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Rapid Production of Mixed-Base Hydrogen Peroxide By Direct-Contact Liquefied Nitrogen Evaporation; Process Design, Scale-up, and Validation

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The deployment and operation of chemically driven, directed-energy weapon systems, such as the Airborne Laser (ABL), require strategies, systems, and training that have not been demonstrated previously in the Air Force, the Department of Defense, or industry. These weapons utilize large quantities of reactive chemicals. Traditional chemical equipment and processes are heavy, large, and permanently installed in fixed facilities. From 1999 to 2002, AFRL/MLQ researchers evaluated various blending techniques and processes for producing mixed-base hydrogen peroxide (MHP). The evaluation criteria for the production facility included deployability, setup time for production, and logistics. This report focuses on the rapid production of MHP using liquefied nitrogen.

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Disclaimer

RAPID PRODUCTION OF MIXED-BASE HYDROGEN PEROXIDE BY DIRECT-CONTACT LIQUEFIED NITROGEN EVAPORATION

Process Design, Scale-up, and Validation

(Unclassified)

EXECUTIVE SUMMARY

Synopsis

The mission capability of Directed Energy Weapons based Chemical Oxygen Iodine Lasers may be severely restricted unless the reagents and chemical engineering processes necessary to produce weapon-grade Mixed-base Hydrogen Peroxide (MHP) at operational rates and under deployed force conditions are available at a Forward Operating Location (FOL).

The deployment and operation of chemically driven, directed-energy weapon systems, such as the Airborne Laser (ABL), require strategies, systems, and training that have not been demonstrated previously in the Air Force, the Department of Defense, or industry. These weapons utilize large quantities of reactive chemicals. Traditional chemical equipment and processes are heavy, large, and permanently installed in fixed facilities. These engineering designs do not meet the requirement for ABL chemical deployment. The necessary chemical equipment for providing MHP must be rapidly deployable, brought quickly into production, and impose the smallest possible logistics burden.

Since the ABL is the most mature of the chemically driven directed-energy laser systems currently under development, it commands the earliest necessity for a demonstration of deployable chemical-production systems that satisfy the weapon Concept-of-Operations (CONOPS) and the Concept-of-Employment (CONEMP).

Scope

The purpose of this report is to document the results of the work performed to date at the Weapons Systems Logistics Branch of the Air Force Research Laboratory (AFRL/MLQL), located at Tyndall AFB, Florida. The scope of work involves the development of rapid blending techniques and processes, for producing mixed-base hydrogen peroxide, from November 1998 to September 2002. Mixed-base hydrogen peroxide possesses properties and characteristics that pose a significant challenge in developing chemical systems for its production in the field. The most critical of these properties are: (1) its meta-stable character with a strong temperature dependence that can lead to high decomposition rates; and (2) the fact that MHP is a multi-component, strong-electrolyte mixture of caustics and hydrogen peroxide that must be kept in solution over a wide range of temperature and component concentrations.

The single most important challenge of MHP production and maintenance is thermal management. The blending of strong caustics and high-concentration hydrogen peroxide is very exothermic. In addition, the introduction of caustic to hydrogen peroxide initiates catalytic decomposition of the peroxide, also an exothermic reaction, which can only be suppressed by keeping the MHP cold. The use of traditional heat exchangers is undesirable because the materials that have acceptable heat-transport properties also catalyze decomposition of peroxide.

A thermal management process has been developed at Tyndall AFB that eliminates the heat exchanger and direct cools the MHP during the blending operation. The process has evolved from using liquefied nitrogen (LN2) in an open system configuration to using a refrigerant based cooling fluid in a closed-recycle configuration. Utilizing the direct contact heat removal process, a rapid blending system has been developed and demonstrated at Tyndall AFB. The process has been scaled up to a 1,000-kilogram batch size. A photo of the 1000-kg MHP production facility is shown in Figure ES. The thermal management technique and blending process developed at Tyndall AFB not only reduces the production time for an ABL magazine from nearly18 hours to under one (1) hour, but also reduces the size of the production facility by as much as a factor of three. This will have a significant impact on the logistics burden of the MHP production and management system.

The results reported herein are limited to the development of the direct-contact cooling process using liquid nitrogen as the cooling agent for rapidly blending mixed-base hydrogen peroxide.

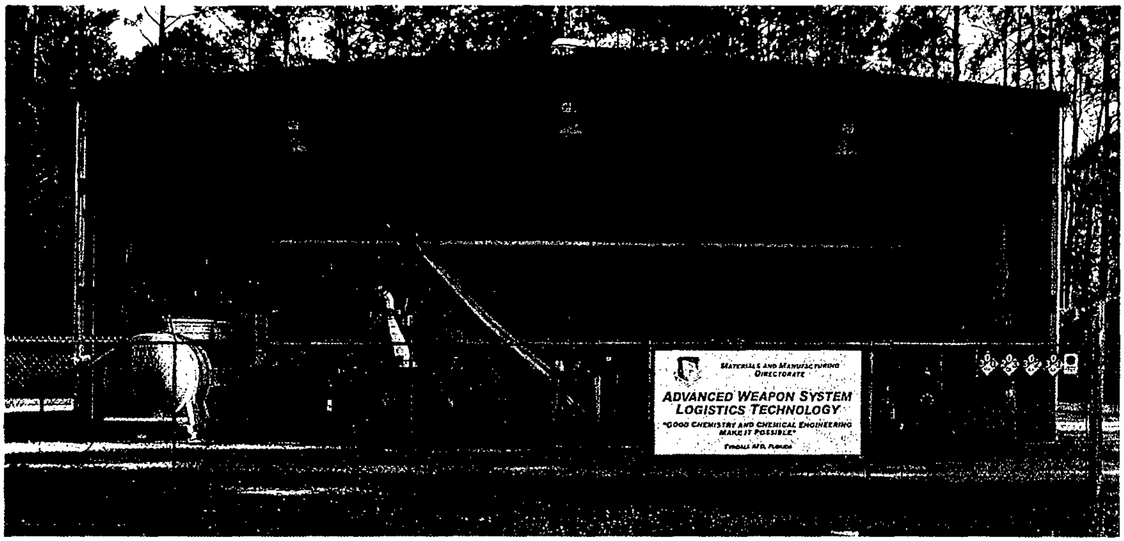


Figure ES. 1000-kg MHP Production Facility at AFRL/MLQL (Tyndall AFB, Florida)

SECTION 1. PRODUCTION OF BASIC HYDROGEN PEROXIDE

1-1. HISTORICAL PERSPECTIVES

The COIL concept was first demonstrated at the Air Force Weapons Laboratory (AFWL), now the Air Force Research Laboratory (AFRL), in 1977 (McDermott et al., 1978; Benard et al., 1979). Unlike other industrial lasers in which the lasing media are generated either in electric discharges or with radiation produced by electric light sources, COIL is produced by reacting chemical fuels: basic hydrogen peroxide, chlorine, and iodine. COIL has many desirable features for military and industrial applications, such as Mega-Watt energy capacity, high energy density and unique beam wavelength (1.315 μm) rendering a powerful directed energy delivery system with minimum atmospheric interference. Advances in the enabling technology and performance of COIL devices during the first decade of its existence have been described in several concise reviews covering R&D efforts at Phillips Laboratory, Kirtland AFB, NM (Truesdell and Lamberson, 1992; Truesdell et al., 1994) and at Rocketdyne Division of Rockwell International, Canoga Park, CA (McDoermott, 1992). The U.S. Air Force ABL weapon system development program began in early 1990's when the concept design effort was initiated. Based on the success of this design phase effort, U.S. Air Force awarded a contract to Team ABL (Boeing/TRW/Lockheed Martin) to design, develop, integrate and test an Airborne Laser weapon system in the Program Definition and Risk Reduction (PDRR) phase in November 1996.

