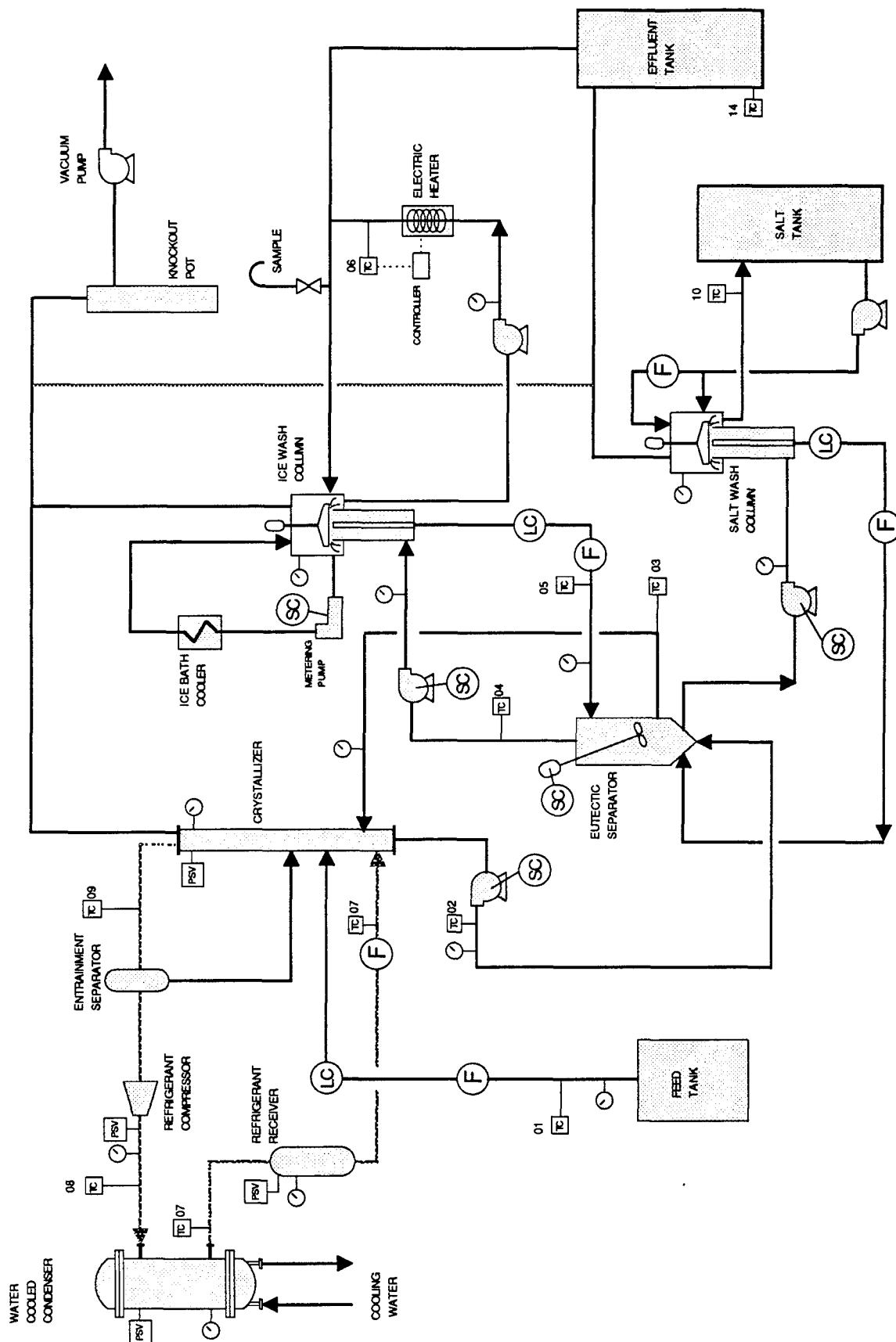
The equipment included in this pilot plant is illustrated in the Process and Instrument Diagram on the next page. The continuous pilot plant (CPP) is set up with a liquid nitrogen refrigerant crystallizer at this time, and will be tested in this configuration. The pilot plant includes:

- a vertical crystallizer, with a supply of liquid nitrogen for cooling and

<u>CONTINUOUS PILOT PLANT TEST CAPABILITY & LIMITATION SUMMARY</u>		
<u>PARAMETER</u>	<u>CAPABILITIES</u>	<u>LIMITATIONS</u>
PHYSICAL PROPERTIES		
- Solid Liquid Equilibria	Demonstrates actual SLE up to the 90% volume conversion.	Residual volume of 8 to 15 gal.
- Viscosity, Surface Tension Foaming Characteristics	Give direct measurement at operating conditions.	
- Vapor Liquid Equilibria	Not involved.	
CRYSTALLIZATION KINETICS		
- Solvent Crystallization	Gives realistic kinetic data at residence times reflecting full scale operations.	
- Solute Crystallization	Shows point where eutectic conditions begin to occur. Most tests also recover the eutectic product(s).	
PRODUCT PURITY		
- Wash Column Performance	Will decrease contamination by a factor of 250 to 10,000.	
- Solute Column Separation	Plant has a salt wash column, and can also use hydrocyclone or centrifuge for recovery.	
DESIGN PARAMETERS		
- Crystallizer	Gives direct scale-up information.	
- Eutectic Salt Separation	Gives direct scale-up information.	
- Wash Columns	Can test at maximum ice production rate, and intermediate rates.	
- Energy Consumption	More directly simulates full scale.	Inefficient equipment at small scale.
- Demonstrated Recovery (= Recovered Product Volumes/Feed Volume)	80 to 90% from a 100 to 150 gallon feed sample.	

CONTINUOUS PILOT PLANT

DirCon™ Secondary Refrigerant Pilot Plant



controls for metering it to the crystallizer.

- a eutectic separator, with provisions for quick interchange of different designs based on the needs of the application. (It won't be needed in this application and will be isolated by valves from the rest of the system.
- a hydrocyclone for removal of heavier-than-solution liquid phases, crystallized salts, and secondary refrigerant liquids.
- an ice wash column, with an electric heater in the repulp slurry line to melt the ice as it is purified and scraped off the top of the column.
- a salt wash column, where salts crystallized in the process are washed to remove mother liquor, and then redissolved in a recirculating brine stream after being scraped from the top of the column. (Redissolving the recovered salt facilitates accurate sampling of the material removed in this stream, as accurate sampling and analysis of solids is much more difficult.)
- A batch melt receiver that holds in excess of 200 gallons, so that the melt can be composited and then stripped by vacuum at the end of the test.
- In this facility the critical process pumps are positive displacement and fitted with variable speed drives, so that flow rates can be controlled without direct measurement. The reslurry pumps on the ice and salt wash columns are centrifugal with no special flow control provisions.
- The instrumentation consists of pressure gauges and high-precision thermocouples.
- Vessel construction is of clear materials (PVC and Acrylic) wherever possible for visual inspection of testing. The liquid nitrogen crystallizer is made of 316L stainless steel.

To begin the tests sample is pumped into the crystallizer from a hold tank. The repulping sections of the wash columns are filled with tap or pure water. As the inventory builds up in the system the various recirculation pumps are started. Liquid nitrogen flow is started by opening a valve from the storage tank to the control system piping. It requires about 30 minutes to get the control piping down to temperature and to reach a steady state flow of nitrogen through the crystallizer.