1-2. BASIC HYDROGEN PEROXIDE

In the early COIL work, either potassium hydroxide (KOH) or sodium hydroxide (NaOH) was the base of choice to produce basic hydrogen peroxide (BHP). Recently, mixed-base hydrogen peroxide (MHP), which involves the mixture of KOH, NaOH, and lithium hydroxide (LiOH) at selected proportions, has been studied extensively for military applications. Properties and performance of several MHP formulations have been documented (Welch and Hurley, 1999). MHP is produced by mixing concentrated aqueous solutions of alkali hydroxides and of hydrogen peroxide (H_2O_2). This process produces large amounts of heat - about 12 kcal/mol base. Since H_2O_2 is known to be extremely unstable at high pHs, MHP is intrinsically unstable particularly at temperatures above the ambient temperature. Therefore, the heat of mixing must be removed rapidly during the mixing operation to keep temperature of the solution below an acceptable level. Typically, temperature of the solution is kept at below 7°C during the production and storage to prevent excessive decomposition of hydrogen peroxide. Typical MHP decomposition profiles over time are shown in Figure 1-1. The strength of an MHP solution is characterized by the concentration of perhydroxyl anions (O_2H^-), which is a function of hydroxide (OH^-) and H_2O_2. The MHP strength may vary, depending on its formulation. Typically, the molar ratio of $[H_2O_2]$ to $[OH^-]$ is about 1.15. The convention is to express the concentration in moles OH^-/kg MHP and moles H_2O_2/kg MHP, respectively. An ideal MHP formulation provides maximum base and peroxide concentrations while maintaining all species in solution during MHP production, storage, and singlet oxygen generation. Several MHP formulations are provided in Appendix A.

1-3. STATE-OF-THE-ART METHODS

As part of test requirements, MHP was routinely prepared at Northrop Grumman (formerly TRW) facilities (Redondo Beach and San Juan Capistrano, CA). Batches as large as 1000-kg have taken up to 20 hours to produce. Since trace amounts of iron, chromium, copper and other metals can accelerate peroxide decomposition, materials of construction of the reactor vessel, piping, and storage containers must be carefully selected. These difficulties are not trivial, but can be managed during the preparation of 10-kg to 100-kg batches of MHP. The difficulties ramp up almost exponentially, as one attempts to scale up to 1000-kg and 10,000-kg batches needed by the ABL program. Because MHP is Air Force unique, there are no commercial processes that can be tapped to obtain science and engineering information about this material. The focus of the ABL program at AFRL/MLQL, the Weapons Systems Logistics Branch of the Air Force Research Laboratory, was to address the thermal management issues for rapid production of MHP. To address the need of projected 10,000-kg of MHP for each ABL mission, AFRL/MLQL proposed a research program to establish the science-base and technical know-how for full-scale, rapid production of MHP meeting ABL weapon system specifications, and develop capabilities for large-scale production of MHP to support field and operational tests.

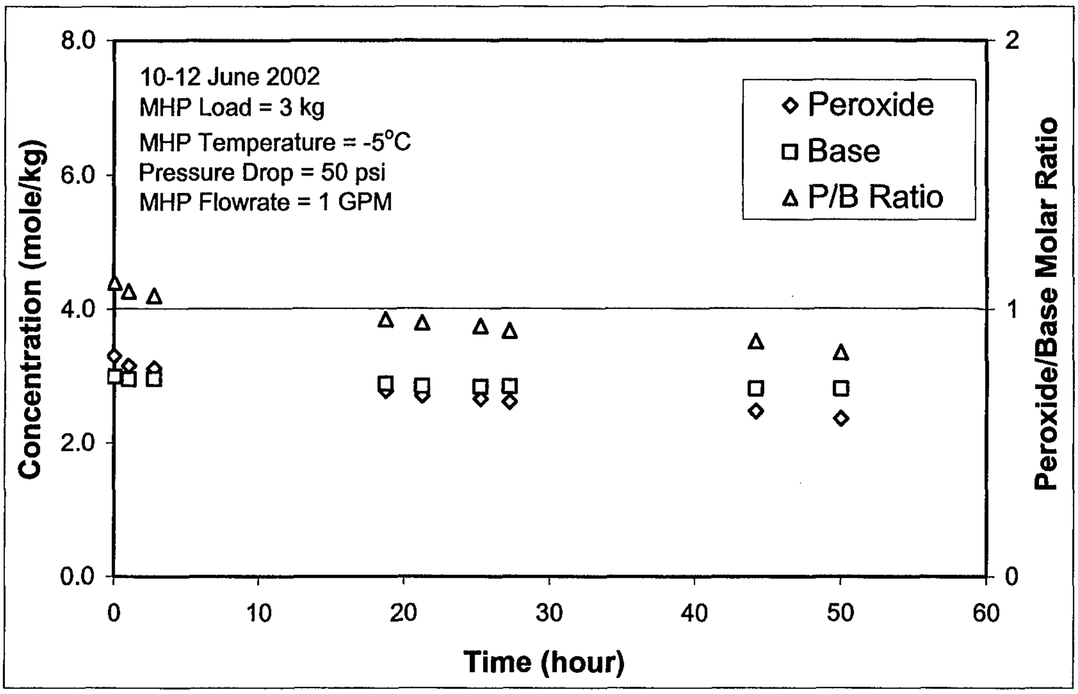


Figure 1-1. MHP Decomposition Profiles (4.20 Formulation)

1-4. PROBLEM DEFINITION

As previously stated, chemically driven, directed-energy weapons, such as the ABL, require large amounts of highly reactive chemicals be transferred, processed, stored, and disposed. The key chemical fuel for COIL is Mixed-base Hydrogen Peroxide (MHP), which is produced by the highly exothermic reaction of concentrated aqueous solutions of bases and hydrogen peroxide. The chemical reagents and chemical processes necessary to rapidly produce weapon-grade MHP under deployed conditions must be made available at a Forward Operating Location (FOL). For the ABL application, the MHP production system must be compact, robust, light in weight, and safe to operate in a confined space. In addition, the support facilities for MHP production, quality control/quality assurance, management, storage and transfer of MHP and other chemicals must meet all deployment and military requirements.

SECTION 2. THERMAL MANAGEMENT FOR MHP PRODUCTION

2-1. OBJECTIVES AND SCOPE

The goals of thermal management were to (1) maximize heat transfer rate per unit volume of MHP and (2) minimize peroxide degradation through effective control of MHP temperature, heat transfer surface area, and materials of construction. To this end, alternative reaction and heat transfer approaches for rapid production of MHP were evaluated. The selection and evaluation of candidate thermal management approaches were primarily based on existing technologies that meet the basic criteria of effectiveness, maturity, and deployability.

2-2. THERMAL MANAGEMENT METHODOLOGY

In general, ABL operations deal with four types of highly exothermic reactions including (1) the mixing of base solids with water to form a homogeneous base solution; (2) the mixing of aqueous solutions of bases with hydrogen peroxide to produce MHP; (3) the reaction of MHP with chlorine gas to generate singlet oxygen $O_2(^1\Delta_g)$; and (4) the deactivation of $O_2(^1\Delta_g)$. Thermal energy transfer requirements are determined by the heats generated from these reactions. Heats of reaction and rates of heat removal are given in Appendix B. Thermal analysis for the MHP production process can be performed in three steps as described below. Typically, MHP blending is performed at temperatures below 280K to minimize peroxide decomposition during the production process, and involves pre-cooled feed streams. For convenience of calculations, it is assumed that all feed materials start at a temperature of 20°C, and the MHP blending process is hypothetically carried out at 20°C.

Step 1 – Mixed Base (MOH) Solution is prepared by adding caustic solids into water, where (1) the temperature of MOH reaches about 65°C if no cooling is provided during the mixing process; and (2) the heat to be removed is calculated from the heat capacity of water with a temperature rise of 45°C.

Step 2 – Peroxide Addition is carried out and maintained at 20°C, where (1) heat is removed continuously to keep the solution temperature constant at 20°C, and (2) the heat generated is based on the following equations developed at AFRL/MLQL:

Q_W/M (kcal/kg MHP) = $230 \times (W_{LiOH\bullet H2O} + W_{NaOH} + W_{KOH})$

Q_M/M (kcal/kg MHP) = $10 \times [OH^-]$

where Q_W and Q_M are heat generation based on weight fractions and mole concentration, respectively, M is the batch mass of MHP (kg), $W_{LiOH\bullet H2O}$, W_{NaOH}, W_{KOH} are the effective mass fractions of the three bases (i.e., discounting the impurities in each base), and $[OH^-]$ is the mole concentration of hydroxide ions (gmole-$[OH^-]$/kg-MHP).

Step 3 – MHP Cooling refers to the cooling of MHP from 20°C to –15°C at which MHP will be delivered to COIL systems, where heat removal is estimated from the heat capacity of water.

Table 2-1 summarizes specific thermal duty for these three processing steps. Calculations show that each of these three steps requires the removal of about the same amount of heat. Since an operating time of one hour is assumed for each step, the total time required to produce a batch of MHP from caustic solids will be three hours. For example, 1000 kg of MHP can be produced in one hour if the process equipment has a cooling capacity of 39 tons of refrigeration (TR = 12,000 BTU/hr). Processes based on these methods can be operated in a batch, semi-batch, or continuous mode. Seven cooling methods have been selected for detailed comparative studies.

Table 2-1. Cooling Duty and Options for Rapid Production of MHP

	MOH Solution	Peroxide Addition	MHP Cooling
Heat Output (kcal/kg MHP)*	-40	-45	-35
Operation Duration (hour)	1	1	1
Start Temperature (°C)	20	20	20
End Temperature (°C)	65 (w/o cooling) 20 (w/ cooling)	20	-15
Specific Thermal Duty (kcal/hr/kg MHP) (TR/1000kgMHP)	 40 13	 45 15	 35 11
Cooling Method			
Forced-Air Cooler	**Preferred**	N/A	N/A
Chiller	Applicable	Applicable	**Preferred**
Surface Evaporator	Applicable	**Preferred**	**Preferred**
Vacuum Evaporator	Applicable	**Preferred**	**Preferred**
Direct Contact LN2 Evaporator	Applicable	**Preferred**	**Preferred**
Direct Contact Freon Evaporator	Applicable	**Preferred**	**Preferred**
Chilled-Air Sparger	Applicable	Applicable	Applicable

* The value is based on a 4.51 MHP formulation and is rounded off to two digits.

The following sections provide detailed discussions on three process design aspects of thermal management. Section 2-3 addresses the issues of how the heat of reaction/mixing is removed from the MHP production process. Section 2-4 compares the efficiencies of unit operations associated with selected approaches, i.e., how rapidly the heat removal process takes place and how much energy is needed to operate a given unit operation. Section 2-5 deals with the issues such as in what order the components of MHP are mixed and when the heat of reaction/mixing is removed from the MHP production process.

2-3. ALTERNATIVE COOLING METHODS

Of the seven cooling methods shown in Table 2-1, the chiller method has been extensively used for MHP production in the past. The rest represent the concepts of alternative cooling methods proposed by AFRL/MLQL researchers for rapid production of MHP. Basic descriptions of these concepts, proof-of-the-concept apparatus and experimental findings are described below. Detailed descriptions of these systems and test results are provided in Appendix C. Descriptions and findings of the direct contact refrigerant evaporator approach have been documented in a separate report.

2-3-1. Forced-Circulation Air-Cooler

This cooling method is only applicable for removing heat from hot MOH solutions. Experimental results show that the temperature of MOH solution rises from ambient (20°C) to about 65°C upon adding all caustic solids into the available amount of water for a typical MHP formulation. In this case, forced-circulation air radiators can be an effective and adequate means to cool the MOH solution. For example, the hot MOH solution is pumped through a series of radiator tubes while air is blown through outside fins of the radiator. This method is energy efficient, but the extent of cooling depends on the ambient temperature. Based on a temperature approach of 5°C typically used in the refrigeration industry, the temperature of MHP would be 5°C above the ambient temperature. The technique is proven and widely used for cooling engines in automobiles as well as refrigeration and air conditioning systems. Therefore, the challenge is primarily the selection of materials of construction, which must be compatible with hot, concentrated aqueous alkali solutions.

2-3-2. Chiller

The conventional refrigeration approach, such as a chiller, is a proven technique to remove heat from reactors. This method relies on a refrigeration loop (compressor, expansion valve, and evaporator), and a secondary fluid medium (coolant) loop to transfer the heat between the evaporator, placed in the coolant reservoir and the process fluid. The coolant flows through a cooling coil submerged in the process fluid or a jacketed reactor vessel. Due to low temperature requirements (less than -15°C), there is limited options for coolant selection. Coolants reportedly used for MHP production include (1) acetone-dry ice solution, whose temperature stays at the dry ice sublimation temperature of -78°C; (2) specialty coolants such as Syltherm XLT (Dow Chemicals) which has a recommended temperature range of -100°C to 260°C; and (3) brine solutions such as 30% calcium chloride aqueous solution. In the latter cases, the use of proper refrigerants is critical for optimum processing results in terms of refrigeration capacity, process temperature, and equipment requirements. Some of the candidate refrigerants include: R22, R404a, R134a, carbon dioxide, and ammonia.

2-3-3. Surface Evaporator

To improve the heat transfer efficiency of the process, the heat transfer unit operation can be accomplished by the refrigeration loop (compressor and evaporator) without the secondary fluid medium (coolant) loop. In this case, cooling coils and jacketed vessels, which are in contact with the processing fluid, act as the evaporator for the refrigerant. The surface evaporator method described herein refers to the production of MHP on the surfaces of a radiator-type evaporator, which is part of the typical close-loop refrigeration cycle. Using R134a as the refrigerant, a production throughput of 2 kg MHP/hr was achieved using a 1/3-HP proof-of-the-concept apparatus. The evaporator temperature was maintained at –2°C. Typical temperature profiles from these tests are shown in Figure 2-1. A larger condenser unit (3 HP) using R-404a as the refrigerant was purchased. R-404a has lower boiling point than R134a, and is suitable for the desired operating temperature of -20°C. For full-scale systems (in 100's HP), ammonia would be a candidate refrigerant from the viewpoint of thermal efficiency and weight penalty.

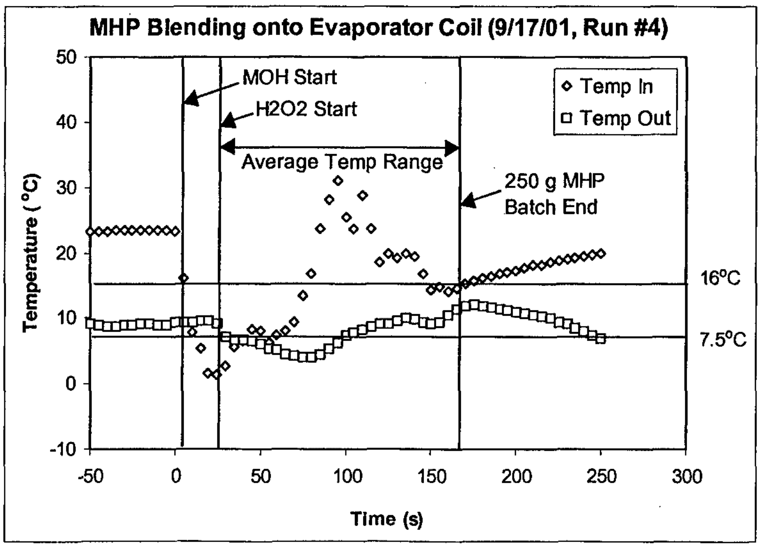


Figure 2-1. Typical Temperature Profiles for Surface Evaporator Tests

2-3-4. Vacuum Evaporator

This method is based on the fact that the boiling temperature of a liquid solution is governed by the pressure maintained above the solution. The normal boiling point of water (at 760 mmHg) is 100°C, whereas at 4.6 mmHg (vacuum), water boils at 0°C. Since MHP is a strong electrolyte solution, there is a rise in the boiling temperature as compared to that of water at a given pressure. The extent of the boiling temperature rise is a function of electrolyte concentration. The approach is to remove the heat of reaction of MHP production by the evaporating water, which has a large heat of evaporation (about 2500 kJ/kg). To minimize the decomposition of MHP during production process, the MHP blending process is typically carried out at a temperature range from 0°C to about -15°C. The approach was experimentally demonstrated and typical temperature profiles from these tests are shown in Figure 2-2.