As ice begins to crystallize, the crystal is trapped in the wash column, and the level in the crystallizer begins to drop. Feed rate is controlled to match

the rate at which material is being removed. As the crystal inventory begins to fill the washing zone of the column(s), the scrapers are started. In the ice wash column, the ice is scraped into water in a repulping zone, and the slurry is pumped through an electrically heated chamber to melt the ice. An automatic temperature control maintains the temperature of this stream after the heater at a few degrees above the normal melting temperature of pure ice. The levels in reslurry chambers are periodically lowered by pumping out to storage tanks.

As the run progresses the variables that can be altered include feed rate, removal rate of concentrate (if any), crystallizer level (which determines residence time for a given pump rate), pumping rates of the various slurries, and refrigerant feed rate (which determines ice production rate). If no concentrate is being removed from the system, the operating temperature will gradually drop. At some point, the heat removal rate by the refrigerant equalizes with the heat leaks into the system, and ice production drops to zero. This point varies with climatic conditions (i.e., ambient heat leaks), but the refrigeration system in this pilot plant is well oversized so that this usually doesn't occur until the freezing temperature has dropped below 0° F. The freezing point of the benzyl alcohol wash water is not expected to drop below 31° F, and capacity should not be a problem.

When the test has been completed, refrigerant flow to the crystallizer is stopped and feed flow is stopped. This completes the run. Several runs are usually necessary on any given waste to test all of the independent parameters. The following table demonstrates the greater flexibility and utility of this pilot plant; the tradeoff is that a much larger volume of sample is required for testing.

3. Methodology

• Test Methods & Data Points

1. Set valves to exclude the eutectic separator / growth column. Isolate the ice and the salt wash columns, including their transfer pumps, from the rest of the system.
2. Charge approximately 12 Gallons of sample 1 to the crystallizer.
3. When the crystallizer level has exceeded 12" of depth, open the valves to the slurry pump and the wash column, then start the ice wash column feed pump and open the recirculation lines. Continue feeding the plant until the level in the crystallizer is at the specified level for the test.
4. Begin refrigerant flow under manual control at a nozzle back pressure of 14

psig and maintain until the nitrogen temperature is -250° F., then switch to automatic control to maintain the temperature at this point.

5. Operations will remain relatively steady while the solution is cooling, before ice is produced. Record data when the system has stabilized, and at [15 minute] intervals. When ice begins to form in the system, it will begin to build up in the upper (drained) portions of the wash column, and deplete liquid inventory from the crystallizer. As the level in the crystallizer drops, begin feed flow to maintain the specified level.
6. Watch the ice rise in the wash column; when it is within 6" of the top, turn on the scraper, activate the automated melt heater, and start the recirculation loop. When scraping begins, start the wash feed pump at a setting of [40% on the feed control and 20% on the pulse length - this will give approximately 2 liter per hour of wash fluid]. Monitor the melt quality, and as it comes in spec turn the wash flow back to [20/20], close the recirculation line and open the line to the effluent tank.
7. Continue adding feed and removing melted product, changing the operating conditions as specified for the individual test.
8. When the desired testing has been done, or when the volume of feed has been achieved, stop the feed, and stop refrigerant flow to the plant. Remove samples as desired, and continue recirculation flows in the plant until all of the ice has been melted, then drain the test material from the plant.

• Data Reduction

The permeability is calculated from the pressure drop and flow rate through the crystal bed, using the equation:

$$\beta_0 = \frac{Q \mu L}{\rho g A h} \quad \text{where: } \beta_0 \text{ is permeability, cm}^2$$

Q is volumetric flow, cc/sec
 μ is viscosity of fluid, gm/cm-sec
 g is gravitational acceleration, cm/sec²
 A is the cross sectional area of the bed, cm²
 L is the length of the flow path, ft
 h is the head loss, ft

The effective average crystal size can be calculated from the permeability that is calculated, using the following formula:

$$\beta_0 = \frac{d_e^2 E^3}{180 (1-E)^2} \quad \text{where } d_e \text{ is the effective particle diameter, cm}$$

and E is the porosity of the bed, cc/cc.

• Analytical

Chromium - total: digestion followed by ICP (ion coupled plasma emission spectroscopy)

Chromium - hexavalent: wet chemistry (s-diphenylcarbazide)

Color - visible light spectroscopy

Benzyl Alcohol and Additives - gas chromatography method to be determined by lab.

4. Health & Safety

See this section under Laboratory Testing section at the beginning of this document. This section is contained on page 6 of this test plan.

14/10/93

12:18

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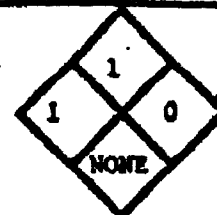
P006/007



801c PSK-125 H
F34650-92-m-1688

SR-125A

POLYSULFIDE REMOVER



MATERIAL SAFETY DATA SHEET

I. PRODUCT IDENTIFICATION

MANUFACTURER'S NAME ELDORADO CHEMICAL COMPANY, INC.		REGULAR TELEPHONE NO. 812-653-83
ADDRESS P.O. BOX 34837, SAN ANTONIO, TEXAS 78266		EMERGENCY TELEPHONE NO. 1-812-653-20
CHEMICAL NAME OR FAMILY N/A		SHIPPING NAME (DOT) NOT REGULATED
TRADE NAME AND SYNONYMS SR-125A		

NOTE: Not intended for consumer use

II. HAZARDOUS INGREDIENTS

MATERIAL OR COMPONENT	CAS NO UN NO.	%	OSHA PEL	ACCOM- PLISH	HAZARD
NONE OF THE MATERIALS USED IN THE MANUFACTURE OF THIS PRODUCT ARE LISTED AS HAZARDOUS BY OSHA.					THE HAZARDS OF SOME INGREDIENTS ARE UNKN CONTACT SHOULD BE AVE TO PREVENT SYSTEMIC C LONG TERM EFFECTS

III. PHYSICAL DATA

BOILING POINT, 760 mm Hg ABOVE 400°F	MELTING POINT BELOW 0°F
SPECIFIC GRAVITY (20/20) 1	VAPOR PRESSURE 0.1 mmHg @ 86°F
VAPOR DENSITY (AIR=1) 3.7	SOLUBILITY IN H ₂ O, % BY WT. LESS THAN 5%
% VOLATILES BY VOL. 92	EVAPORATION RATE (WATER =1) MUCH THAN
APPEARANCE AND ODOR CLEAR VISCOUS LIQUID	pH (AS IS) N/A pH AT DILUTION N/A

IV. FIRE AND EXPLOSION DATA

FLASH POINT (TEST METHOD) ABOVE 200°F C.C.C.	AUTO IGNITION TEMPERATURE ABOVE 600°F	FLAMMABLE LIMITS IN AIR, % BY VOL. LOWER: 1.5% UPPER: 15%
EXTINGUISHING MEDIA WATER SPRAY, DRY CHEMICAL, CO₂		
SPECIAL FIRE FIGHTING PROCEDURES AVOID SKIN CONTACT		
UNUSUAL FIRE AND EXPLOSION HAZARD NONE		

SAL...