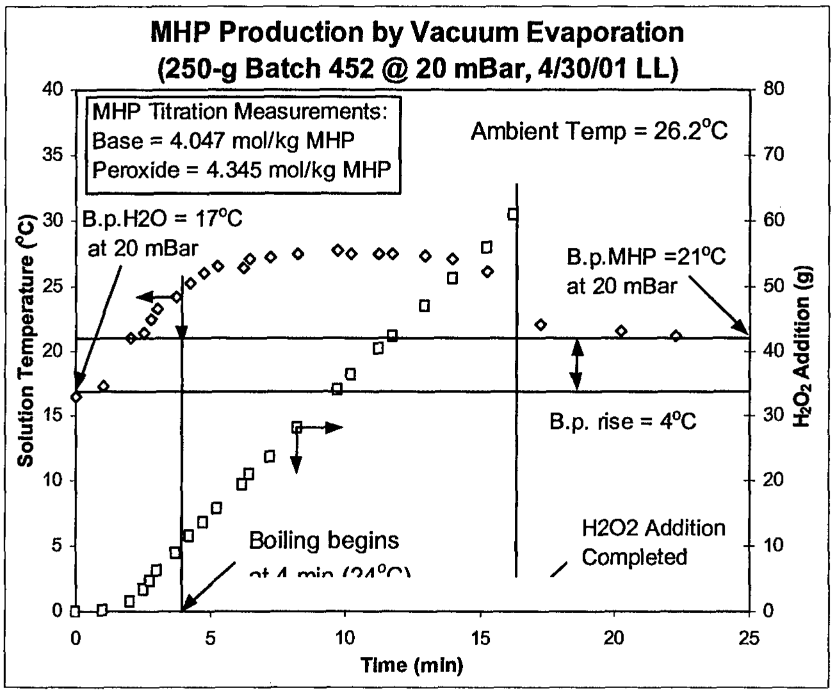


Figure 2-2. Typical Temperature Profiles for Vacuum Evaporation Tests

2-3-5. Direct Contact LN2 Evaporator

Direct contact heat transfer is widely practiced in chemical industries (Kreith and Boehm, 1988). As the name implies, this approach takes advantages of two physical processes: (1) bringing a higher temperature stream and a lower temperature stream into contact; and (2) evaporating the lower temperature stream to achieve rapid heat removal from the higher temperature stream. For example, direct contact heat transfer using liquefied nitrogen (LN2) was recognized by some researchers to be an effective means for rapid production of MHP, but had not been demonstrated experimentally in any scale of operation. The developmental work at AFRL/MLQL was successful in scaling up the MHP production using LN2 as direct contact coolant from 1-kg/batch to 1000-kg MHP/batch. The time for mixing hydrogen peroxide with base solutions was reduced to about 45 minutes. However, the mass ratio of LN2 consumption to MHP production is about 0.8 excluding the cooling requirement for preparing the caustic solutions. Field deployment of LN2 for ABL operations represents additional logistics burdens. Details of this approach are covered in Section 3 – Scale-up of LN2-Based MHP Production.

2-3-6. Chilled-Air Sparger

Another approach similar to the direct contact LN2 evaporation, but without the benefit of the latent heat of the carrier fluid, is the use of chilled air for cooling. The atmospheric air can be cooled by means of Vortex Tubes. The ambient air is first compressed and dehumidified. The compressed air enters the Vortex Tube, which separates the air into a hot fraction and a cold fraction. Vortex Tubes are typically operated in one of the two modes to achieve: (1) maximum refrigeration which occurs at about 60% cold fraction; or (2) lowest possible cold temperature which occurs at about 20% cold fraction. The chilled air is then sparged into the aqueous MHP solution to remove heat by means of moisture pickup.

2-4. UNIT OPERATION EFFICIENCY AND SELECTION CRITERIA

To further evaluate the feasibility of the proposed concepts, the methods described above are compared in terms of two critical process parameters. The first parameter is the power input requirement per unit mass of MHP produced, and the second parameter is the overall process efficiency. The latter is defined as effectiveness of energy utilization (%), which is estimated by the efficiencies of motive devices and complexity of the process. The net power requirements for the proposed methods can be estimated from these two terms as given in Table 2-2.

Table 2-2. Power Requirement and Efficiency for Various MHP Cooling Methods

Cooling Method	Motive Device	Medium	Process Step	Power Req't (W/kg MHP)	Process Efficiency(%)
Forced-Circulation Air-Cooler	Fan Pump	Air MOH	1	2.82	80
Chiller	Compressor Pump A Pump B	Refrigerant Coolant MHP	2, 3	15.5	70
Surface Evaporator	Compressor Pump	Refrigerant MHP	2, 3	15.5	80
Vacuum Evaporator	Jet Pump Pump	Water MHP	2	17.0	70
Direct Contact LN2 Evaporator	Sparger	LN2	2, 3	0	95
Chilled-Air Sparger	Compressor	Chilled Air	2, 3	-	70

Further comparisons of hardware associated with these unit operations are made in terms of other logistical issues, such as weight, volume, consumables, and costs. In particular, one of the most critical evaluation criteria for field deployment is the "weight penalty," which is defined as the total deployed weight (weights of equipment and consumables) per kg of MHP produced. Table 2-3 shows the comparison of several thermal management systems based on the MHP production rate of 5000 kg/hr. At this production rate, 1.43 MBTU/hr or 119 TR are required. The baseline system, i.e., the indirect cooling by air-cooled chiller system with conventional heat exchangers, has a weight penalty of 3 for the first 5000-kg MHP produced. Under the same conditions, the vacuum evaporation method has a weight penalty of 0.6, while the LN2 injection method has a weight penalty of 8.8. If LN2 were to be generated on-site, the weight penalty would be 33. Table 2-4 summarizes the selected thermal management options, and their respective process equipment requirements in relationship to deployment logistics. Finally, the development milestones and pro's and con's of the key thermal management options are summarized in Table 2-5.

Table 2-3. Comparison of Thermal Management Systems for MHP Production (5000 kg MHP/batch)

Cooling Method	Equipment Type			Modular Equipment Specifications						Total Equipment			Elec.	Consumable		Weight	Heat Transfer
	Operating Mode	Key	Capacity	Wt.	LxHxW	Motor	Cost	# of	Capacity	Wt	C17 FP	Cost	Power	LN2	Fuel	**Penalty**	**Limitations**
		Feature	(TR)	(ton)	(ft)	(hp)	(k$)	Unit	(TR)	(ton)	(%)	(k$)	(kW)	(kg)	(kg)		
	Batch																
LN2 Direct Contact*	LN2 Tank	3000 gal	284	10.0	16x7x7	0	10	4	1136	40.0	36.6	40	0.0	4000	200	8.8	1.43 MBTU/hr
	Continuous-Flow																
LN2 Injection**	LN2 Generator	7.5 TPD	15	20.5	33x14x10	500	1,500	8	120	164	216	12,000	2983	0	812	32.9	1.43 MBTU/hr
Indirect Cooling***	Chiller System/ Air Cooled	45°F/14°F	150	15.0	20x9x8	200	135	1	150	15.0	13.1	135	149	0	40.6	3.0	100 BTU/hr°Fft^2
Vacuum Evaporation	SP Evaporation System	9 m^2	144	3.0	8x20x6	50	1,000	1	144	3.0	13.1	1,000	37	0	10.1	0.6	1.92 MBTU/hr
Indirect Cooling #	Contact Evaporator																
See Assumption No.			*(3)*						*(1,2)*		*(4)*				*(5,6)*	*(7)*	

Assumptions:

(1) Thermal Load/kg MHP = 72 kcal; 301 kJ; 286 BTU (Assuming temperature for all feed solutions = 20°C, and blending temperature = 0°C)

(2) Heat Flux Required/kg MHP= 0.0837 kW; 286 BTU/hr (Assuming Time for blending peroxide with base solutions = 1 hour)
Heat Flux for 5000 kg MHP = 1430000 BTU/hr = 119 TR

(3) 1 ton of refrigeration (TR) = 12,000 BTU/hr
1 kg LN2 = 90 kcal = 357.5 BTU cooling capacity
Heat of Evaporation for Water (at 30°C and 42.5 mBar) = 581 kcal/kg = 1048 BTU/lb

(4) C-17 Aircraft footprint = 68 ft by 18 ft (Height = 9 ft)

(5) Fuel to Electricity Conversion Efficiency = 30%

(6) Diesel Fuel Heat Value = 19000 BTU/lb

(7) Weight Penalty is defined as total weight (sum of equipment and consumables) per unit weight of MHP produced

* Option 1 – LN2 is transported to production site and stored in four tanks (3000-gal capacity each) sufficient for two 5000 kg MHP batches

** Option 2 – LN2 is generated on site

*** Conventional refrigeration chiller system in combination with cooling coils and/or jacketed vessels

Blending the MHP directly on the surface of an evaporator and eliminating the coolant loop.