ON

HEALTH HAZARD DATA		HAZARD	EFFECTS OF OVEREXPOSURE
ROUTES OF EXPOSURE			
INHALATION	Acute:	SLIGHT - (LOW VAPOR PRESSURE)	MAY CAUSE IRRITATION OF THE UPPER RESPIRATORY TRACT AND COUGHING
	Chronic:	SLIGHT - (LOW VAPOR PRESSURE)	UNKNOWN-SYSTEMIC EFFECTS MAY OCCUR WITH CHRONIC EXPOSURE
SKIN CONTACT	Acute:	MILD IRRITANT	CONTACT DERMITITIS MAY OCCUR
	Chronic:	IRRITANT	MAY CAUSE ALLERGIC REACTIONS
SKIN ABSORPTION	Acute:	UNKNOWN	UNKNOWN - SYSTEMIC EFFECTS MAY OCCUR
	Chronic:	UNKNOWN	UNKNOWN - SYSTEMIC EFFECTS MAY OCCUR
EYE CONTACT	Acute:	SEVERE IRRITANT	MAY CAUSE TEMPORARY BLURRED VISION
	Chronic:	SLIGHT	PAIN WILL PREVENT CHRONIC EXPOSURE

EMERGENCY AND FIRST AID PROCEDURES**EYES:** FLUSH EYES WITH WATER FOR 15 MINUTES.**SKIN:** FLUSH WITH WATER FOR 10 MINUTES. WASH WITH SOAP AND WATER.**INHALATION:** REMOVE TO FRESH AIR. IF BREATHING BECOMES DIFFICULT, GIVE OXYGEN.**VI. REACTIVITY DATA****INCOMPATIBILITY (MATERIALS TO AVOID)**

MINERAL ACIDS, STRONG OXIDIZERS

HAZARDOUS DECOMPOSITION PRODUCTSCARBON MONOXIDE, CO₂**VII. SPILL OR LEAK PROCEDURES**

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED SMALL SPILLS CAN BE CLEANED UP WITH ABSORBANT.
 LARGE SPILLS SHOULD BE PUMPED INTO CONTAINERS

DISPOSAL METHODS

USEPA HAZARDOUS WASTE NO.'S

NONE

CONSULT FEDERAL, STATE AND LOCAL REGULATORY AGENCIES FOR PROPER DISPOSAL

VIII. CONTROL MEASURES

SAFETY REQUIREMENTS	MATERIAL TRANSFER OR SPILL	MATERIAL USE
VENTILATION	0.5 FT/MIN	0.5 FT/MIN
RESPIRATORY	NONE	PARTICULATE FILTER
EYE PROTECTED EQUIPMENT	SAFETY GOGGLES, FACE MASK	FACE MASK
GLOVES	RUBBER	RUBBER
OTHER EQUIPMENT	RUBBER BOOTS, APRON	RUBBER BOOTS, APRON
WORK PRACTICES	AVOID ALL SKIN CONTACT	AVOID ALL SKIN CONTACT

NOTICE: The data contained in this MSDS is based on information believed to be accurate at this date. Eldorado Chemical Co., Inc. makes no guarantee as to the completeness or accuracy of this MSDS and assumes no liability in connection with the use of this information.

PREPARED BY: PAT E. SMITHDATE PREPARED: 3/20/92

SIGNATURE

Pat E. Smith

SODIUM CHROMATE

SCH

Common Synonyms Sodium chromate (VI) Neutral sodium chromate anhydrous		Solid	Yellow	Odorless
		Sinks and mixes with water.		
Avoid contact with solid and dust. Keep people away. Stop discharge if possible. Isolate and remove discharged material. Notify local health and pollution control agencies.				
Fire		Not flammable. Will increase the intensity of a fire. May cause fire on contact with combustibles. Flood discharge area with water. Cool exposed containers with water.		
Exposure		CALL FOR MEDICAL AID. DUST Irritating to eyes, nose and throat. If inhaled will cause coughing or difficult breathing. If in eyes, hold eyelids open and flush with plenty of water. If breathing has stopped, give artificial respiration. If breathing is difficult, give oxygen. SOLID POISONOUS IF SWALLOWED. Irritating to skin and eyes. If swallowed will cause nausea or loss of consciousness. Remove contaminated clothing and shoes. Flush affected areas with plenty of water. IF IN EYES, hold eyelids open and flush with plenty of water. IF SWALLOWED and victim is CONSCIOUS, have victim drink water or milk and have victim induce vomiting. IF SWALLOWED and victim is UNCONSCIOUS OR HAVING CONVULSIONS, do nothing except keep victim warm.		
Water Pollution		Dangerous to aquatic life in high concentrations. May be dangerous if it enters water intakes. Notify local health and wildlife officials. Notify operators of nearby water intakes.		
1. RESPONSE TO DISCHARGE (See Response Methods Handbook) Disperse and flush		2. LABEL 2.1 Category: None 2.2 Class: Not pertinent		
3. CHEMICAL DESIGNATIONS 3.1 CG Compatibility Class: Not listed 3.2 Formula: Na ₂ CrO ₄ 3.3 IMO/UN Designations: Not listed 3.4 DOT ID No.: Data not available 3.5 CAS Registry No.: 7775-11-3		4. OBSERVABLE CHARACTERISTICS 4.1 Physical State (as shipped): Solid 4.2 Color: Yellow 4.3 Odor: None		
5. HEALTH HAZARDS 5.1 Personal Protective Equipment: U.S. Bu. Mines approved respirator; rubber gloves; chemical safety goggles; rubber apron and sleeves, face shield, rubber shoes, protective clothing. 5.2 Symptoms Following Exposure: Inhalation causes irritation and may ulcerate mucous membranes; continued irritation of the nose may lead to perforation of the septum. Ingestion causes severe circulatory collapse and toxic nephritis; may be fatal. Contact with eyes causes severe irritation and possible conjunctivitis. Irritates skin and can cause ulcers; if skin is broken, prolonged contact may cause "chrome sores" (slow-healing, hard-rimmed ulcers), which leave the area vulnerable to infection as a secondary effect. 5.3 Treatment of Exposure: INHALATION: remove victim to fresh air; get medical attention. INGESTION: get immediate medical help; if vomiting is not spontaneous, give an emetic such as soapy water followed by copious water intake. EYES: immediately flush with plenty of water for at least 15 min; consult physician promptly. SKIN: immediately flush with plenty of water for at least 15 min; persistent dermatitis should be referred to a physician; wash contaminated skin or clothing until chromate color disappears. 5.4 Threshold Limit Value: 0.05 mg/m ³ as Chromium 5.5 Short Term Inhalation Limits: Data not available 5.6 Toxicity by Ingestion: Grade 3; LD ₅₀ = 50-500 mg/kg 5.7 Late Toxicity: Possible lung cancer. 5.8 Vapor (Gas) Irritant Characteristics: Data not available 5.9 Liquid or Solid Irritant Characteristics: Data not available 5.10 Odor Threshold: Data not available 5.11 IDLH Value: 250 mg/m ³				