Table 2-4. Thermal Management Logistics for MHP Production

Basic Approach	Thermal Management Requirements	Heat Transfer (HT) Surface Area (ft^2/1000 kgMHP/hr)	HT Medium Weight (kg/1000kgMHP)
Coolant/ Indirect Heat Exchange (HE)	- Coolant - Refrigerant - Heat Exchangers - Rec Pumps - Refrig System	60* mininum required	~ 2000 (recycled)
LN2/ Direct HE	- Cryogenic Storage - LN2 Mixer	8,000** available	800 (non reusable)
Water/ Direct HE	- Vacuum System - Auxiliary Cooling System	1,200** available	120 (discharged or recycled)
Refrigerant/ Indirect HE	- Refrigerant - Heat Exchangers - Refrig System	Less than 60* required	1,000*** (recycled)
Refrigerant/ Direct HE	- Refrigerant - Refrig System	10,000** available	1,000*** (recycled)

* Assuming: 150 Btu/hr F ft^2, Temperature difference = 20°F, H_R = 180 Btu/kg MHP

** Assuming the average bubble diameter is ¼ inch

*** Based on R-134a (Heat of vaporization = 90 Btu/lb)

Table 2-5. Thermal Management Options for MHP Production

Medium/ Basic Approach	Status/ Developer	Pro's and Con's
Coolant/Heat Exchanger	1000 kg/batch DELC, TRW	• Proven technology • Need large HE surface or long blend time • Two HE loops (refrigerant and coolant)
LN2/Direct Contact Evaporative Cooling	1000 kg/batch MLQL (9/2000)	• Proven technology • Direct contact heat exchange • Logistical issues for deployment
Water/Direct Contact Evaporative Cooling	Bench-scale MLQL (3/2001)	• Vacuum system • Direct contact heat exchange • Need auxiliary cooling to achieve a delivery and/or storage temp of –15°C
Refrigerant/ Heat Exchanger	Bench-scale MLQL (9/2001)	• Proven technology • Less surface area required than the coolant approach (larger temp difference)
Refrigerant/Direct Contact Evaporative Cooling	Proposed MLQL (12/2001)	• Direct contact heat exchange • Need proof-of-the-concept tests • Potential cross contamination issues need to be addressed
Refrigerant/Direct Contact Evaporative Cooling	Bench-scale MLQL (3 to 8/2002)	• Proof-of-the-concept tests for MHP production conducted • Oil-less compressor identified • Effect of selected refrigerants on stability and quality of MHP studied

2-5. IMPACT OF BLENDING SEQUENCE

The blending sequence refers to the order the five components (water, hydrogen peroxide and three bases) of MHP are added together and when the heat of reaction/mixing is removed. For example, the most common procedure to produce a batch of MHP is to first make an aqueous solution from solids of the three bases, which contribute about 30% of the total heat evolved from the MHP production process. Since the MOH solution is stable, it can be made and stored prior to MHP production. This approach results in the total time required for the MHP production to be compressed, and thus the peak demand for the refrigeration power is reduced.

The blending sequence of the five components of MHP is relevant to the batch production process. Typically, either 70 wt% or 50 wt% hydrogen peroxide aqueous solution is used, with and without stabilizers. Both types are commercially available. The three solid bases used for MOH production are lithium hydroxide monohydrate (LiOH•H2O), sodium hydroxide (NaOH), and potassium hydroxide (KOH). The use of solids allows numerous variations of blending sequence and heat removal. The MHP blending sequences that have been tested at AFRL/MLQL are listed in Table 2-6. Most bench-scale MHP blending tests were made according to procedure AFRL-A. Most 1000-kg batch MHP production tests were made according to procedure AFRL-B.

Table 2-6. Processing Sequence for MHP Production

Method	Step 1 (Preparation)	Step 2 (Preparation)	Step 3 (MHP Mixing*)
AFRL-A	Prepare MOH solution (Add LiOH•H_2O, NaOH, and KOH to H_2O)	Transfer RT MOH solution to MHP reactor	Add H_2O_2 solution** to MOH solution
TRW	Prepare MOH solution	Transfer RT H_2O_2 solution to MHP reactor	Add MOH solution to H_2O_2 solution
AFRL-B	Prepare (1) LiOH solution and (2) MOH solution (NaOH/KOH)	Transfer RT LiOH solution to MHP reactor	(1)Add H_2O_2 solution to LiOH solution; (2) Add MOH solution
AFRL-B2	Prepare (1) LiOH solution and (2) MOH solution (NaOH/KOH)	Transfer RT H_2O_2 solution to MHP reactor	(1)Add LiOH solution to H_2O_2 solution; (2) Add MOH solution
AFRL-B3	Prepare (1) LiOH solution, (2) NaOH solution, and (3) KOH solution	Transfer RT LiOH solution to MHP reactor	(1)Add H_2O_2 solution; (2) Add NaOH solution (3) Add KOH solution
AFRL-C	Add H_2O to MHP reactor	Transfer RT H_2O_2 solution to MHP reactor	(1)Add LiOH•H2O (2)Add NaOH (3)Add KOH
AFRL-D	Prepare MOH solution according to AFRL-A	Cool MOH solution Cool H_2O_2 solution	Blend in PC MOH and H_2O_2 solutions rapidly and proportionally

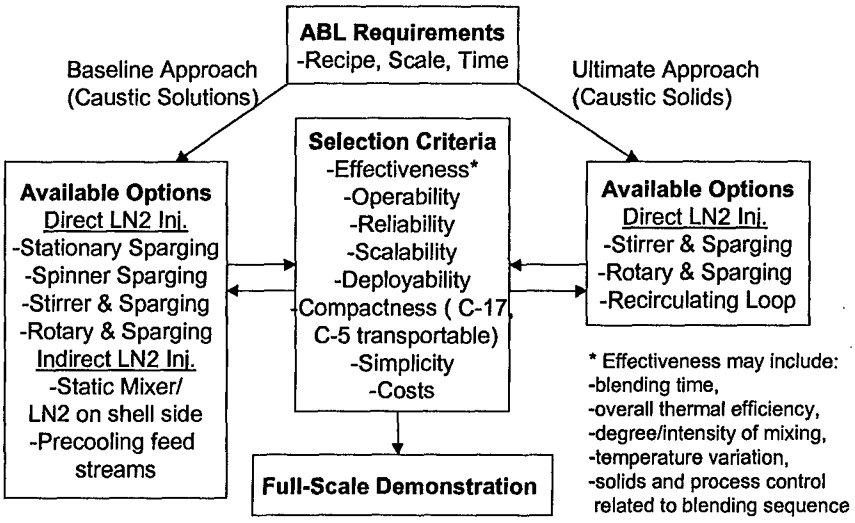
RT – room temperature; PC – pre-cooled.

* - Means to remove heat required; ** - Either 70% or 50% H_2O_2 solution can be used.

SECTION 3. SCALE-UP OF LN2-BASED MHP PRODUCTION

Early in the AFRL/MLQL's ABL program, it was decided that the use of liquefied nitrogen (LN2) would be considered as the baseline approach for rapid production of MHP. Because of the logistics of LN2 supply, this approach would be more appropriate for a fixed-base MHP production facility. During the first two years of this program (1999 and 2000), significant amount of effort was dedicated to the LN2 approach. Figure 3-1 summarizes ABL requirements, system selection criteria, and available options for the research and development of LN2-based MHP production systems. This section discusses the literature database, system design, hardware, operating procedures, and findings pertaining to the available options shown in Figure 3-1 in an effort to scale-up the LN2-based MHP production process. Specific scales of operation include (1) bench-scale systems (250-g, 1-kg, 10-kg); (2) demonstration-scale systems (100-kg); and (3) sub-scale system (1000-kg). All of these systems were operated in the semi-batch mode. In addition to demonstrating the feasibility of direct-contact heat transfer for MHP production, a more complete understanding of the heat-transfer and cooling requirements was established from the operation of these systems. Bases on these findings, a full-scale (2,500 kg/hr) MHP production system using conventional heat exchangers was contracted for and designed by CASE Engineering, Inc. (Mulberry, Florida). This base-line design package is available in a separate report (Spears and Hurley, 2002).

Figure 3-1. System Engineering Methodology and Pathways
To Explore and Demonstrate Alternative Methods for
Rapid Production of Mixed Base Hydrogen Peroxide (MHP)



3-1. LITERATURE REVIEW

Beginning in early 1999, systematic literature searches were conducted on heat transfer techniques involving LN2 or other cryogenic fluids as a rapid and direct cooling medium, particularly applied to controlling exothermic reactions. Direct-contact heat transfer, defined as the heat transfer process accomplished by contacting (mixing) a higher temperature stream with a lower temperature stream, has been an area of chemical engineering practice for many years (Kreith and Boehm, 1988; Sideman and Moalem-Maron, 1982). The advantages of direct contact heat transfer over those using metallic transfer surfaces include (1) the relative simplicity of design, (2) less corrosion and scaling problems, (3) lower maintenance costs, and (4) higher specific transfer areas and overall heat transfer rates. In the application of direct-contact heat transfer for rapid production of MHP, the lower temperature stream can be a cryogenic fluid, which evaporates upon contacting with the higher temperature stream and rapidly removes a large amount of thermal energy from the process, significantly more than a lower temperature fluid without phase change.