6. FIRE HAZARDS 6.1 Flash Point: Not flammable 6.2 Flammable Limits in Air: Not flammable 6.3 Fire Extinguishing Agents: Not pertinent 6.4 Fire Extinguishing Agents Not to be Used: Not pertinent 6.5 Special Hazards of Combustion Products: Toxic chromium oxide fumes may form in fire. 6.6 Behavior in Fire: May increase intensity of fire when in contact with combustible material 6.7 Ignition Temperature: Not pertinent 6.8 Electrical Hazards: Not pertinent 6.9 Burning Rate: Not pertinent 6.10 Adiabatic Flame Temperature: Data not available 6.11 Stoichiometric Air to Fuel Ratio: Data not available 6.12 Flame Temperature: Data not available		10. HAZARD ASSESSMENT CODE (See Hazard Assessment Handbook) SS	
7. CHEMICAL REACTIVITY 7.1 Reactivity With Water: No reaction 7.2 Reactivity with Common Materials: In contact with combustible materials may cause fire. 7.3 Stability During Transport: Stable 7.4 Neutralizing Agents for Acids and Caustics: Not pertinent 7.5 Polymerization: Not pertinent 7.6 Inhibitor of Polymerization: Not pertinent 7.7 Molar Ratio (Reactant to Product): Data not available 7.8 Reactivity Group: Data not available		11. HAZARD CLASSIFICATIONS 11.1 Code of Federal Regulations: ORM-E 11.2 NAS Hazard Rating for Bulk Water Transportation: Not listed 11.3 NFPA Hazard Classification: Not listed	
8. WATER POLLUTION 8.1 Aquatic Toxicity: 300 mg/l/24 hr/bluegill/TL ₅₀ /fresh water 40-60 ppm/288 hr/shore crab/toxic/salt water 8.2 Waterfowl Toxicity: Data not available 8.3 Biological Oxygen Demand (BOD): None 8.4 Food Chain Concentration Potential: Bioconcentrative to 2,000 fold but not likely to be a problem in a spill situation.		12. PHYSICAL AND CHEMICAL PROPERTIES 12.1 Physical State at 15°C and 1 atm: Solid 12.2 Molecular Weight: 162 12.3 Boiling Point at 1 atm: Not pertinent (decomposes) 12.4 Freezing Point: Not pertinent 12.5 Critical Temperature: Not pertinent 12.6 Critical Pressure: Not pertinent 12.7 Specific Gravity: 2.723 at 25°C (solid) 12.8 Liquid Surface Tension: Not pertinent 12.9 Liquid Water Interfacial Tension: Not pertinent 12.10 Vapor (Gas) Specific Gravity: Not pertinent 12.11 Ratio of Specific Heats of Vapor (Gas): Not pertinent 12.12 Latent Heat of Vaporization: Not pertinent 12.13 Heat of Combustion: Not pertinent 12.14 Heat of Decomposition: Not pertinent 12.15 Heat of Solution: -24.5 Btu/lb = -13.6 cal/g = -0.57 X 10 ⁴ J/kg 12.16 Heat of Polymerization: Not pertinent 12.25 Heat of Fusion: Data not available 12.26 Limiting Value: Data not available 12.27 Reid Vapor Pressure: Data not available	
9. SHIPPING INFORMATION 9.1 Grades of Purity: Reagent; Commercial; Tetrahydrate grade 9.2 Storage Temperature: Ambient 9.3 Inert Atmosphere: No requirement 9.4 Venting: Open		NOTES	

SCH	SODIUM CHROMATE
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12.17 SATURATED LIQUID DENSITY		12.18 LIQUID HEAT CAPACITY		12.19 LIQUID THERMAL CONDUCTIVITY		12.20 LIQUID VISCOSITY	
Temperature (degrees F)	Pounds per cubic foot	Temperature (degrees F)	British thermal unit per pound-F	Temperature (degrees F)	British thermal unit-inch per hour- square foot-F	Temperature (degrees F)	Centipoise
	N O T P E R T I N E N T		N O T P E R T I N E N T		N O T P E R T I N E N T		N O T P E R T I N E N T

12.21 SOLUBILITY IN WATER		12.22 SATURATED VAPOR PRESSURE		12.23 SATURATED VAPOR DENSITY		12.24 IDEAL GAS HEAT CAPACITY	
Temperature (degrees F)	Pounds per 100 pounds of water	Temperature (degrees F)	Pounds per square inch	Temperature (degrees F)	Pounds per cubic foot	Temperature (degrees F)	British thermal unit per pound-F
34	34.190		N O T		N O T		N O T
36	36.790						
38	39.390						
40	41.990						
42	44.590		P E R T I N E N T		P E R T I N E N T		P E R T I N E N T
44	47.190						
46	49.790						
48	52.390						
50	54.990						
52	57.590						
54	60.190						
56	62.790						
58	65.389						
60	67.990						
62	70.589						
64	73.190						
66	75.790						
68	78.389						
70	80.990						
72	83.589						
74	86.190						
76	88.790						
78	91.389						
80	93.990						
82	96.589						
84	99.190						

LABORATORY AND TEST FACILITIES

GENERAL

FTC Acquisition Corporation (FTCAC) occupies 1500 square feet of space in a multi-purpose building at 3812 Tarheel Drive, Raleigh, NC 27609. Approximately 600 square feet is used for offices, and the remainder contains fabrication, assembly, laboratory and pilot plant areas.

The shop and testing area has 18 foot clearance and is accessed through a 12 foot door. The shop is equipped to assemble pilot plants, and perform minor fabrication activities. Most fabrication requiring sophisticated machining and welding is contracted to local shops.

FTCAC's laboratory is equipped to perform a variety of crystallization equilibrium, kinetic and physical property measurements. The lab has nominal analytical capabilities, including pH, specific ion, and a variety of wet chemical tests. It also has a visible light spectrophotometer and a polarimeter.

A multi-purpose freeze crystallization pilot plant is set up in the shop area that is used to test both recirculated (HCFC) and single-use (Liquid nitrogen) secondary refrigerant freeze cycles and primary (vacuum) direct contact refrigeration cycles. It is mounted in frame structures that allows quick changes, and the addition of new equipment components as needed for different applications, or to test new concepts. The pilot plants makes extensive use of clear vessel construction - clear PVC or acrylic; the ability to see what is happening in a process is a distinct advantage in understanding the basic operation of the process and in designing full-scale equipment. The pilot plants are described in greater detail below. Photographs of recent configurations of the pilot plants are shown in Figure A3-1.

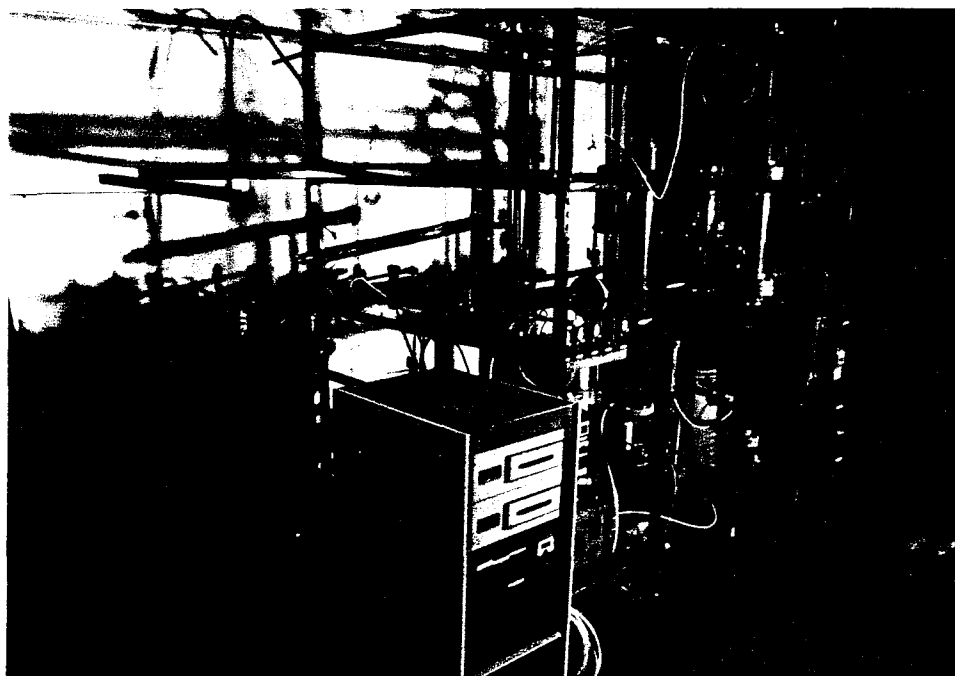
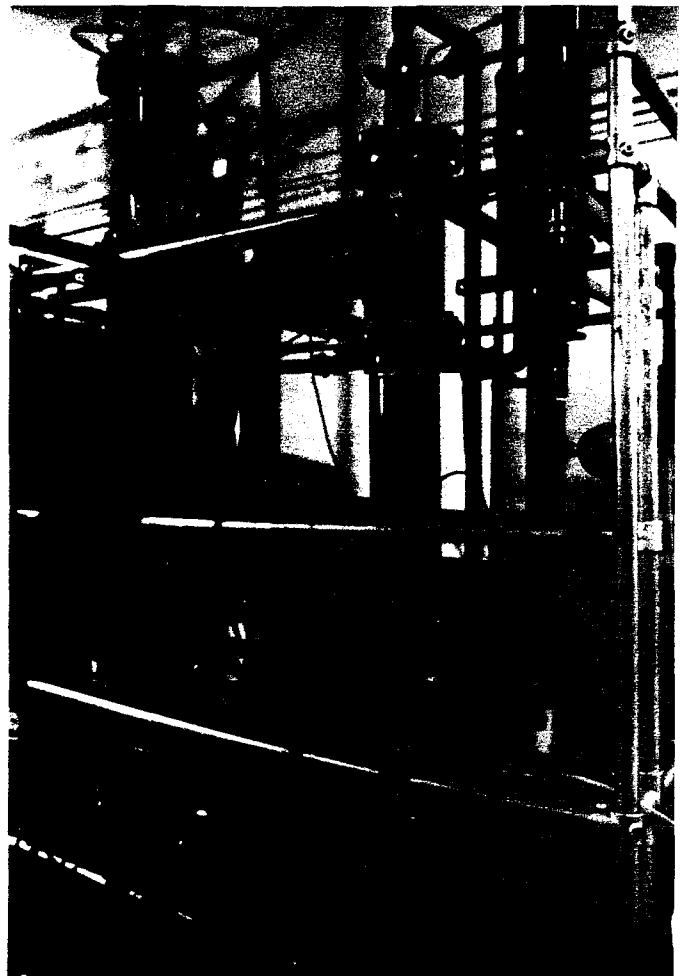
Major fabrication and assembly activities are subcontracted to any of several companies that have demonstrated the ability to provide the necessary services. Detailed design and modular equipment fabrication services have been provided by Applied Engineering, a wholly owned subsidiary of the Jacobs Group.

PILOT PLANT FACILITIES

FLASH VACUUM FREEZE CRYSTALLIZATION (FVFC) PLANT

This plant was originally designed as a secondary refrigerant plant, but has since been altered so that it can also be used as an FVFC process plant. The original objective was to build a pilot plant that would demonstrate process feasibility on a sample of no more than 5 gallons, which this plant does. The volume limitation imposes some restrictions on the data that is gathered from the tests. The foam-suppressing crystallizer anticipated for use in several ALC applications was developed in this test bed.

THE FLASH VACUUM
FREEZE CRYSTALLIZATION
PILOT PLANT. . .



AND THE SECONDARY REFRIGERANT PILOT PLANT.

FIGURE A3-1
PILOT PLANT FACILITIES

A flow diagram for this pilot plant is shown in Figure A3-2. A photograph of the plant is shown in Figure A3-1. It consists of:

- a vertical crystallizer column, with recycle of condensed volatiles in the bottom, through small orifices that promote fine dispersions into the process solution in the crystallizer.
- a variable speed slurry pumps that pumps crystal slurry from the crystallizer to ...
- a drain column where crystals are pumped in a slurry, with a center drain through which the liquid portion drains, holding the crystals in the column.
- diaphragm refrigerant compressors that achieve about a 1.5:1 compression ratio, so that the vapors can be condensed on a cold condensing coil. With most applications these compressors are not in operation, and the flow is natural convection from the higher pressure crystallizer to the lower pressure condenser.
- a refrigerant recirculation pump with a variable speed control that takes this condensed refrigerant and recycles it to the crystallizer, or out to a collection tank.
- a heat removal system, consisting of a closed cycle compressor and vapor-to-air condensers.
- a vacuum system to remove air from the system before the tests are started.

This pilot plant provides basic data on the solid-liquid equilibrium of the application, defines the operating pressures at the solution freezing point, and generates samples for analysis. A list of abilities and limitations of this pilot plant is presented below. To summarize, while this pilot plant doesn't generate as clean a product (ice), or reach the same degree of recovery of product from the feed stream, it does demonstrate the ability of the process, and provides sufficient design data to build larger plants.

A test run in the batch system begins by totally evacuating the system, to a vacuum below 5 mm Hg. absolute pressure. Approximately 4 gallons of feed solution is added to the crystallizer and recirculating flow to the drain column is started. The refrigeration system is started, so that the condensing coil is being cooled, which induces a lower pressure in the condenser, and flashing of the volatile components in the crystallizer. After about 15 minutes, when the condensate level has built up, the refrigerant pump is started and flow of volatiles is set to maintain either a specific cooling rate or a pressure level in the crystallizer. As these flows are maintained, the temperature of the process liquid drops, until a crystallizing point is reached and either solvent or solute (or both) begin to crystallize. The slurry is then pumped to the drain column, where the solids are captured and build up, and that allows the liquid portion to drain back into the crystallizer by gravity.

Typically it takes from 30 minutes to 3 hours to reach the point that crystallization begins. It can take another 2 to 6 hours to convert 50% of the liquid to crystals. The run is stopped by one of three conditions: 1) the drain column is full of crystals, blocking the discharge of the slurry pump; 2) there is too little liquid remaining in the crystallizer to maintain flow in the slurry pump; or 3) the freezing point is so low that an equilibrium between ice production and ice melting has occurred. At that point, condensate recirculation is stopped, and the process is operated for another 15 to 30 minutes to strip as much volatiles from the remaining liquid as is possible. The slurry pump is then stopped and the concentrate is isolated in the crystallizer. The drain line from the drain column is closed, and a drain to atmosphere is opened. Wash water is distributed over the crystal pack in the drain column. If samples of ice fractions are desired, the drain column is opened and appropriate samples are taken. If a composite sample is desired, the ice inventory is melted, and then a sample taken of the liquid.