Highlighted below is the most relevant U.S. patent literature dealing with LN2 processes.

- Stowasser and Miller (US Patent No. 3,672,182, June 27, 1972) described a process of cooling water by direct injection of LN2, where heat is applied in the vicinity of the injection zone, and the injection of LN2 is intermittent with inert gas being injected when LN2 is not injected to eliminate the tendency of the injector to be plugged by ice formation.
- Bridden (US Patent No. 5,207,068, May 4, 1993) described a similar apparatus for cooling water by direct injection of LN2. Perforated plates are placed in the process vessel to dampen the turbulence and disengage the vaporized LN2 from water. Pressurized gas is introduced from an inlet into the water beneath LN2 to prevent local freezing of water in the mouth of the LN2 injector.
- Cheng et al. (US Patent No. 5,943,869, Aug. 31, 1999; US Patent No. 5,763,544, June 9, 1998) used LN2 to cool a reactor vessel housing an exothermic reaction wherein LN2 is introduced into the reactor in a downward direction, and the LN2 injector is shielded by annular coaxial shielding gas. These prior arts indicate the feasibility of using LN2 to remove heat from MHP production processes, and provide some design considerations for introducing LN2 into an aqueous reaction mixture.

3-2. BENCH-SCALE SYSTEMS

Experimental efforts first focused on developing and testing bench-scale systems to explore different ways of introducing liquefied nitrogen (LN2) into the blending process as a direct contact coolant for rapid MHP production. The first experiment attempted was to freeze 70% H_2O_2 aqueous solution (m.p. = - 40°C) using LN2, and then add the peroxide "ice" into the MOH solution. The heat of melting of peroxide effectively balanced the heat of mixing. However, it is deemed that transformation and transport peroxide "ice" in large-scale would be energy-intensive as in the case of ice machine operations and could encounter other technical challenges. Therefore, subsequent tests focused on injecting LN2 directly into the liquid phase of MOH, H_2O_2, or MHP involving different blending apparatus configurations. Descriptions of these experiments are provided below.

3-2-1. The Jacketed Beaker System

In March 1999, AFRL/MLQL researchers began experimenting with batch production of 4.20 MHP formulation using a 500-ml jacketed glass beaker. For each batch of 250 grams of MHP, it took about one hour to complete the blending of hydrogen peroxide with MOH solution, while the temperature of MHP was kept in the range of 0°C to 5°C during the blending process. The purpose of these experiments was to gain first-hand experience in MHP material handling, production, storage and characterization.

3-2-2. The Recirculation Systems

Between April and June 1999, several recirculation blending configurations were tested under simulated conditions using LN2 and water. Descriptions of most of these setups and results are provided in Appendix D. One of the key components involved in the recirculation systems was the pump. Progressive cavity and modified peristaltic pumps were used. In both cases, MHP must pass through the pump head under high shear rate conditions, which was a concern for accelerating the decomposition of peroxide and temperature rise in MHP.

3-2-3. The LN2 Spinner System

In August 1999, a new apparatus design was proposed and tested for MHP production. This apparatus design involved two spinning arms propelled by the evaporating nitrogen perpendicular to a stationary shaft, which also serves as the LN2 carrying duct as shown in Figure 3-2. The idea was to eliminate the need for a recirculation pump, and provide fluid mixing through perturbation as result of the rapidly expanding nitrogen in the bulk fluid mixture.

Using compressed air as the motive fluid and water as the liquid medium, the effectiveness of the spinner mechanism was experimentally simulated. Direct observation of mixing of colored plastic beads indicated the spinner mechanism was effective in enhancing fluid mixing. The head pressure in the LN2 dewar (20 psig) was sufficient to drive the spinner in MHP solution resulting in adequate fluid motion and mixing. Because of the effectiveness and simplicity of this blending system, it was decided that the spinner mixer design with multiple injection ports would be used in the 1st generation of 100-kg MHP systems.

3-2-4. The Rotary System

Although the LN2 spinner system worked well in both small-scale and large-scale systems, the search for a better and simpler system continued. On 28 February 2000, a rotary MHP blender in the capacity of 1-kg batch was successfully tested. The mixing was achieved by the rotating the blending vessel at a pre-determined speed, while the LN2 and hydrogen peroxide were injected into the MOH solution via two parallel stationary conduits. This system was later scaled up to the 10-kg batch size.

This system worked well for blending small batches of MHP (1 kg to 10 kg). It appeared that more effort would be needed to build larger rotating vessels and motor assemblies. A large-scale cement transportation truck would be a close representation of a full-scale rotary MHP blending system. At the time, the decision to select a design for larger systems was in favor of a stationary vessel system. Therefore, further scale-up of the rotary system was not pursued.

3-2-5. Thermal Efficiency of LN2-Based MHP Blending Systems

The evaluation of MHP production systems was based on system features (i.e., simplicity, light weight, process stability) as well as the thermal efficiency of the process. In the case of the LN2-based MHP blending process, the thermal efficiency is defined as the measured heat removal divided by the amount of heat required to vaporize LN2. Table 3-1 shows the thermal efficiencies and GN2 flow rates recorded in different scales of MHP blending processes. The results were derived from the 5-kg, 10-kg, and 100-kg batch tests. The thermal efficiency of a MHP blending test is treated in two steps: (1) the step of pre-cooling the MOH solution and (2) the step of adding hydrogen peroxide solution.

3-3. SUB-SCALE SYSTEM TESTING

After demonstrating the efficacy of 1-kg and 10-kg MHP batch production systems using LN2, scale up of the process to 100-kg batch-size was justified. Two generations of the demonstration-scale systems (100-kg batch size) were designed, constructed, and tested. The purpose of the 10X scale-up was to (1) produce a system that more closely resembled a production type configuration, (2) fully instrument a system to close all material and energy balances, and (3) develop a first generation control strategy.