EVFC PILOT PLANT PERFORMANCE SUMMARY

<u>PARAMETER</u>	<u>CAPABILITIES</u>	<u>LIMITATIONS</u>
PHYSICAL PROPERTIES		
- Solid Liquid Equilibria	Demonstrates actual SLE up to the 50% volume conversion.	SLE data at >50% volume conversion requires sequential tests and greater sample volume.
- Viscosity, Surface Tension Foaming Characteristics	Give direct measurement at operating conditions.	
- Vapor Liquid Equilibria	Give direct measurements of vapor pressure and vapor compositions at operating conditions.	
CRYSTALLIZATION KINETICS		
- Solvent Crystallization	Provides growth rates from tests at limited residence times. Gives good approximation of growth & nucleation rates.	Crystallizer residence time is short, and may not grow anything but very small crystals, which will be difficult to purify.
- Solute Crystallization	Shows point where eutectic conditions begin to occur. Will give some idea of crystal growth rates, which may be very slow.	Does not provide good growth conditions and long residence times needed to grow large crystals. May be difficult to harvest high purity material for demonstration.
PRODUCT PURITY		
- Wash Column Performance	Will decrease contamination by a factor of 10 to 100.	Continuous operation in a true wash column achieves 1 to 2 orders of magnitude better performance.
- Solute Column Separation		Plant has no proactive method to remove solute solids, or to purify them.
DESIGN PARAMETERS		
- Crystallizer	Gives some idea of mass transfer rates and crystal kinetics.	No direct scale-up because of differences in crystallizer construction.
- Eutectic Salt Separation		No ability in this system.
- Wash Columns	Get performance data at a few conditions.	No ability to define maximum column productivity, so optimization is limited.
- Energy Consumption	Operating conditions are demonstrated, which allow accurate calculation of energy consumption.	Pilot plant is very inefficient and performance can't be directly correlated to full-scale operations.
- Demonstrated Recovery (= Recovered Product Volumes/Feed Volume)	80 to 90% from a 20 gallon feed sample.	

Since the batch unit is limited by the amount that can be crystallized from a 4 gallon feed charge, and is about 50% of the feed, demonstrating operations at high conversion ratios (ratio of the crystallized product amount to the feed amount) requires that a number of tests be run and feed added to the concentrate each time.

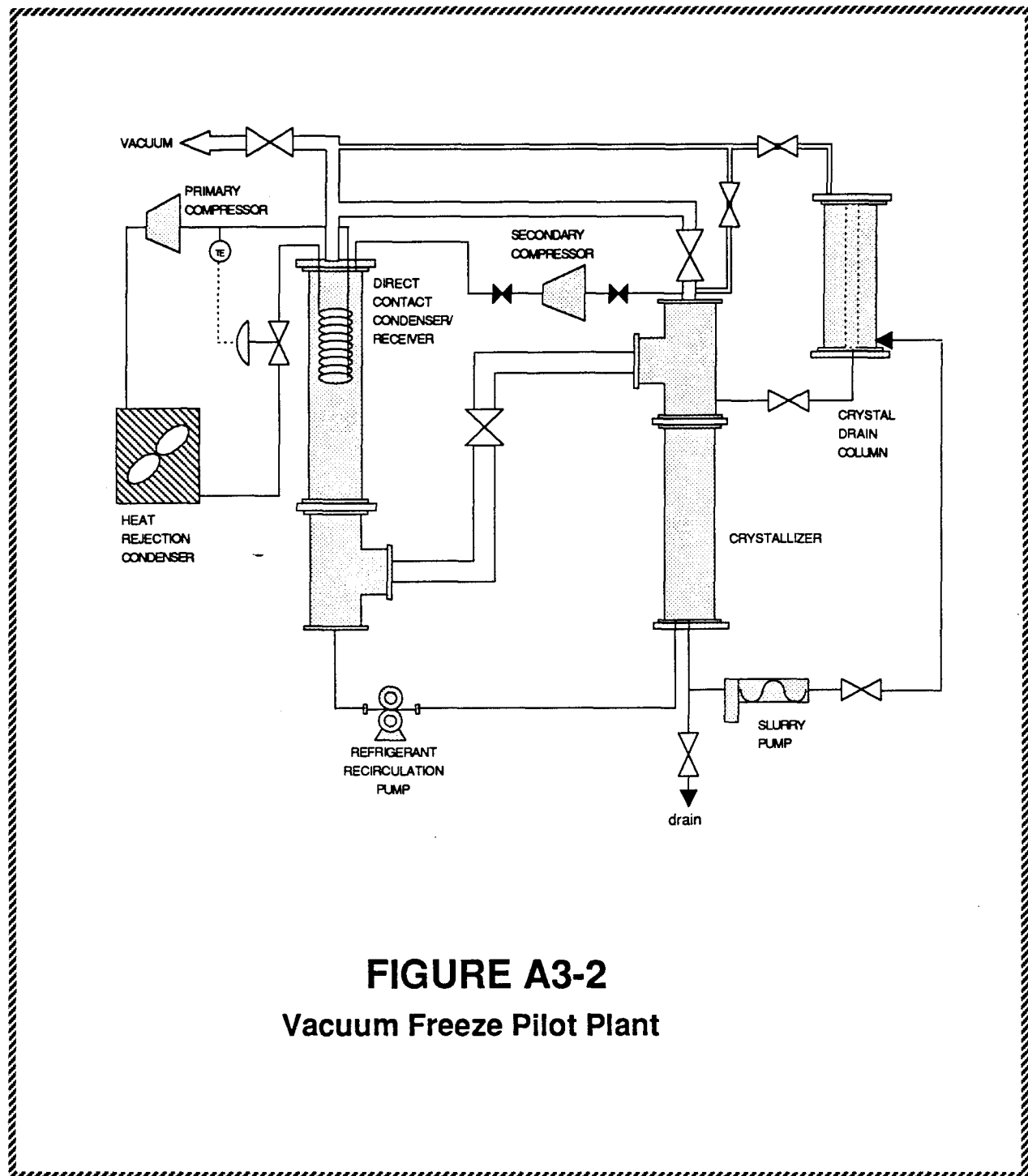


FIGURE A3-2
Vacuum Freeze Pilot Plant

Secondary Refrigerant Pilot Plant:

This pilot plant was used in this program and is described in the Test Plan, Appendix 2. A photo of the pilot plant as used in this program is shown in Figure A3-1.



Southern Testing & Research Laboratories, Inc.

3709 Airport Drive

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Wilson, NC 27893

REPORT OF ANALYSIS

LAB SAMPLE NO.(s) : 3581C1-4 of: 4

Date Received: 93/12/08

Sample(s) of : WASTEWATER

Date Reported: 93/12/30

NAM : JIM HEIST

ORG : FTC ACQUISITION CORPORATION

ADD : P.O. BOX 40968

CSZ : RALEIGH, NC 27609

Telephone : 919-850-0600

PO/Job No. : 3055

* FINAL REPORT 1-10-94

Marked A: JOB 31 CONCENTRATE SAMPLE NO.002 B: JOB 31 MELT SAMPLE NO. 003

C: JOB 31 FLOAT SAMPLE NO. 004

D: JOB 31 2% BA SAMPLE NO. 005

Lab Sample No.=> A: 3581C1 B: 3581C2 C: 3581C3 D: 3581C4

CAT. NO.	ANALYSES	UNITS				
: EO-5	: BENZYL ALCOHOL		: FORM 0_1:	FORM 0_1:	FORM 0_1:	FORM 0_1
: EW-14	: COLOR, APPARENT	(mg/L)	: <70 >50	: <70 >50	: <50 >40	: <50 >40
: EW-12	: CHROMIUM (HEXAVALENT)	(mg/L)	: 20.0	: 5.49	: 12.3	: <0.1
: EM-24	: CHROMIUM (ICP)	(mg/L)	: 65.0 *	: 10.8 *	: 56.0 *	:
: EP-1	: DIGESTION		: Y	: Y	: Y	:
:	:		:	:	:	:
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Comments:

:
:
:
:

Laboratory Contact For Above Report

Reviewed and Approved

Name : Jeff Whaley, B.S.

Title: Chemist

Thomas A. Dean, Jr. Ph.D.