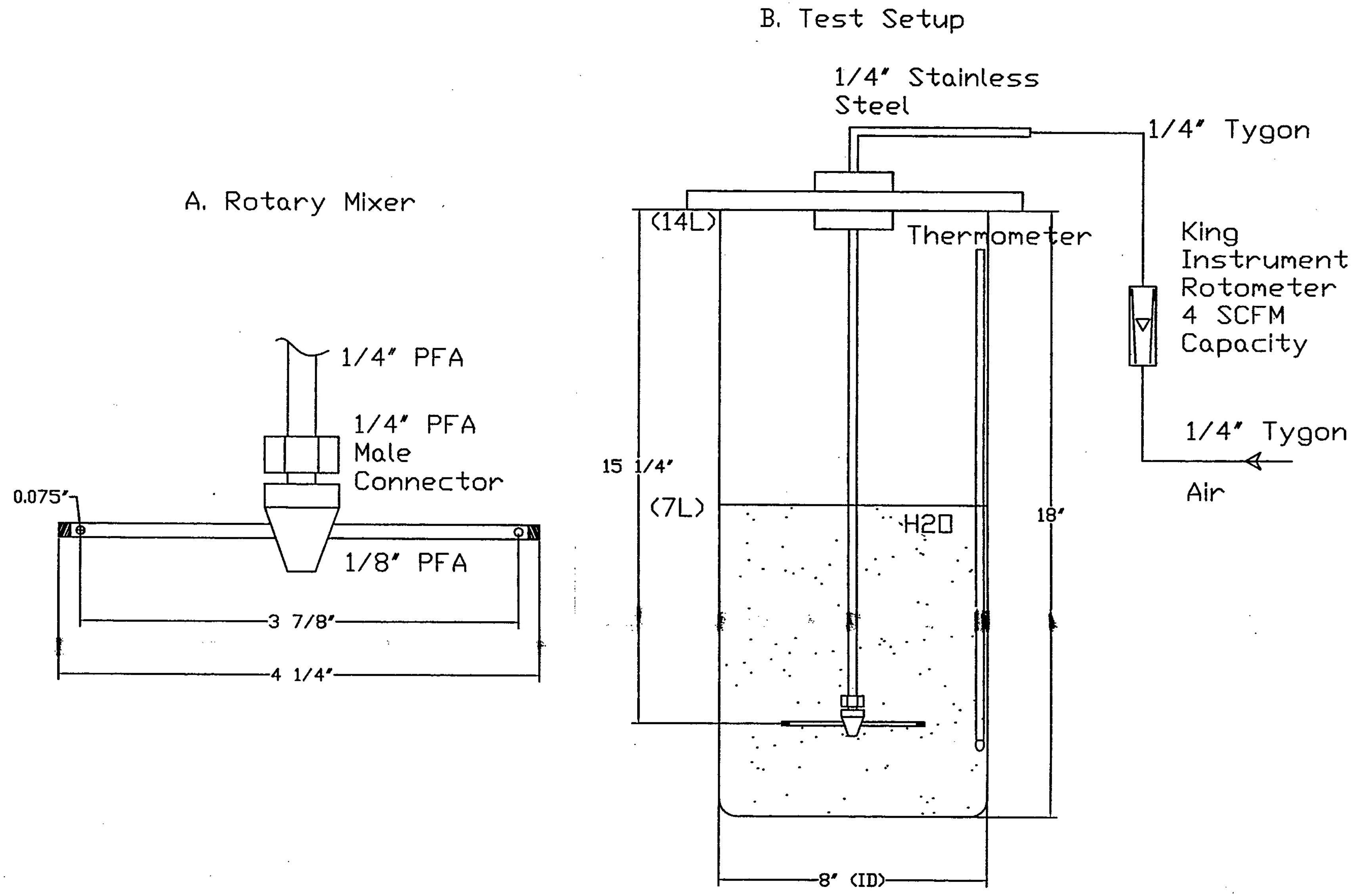


Figure 3-2. Schematic of LN2 Spinner and Setup for MHP Blending

Table 3-1. Thermal Efficiencies and GN2 Flow Rates for LN2-Based MHP Production Processes

Test Date	Description	Process	Time	Temperature			Feed	Heat	LN2 Consumption				Thermal	Precool/	Volumetric	
		Stage		Start	End	Diff.	Load	Burden	Start	End	Total	Rate	Efficiency	Total LN2	Gas Flow Rate	
			(min)	(C)	(C)	(-C)	(kg)	(kJ)	(kg)	(kg)	(kg)	(g/min)	(%)	(%)	(ACFM)	(SCFM)
13-Jul-99	10 kg batch	Precooling	27	21.0	4.0	17.0	7.74	550	57.48	54.36	3.12	116	43.2	28.1	0.93	3.29
8-Jul-99	4.50 recipe	Blending	67.5	~4	~4	0	10	1881	71.28	63.28	8.0	119	57.6		0.95	3.37
											11.12					
6-Aug-99	10 kg batch	Precooling	21.3	23.0	7.0	16.0	7	468	46.26	44.2	2.06	97	55.6		0.78	2.75
	Water only															
9-Aug-99	5 kg batch	Precooling	17	32.0	-2.0	34.0	3.873	550	73.44	71.5	1.94	114	69.5	32.1	0.92	3.25
	4.50 recipe	Blending	31	~4	~7	-3	5	877.8	71.5	67.4	4.1	132	52.4		1.06	3.76
											6.04					
13-Aug-99	5 kg batch	Precooling	8	26.1	-0.6	26.7	3.87	432	63	61.26	1.74	218	60.8	28.5	1.75	6.19
	4.86 recipe	Blending	38.4	~14	~4	10	5	1225	61.26	56.9	4.36	114	68.8		0.91	3.23
											6.1					
27-Aug-99	10 kg batch	Precooling	8	17.8	-1.0	18.8	7.34	577	74.26	72.46	1.8	225	78.5	24.8	1.81	6.40
	4.86 recipe	Blending	25	~0	~0	0	10	2031	72.46	67	5.46	218	91.1		1.75	6.21
											7.26					
30-Aug-99	10 kg batch	Precooling	9	19.9	-1.2	21.1	7.34	647	60	57.96	2.04	227	77.7	28.3	1.82	6.45
	4.86 recipe	Blending	22.5	~-1	~-2	1	10	2073	57.96	52.8	5.16	229	98.4		1.84	6.53
											7.2					
2-Nov-99	100 kg batch	Precooling	35	21.0	6.0	15.0	58.67	3678	73	61.5	11.5	329	78.3	23.0	2.64	9.35
	Water only	Blending														
								Available LN2 =			50					

Assuming:

(1) GN2 density (20 psig) 0.0044 g/ml @ -196C
0.00124 g/ml @ 0C

(2) Heat of Mixing (kcal/kg MHP) = 10 x [OH-] (mol/kg)

(3) Cooling Capacity of LN2 = Heat of Evaporation + Heat Capacity x 200C = 408.4 kJ/kg LN2

3-3-1. 1st Generation of 100-kg Batch System

The first blending vessel design was based on envisions that a full-scale MHP production system was a horizontally oriented tank, such as the one used on a diary transportation truck. The mixing mechanism was based on the LN2 spinner design demonstrated by the 10-kg scale batch systems. Most activities in support of the design, construction, and testing of the 1st Generation 100-kg MHP Batch System took place between September 1999 and January 2000. The system hardware, computer control system, control software programming was developed in September through December 1999, whereas five preliminary MHP blending tests were conducted from 15 December 1999 through the end of January 2000.

Analytical validation results, in terms of concentrations of hydrogen peroxide and base, for seven selected tests based on the 4.86 MHP formulation ranging from 250-g batch to 100-kg batch sizes are summarized in Table 3-2. Since the 100-kg batch operation was conducted at an open structure without environmental controls, the ambient temperature could have dropped near 0°C at night. As shown in Table 3-2, the test conducted on 7 January 2000 involved an MOH solution prepared on 5 January 2000, significant amounts of solids were observed before and after addition of hydrogen peroxide. It was believed that the solids were formed in the MOH solution overnight, and it was hard to re-dissolve without raising the temperature of the solution. Two smaller batches (250 g and 5 kg) of MHP were made to evaluate the observed solid formation. It seemed that the MOH solution prepared according to the 4.86 MHP formulation was near a phase boundary and thus had a higher propensity for precipitating solids. If the MOH solution was used soon after it was prepared, the solids formed were loose and less packed. The addition of hydrogen peroxide tended to re-dissolve the solids. Also, both of the small batches were made using a mechanical stirrer. Although the spinner mechanism worked well for mixing fluids in solution in the 100-kg batch operation, it was believed that a stronger agitation device, such as a stirrer, was needed to deal with fluid mixtures containing suspended solids.

3-3-2. 2nd Generation of 100-kg Batch System

The second generation 100-kg batch system was designed based on standard industrial practices for mixing and rapidly cooling chemical mixtures. The system was a simple process comprising three metering pumps, a vertical mixing tank, a mechanical agitator, a liquid nitrogen sparging system, and a computer control system. All the base solids were dissolved into the proper amount of water. The $LiOH \bullet H_2O$ was dissolved in water and stored in a separate storage container. This was done due to the limited solubility of LiOH in water. A majority of the available water was used to dissolve the $LiOH \bullet H_2O$. The remainder of the water to be added to the batch was used to dissolve NaOH and KOH. The NaOH and KOH were dissolved in water and put into the same storage container. The base solutions were metered into the mixing tank one at a time. The amount of each ingredient added was monitored and controlled with a computer control system. LN2 was used as the cooling medium for this mixing process and it was sparged into the bottom of the tank while the peroxide was being added. When peroxide was being added to the base, or vice versa, the computer control system regulated the flow rate of the ingredient being added to keep the mixture temperature at or below 0°C, while maintaining a constant flow of LN2. Once the mixing process was complete and the final desired temperature of the mixture was reached the liquid nitrogen was turned off. Parameters quantified for each batch of MHP included the weights of MHP produced and liquid nitrogen consumed, and the concentrations of peroxide and base in the MHP. The effort of this task began in February 2000. The system was completed in May 2000, and testing was conducted from May through July 2000. Details of this process and typical test results are presented in Appendix F.