Manager, Environmental Dept

-----SUBMISSION INFO-----
Analyst(s): JW No. Containers: 4 Sample Submission: Y C-O-C: N
Samp Admin: Pickup: Y Time: N Miles: N RUSH : N

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FORM 0 1

MISCELLANEOUS COMPOUND REPORT FORM

METHOD: EPA 8015

Catalog No.: EO-5

Sample Specific Information For STRL Sample No.: 3581C1

Client Sample ID: JOB 31 CONC. SAMPLE NO.002 Sample Matrix : WATER

Date Sampled : 12-7-93

Date Analyzed : 12-28-93

Date Received : 12-8-93

Date Reported : 12-30-93

Date Prepared : NA

[illegible]

COMMENTS: NA = NOT APPLICABLE

Laboratory Contact For Above Report

Name : Jeff Whaley, B.S.
Title: Chemist

J. Whaley
Reviewed and Approved

Thomas A. Dean, Jr. Ph.D.
Manager, Environmental Dept

Southern Testing & Research Laboratories, Inc.

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Wilson, NC 27893

FORM 0 1

MISCELLANEOUS COMPOUND REPORT FORM

METHOD: EPA 8015

Catalog No.: EO-5

Sample Specific Information For STRL Sample No.: 3581C2

Client Sample ID: JOB 31 MELT SAMPLE NO.003 Sample Matrix : WATER

Date Sampled : 12-7-93

Date Analyzed : 12-28-93

Date Received : 12-8-93

Date Reported : 12-30-93

Date Prepared : NA

[illegible]

COMMENTS: NA = NOT APPLICABLE

Whaley

Laboratory Contact For Above Report

Reviewed and Approved

Name : Jeff Whaley, B.S.

Thomas A. Dean, Jr. Ph.D.

Title: Chemist

Manager, Environmental Dept

Southern Testing & Research Laboratories, Inc.

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FORM 0 1

MISCELLANEOUS COMPOUND REPORT FORM

METHOD: EPA 8015

Catalog No.: EO-5

Sample Specific Information For STRL Sample No.: 3581C3

Client Sample ID: JOB 31 FLOAT SAMPLE NO.004 Sample Matrix : WATER

Date Sampled : 12-7-93

Date Analyzed : 12-28-93

Date Received : 12-8-93

Date Reported : 12-30-93

Date Prepared : NA

[illegible]

COMMENTS: NA = NOT APPLICABLE

Laboratory Contact For Above Report

Name : Jeff Whaley, B.S.
Title: Chemist

J. Whaley
Reviewed and Approved

Thomas A. Dean, Jr. Ph.D.
Manager, Environmental Dept

Southern Testing & Research Laboratories, Inc.

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FORM 0 1

MISCELLANEOUS COMPOUND REPORT FORM

METHOD: EPA 8015

Catalog No.: EO-5

Sample Specific Information For STRL Sample No.: 3581C4

Client Sample ID: JOB 31 2% BA SAMPLE NO.005 Sample Matrix : WATER

Date Sampled : 12-7-93

Date Analyzed : 12-28-93

Date Received : 12-8-93

Date Reported : 12-30-93

Date Prepared : NA

[illegible]

COMMENTS: NA = NOT APPLICABLE

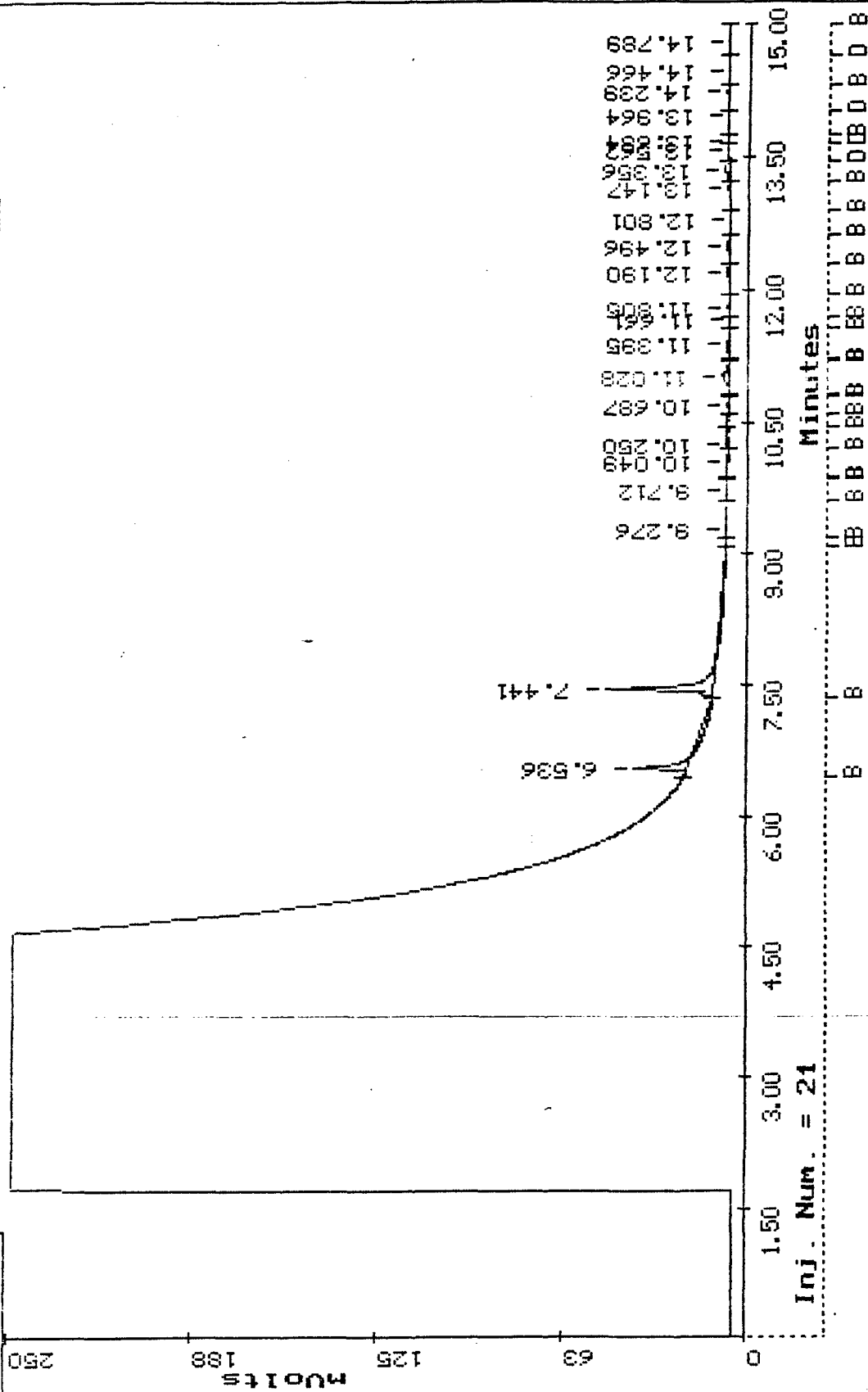
Laboratory Contact For Above Report

Name : Jeff Whaley, B.S.
Title: Chemist

J. Whaley
Reviewed and Approved

Thomas A. Dean, Jr. Ph.D.
Manager, Environmental Dept

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Inj. Num. = 21

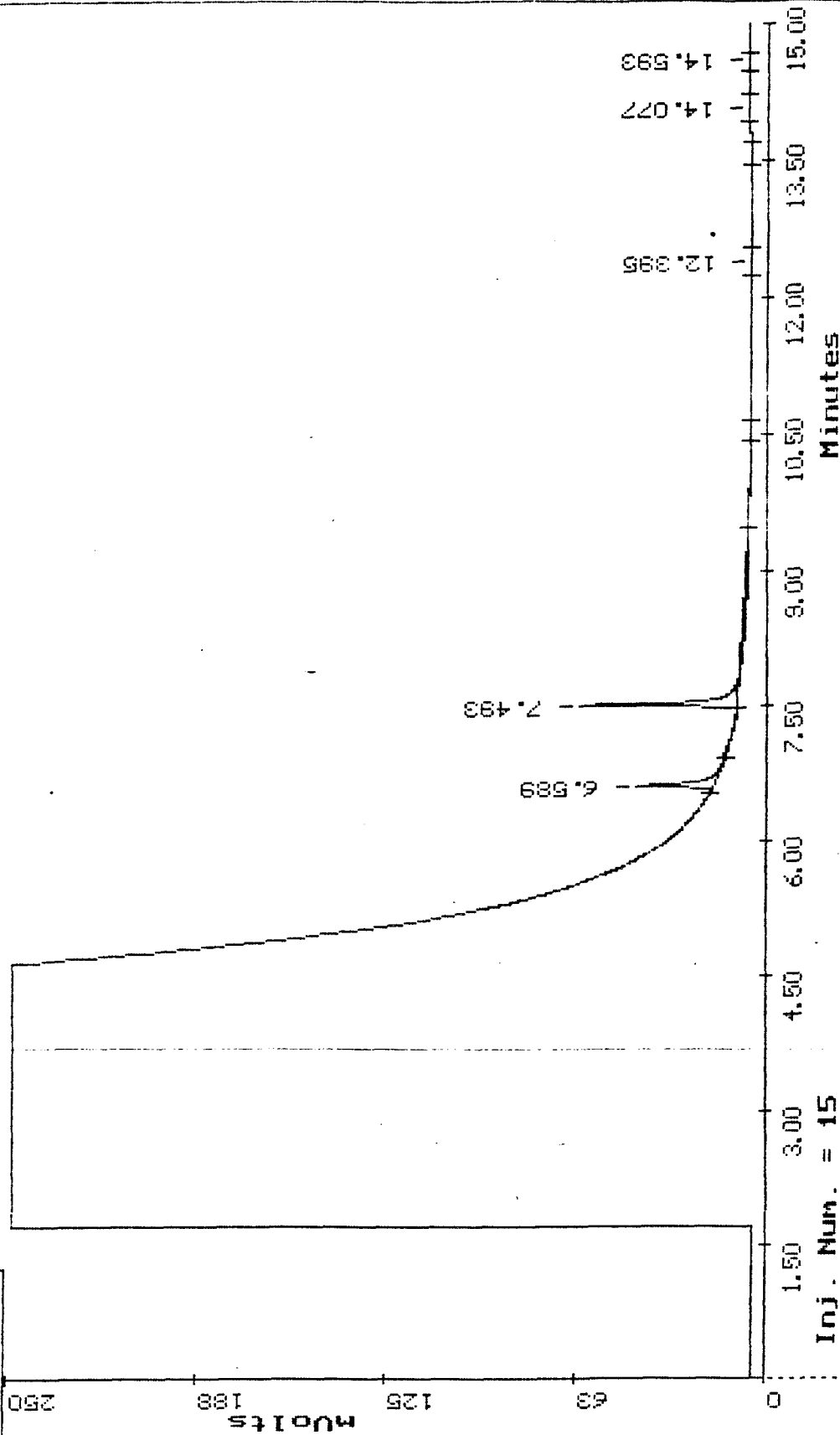
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PC/Chrom

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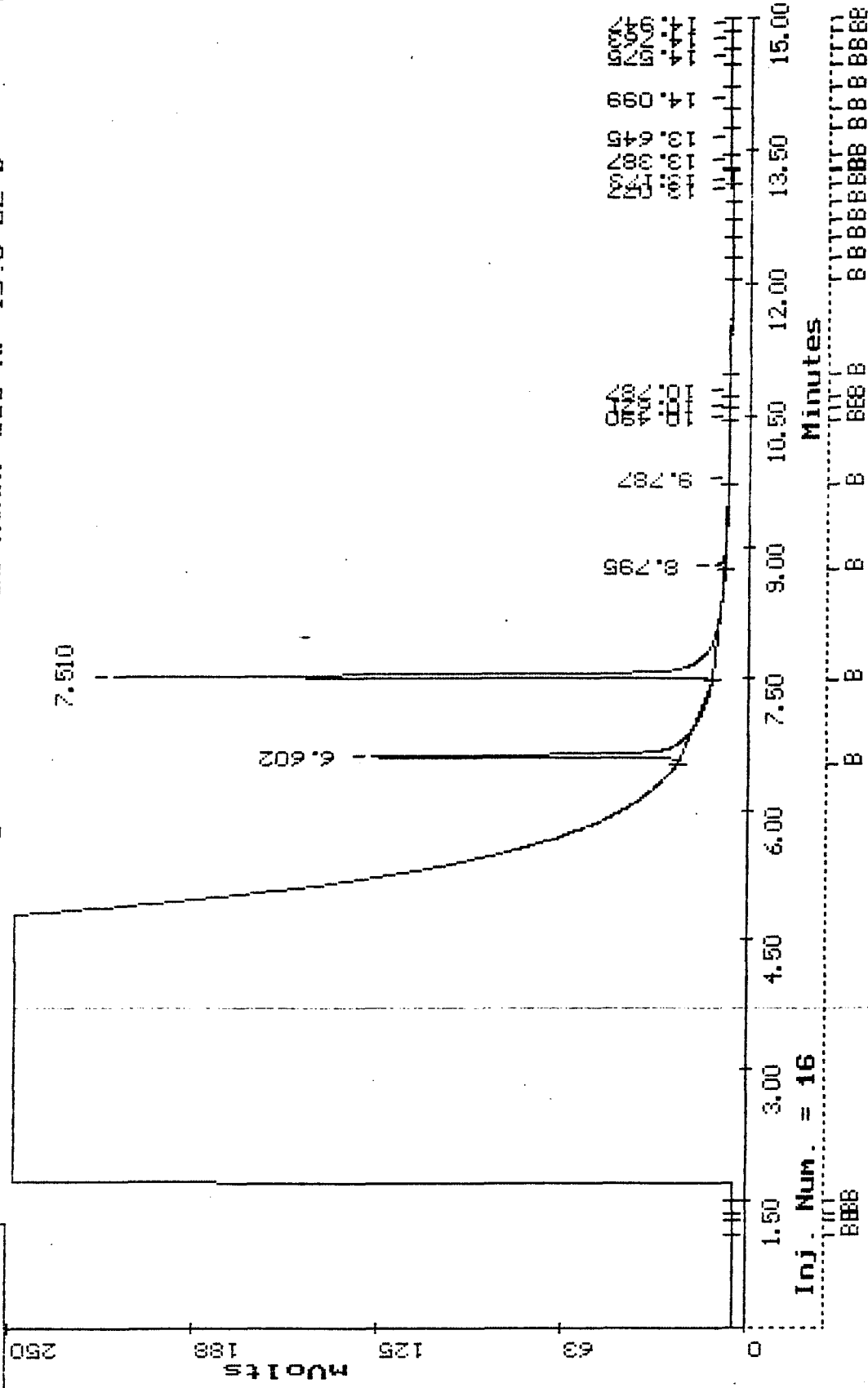


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Sequence: AUTOINJ
ID :