Table 3-2. Analytical Validation Results Derived from the LN2-Based MHP Blending Tests Using the 4.86 Formulation

Date	Scale	Blending Tank Configuration	Ingredient	Loading (kg)*	Peroxide Strength (gmol/kg MHP)		Base Strength (gmol/kg MHP)**		Note
					Target	Actual	Target	Actual	
12/15/ 1999	100 kg	Horizontal, six LN2 spinners, 4-inch above the curved tank bottom	H_2O $LiOH \bullet H_2O$ NaOH KOH H_2O_2(70%)	50.08 6.38 4.24 12.78 26.7	5.70	6.13	4.447	N/A	-MOH solution was prepared on 12/14/1999 using a mechanical mixer -Base precipitates were apparent at the tank bottom before H_2O_2 blending -Samples drawn at the middle level of MHP solution
12/20/ 1999	100 kg	Horizontal, six LN2 spinners, 4-inch above the curved tank bottom	H_2O $LiOH \bullet H_2O$ NaOH KOH H_2O_2(72.8%)	50.04 6.38 4.24 12.78 25.5	5.474	6.10	4.447	4.07	-MOH solution was prepared on 12/17/1999 using a mechanical mixer -Base precipitates were apparent at the tank bottom before H_2O_2 blending -Samples drawn at the middle level of MHP solution
12/21/ 1999	250 g	Jacketed beaker with a magnetic stirring bar	H_2O $LiOH \bullet H_2O$ NaOH KOH H_2O_2(68.3%)	0.1261 0.016 0.01068 0.032 0.06602	5.29	5.18	4.447	4.56	-MOH solution was prepared prior to blending using a magnetic mixer -Base precipitates were apparent at the tank bottom before H_2O_2 blending -No precipitates after H_2O_2 blending
1/7/ 2000	100 kg	Horizontal, six LN2 spinners, 4-inch above the curved tank bottom	H_2O $LiOH \bullet H_2O$ NaOH KOH H_2O_2(72.8%)	50.04 6.38 4.24 12.78 25.5	5.474	Top: 5.95 5.93 Bottom: 5.39 4.12	4.447	Top: 3.68 3.60 Bottom: 3.94 4.67	-MOH solution was prepared on 1/5/2000 using LN2; blending test delayed due to depletion of LN2 -Base precipitates were apparent at the tank bottom before and after H_2O_2 blending -Samples were drawn at the bottom and top levels of the MHP solution
1/18/ 2000	5 kg (4.94 kg actual wt.)	Vertical, flat bottom glass vessel, single LN2 spinner, ½ inch above the bottom of the vessel	H_2O $LiOH \bullet H_2O$ NaOH KOH H_2O_2(72.8%)	2.56 0.318 0.212 0.640 1.275	5.474	5.24	4.447	4.57	-MOH solution was prepared prior to blending using a mechanical mixer -Base precipitates were apparent at the tank bottom before H_2O_2 blending -No precipitates after H_2O_2 blending -Samples drawn at the middle level of MHP solution

Table 3-2. Analytical Validation Results Derived from the LN2-Based MHP Blending Tests Using the 4.86 Formulation (Cont.)

Date	Scale	Blending Tank *Configuration*	Ingredient	Loading (kg)*	Peroxide *Strength (gmol/kg MHP)*		Base Strength *(gmol/kg MHP)***		Note
					Target	Actual	Target	Actual	
1/24/ 2000	100 kg	Horizontal, four LN2 spinners, ½ inch above the curved tank bottom (the new supply manifold)	H_2O $LiOH \bullet H_2O$ NaOH KOH H_2O_2(72.8%)	51.14 6.38 4.24 12.78 25.5	5.474	Top: 5.32 Bottom: 5.30	4.447	Top: 4.50 Bottom: 4.55	-MOH solution was prepared prior to blending using a mechanical mixer -No precipitates after H_2O_2 blending -Samples were drawn at the bottom and top levels of the MHP solution
1/28/ 2000	100 kg	Horizontal, four LN2 spinners, ½ inch above the curved tank bottom (the new supply manifold)	H_2O $LiOH \bullet H_2O$ NaOH KOH H_2O_2(72.8%)	51.14 6.38 4.24 12.78 25.5	5.474	Top: 5.33 Bottom: 5.31 5.38	4.447	Top: 4.65 Bottom: 4.56 4.59	-MOH solution was prepared prior to blending using a mechanical mixer -No precipitates after H_2O_2 blending -Samples were drawn at the bottom and top levels of the MHP solution

Notes: * For 100-kg MHP blending tests, the weight of 70% H2O2 was monitored by an Ohaus scale with a readability of 0.005 kg; individual weight of all other materials was measured by using a First-Weigh scale with a readability of 0.02 kg.

** Lab assay values (manufacturer specifications): KOH = 88% (min 90%); NaOH = 94% (96.6%); LiOH = 96% (99%); and H_2O_2 = 72.76% (72.9%).

3-4. PILOT-SCALE SYSTEM DEVELOPMENT AND TESTING

A 1000-kg MHP production system was designed and constructed based on the 2nd generation 100-kg batch system. The larger process consisted of tanks for diluting and storing caustic solutions, an agitated tank for mixing MHP (MHP production tank), and a liquid nitrogen vessel. A process monitoring/control and data acquisition system was equipped to control the weights of reagent addition so that the temperature of MHP can be maintained at a constant level for a given LN2 injection rate. As with the 100-kg system the solid caustics were dissolved in water and stored in individual tanks prior to MHP blending. However, due to the increase in scale, the caustic solids were transferred by a solid conveying system (Flexicon), which was selected, procured, and installed in 1999. The system was equipped with a weigh hopper to quantify and control the amount of caustic transferred. To ensure the proper weight ratio of the solids of each hydroxide, the MOH solution was prepared in the MOH mixing tank, where the deionized water was added by using a standard water meter (volumetric), and the weight of each hydroxide was monitored by the weigh hopper. The MOH solution was then transferred to the MHP production tank.

The MHP production tank was installed on the top of a scale that was used to determine the amount of each ingredient added to the mixture. Air-operated pumps were used to transfer liquid ingredients from their storage containers to the MHP production tank. The airflow that operated the pumps was controlled by the computer control system. This control system monitored the weight in the MHP production tank. This allowed the operator to add specific weights of each ingredient to the mixing tank. The computer control system added each ingredient to the mixture one at a time by sending air to the pump that was used to transfer that ingredient to the mixing tank. The computer control system controlled the temperature in the mixing tank by increasing or decreasing the flow rate of ingredients to the MHP mixing tank. The liquid nitrogen addition causes the temperature to decrease while the reaction between the MOH solution and the peroxide causes the temperature of the mixture to increase. As ingredients are added to the mixing tank and the computer controls the flow of each ingredient to the tank, a mechanical agitator ensures the ingredients are well mixed and helps disperse the liquid nitrogen into the mixture. Upon contacting the reaction liquid, the LN2 rapidly boils off. To accommodate the nitrogen gas generated, a vent was placed in the top of the MHP production tank discharging the gas to the outside.

The preliminary design evaluation of the feed tanks, MOH mixing tank, MHP production tank, weighing system, and LN2 delivery system began in March 2000, and the system construction was completed in September 2000. The first 1000-kg batch of MHP was prepared on 29 September 2000. From October 2000 to August 2001, several 1000-kg batches of MHP were made with this system. Typical MHP blending time was about 45 minutes excluding pre-cooling time for the base solutions. Detailed description of the process and results from typical batch runs are provided in Appendix G.

SECTION 4. SUMMATIVE ANALYSIS AND RECOMMENDATIONS

Thermal management is one of the most critical engineering issues for rapid production of MHP. Thermal management for rapid production of MHP encompasses three key process design aspects: (1) heat transfer equipment; (2) heat generation and removal rates; and (3) processing (blending) sequence as related to reduction of the peak refrigeration power requirement during the MHP production. During the AFRL/MLQ ABL program period, issues related to these three design aspects were analyzed, and in many cases experimentally evaluated. Findings and approaches developed from these studies are summarized and presented in this report.

There are two general approaches for thermal management: indirect-contact heat transfer and direct-contact heat transfer. The former involves heat transfer through heat exchangers, and the latter refers to the heat transfer achieved by direct contact between the cooling medium and the process fluid. In the case of direct-contact heat transfer for MHP production, the cooling medium can be a liquid that evaporates under controlled conditions. The phase change from liquid to vapor of the cooling medium has three major positive effects: (1) utilization of the latent heat of the cooling medium, (2) rapid removal of heat as the cooling medium vapor leaves the system, and (3) the rapidly expanding vapor bubbles enhance the agitation of the mixing fluids. Specifically, the cooling medium can be either water itself in which case the process is called vacuum evaporation, or a liquid with low vapor pressures such as a cryogen or a refrigerant.

One of the highlights of the AFRL/MLQ ABL program was the successful scale-up of the LN2-based MHP production process by a factor of 4000. The direct-contact LN2 evaporation approach was demonstrated at incremental batch scales of 0.25-kg, 1-kg, 10-kg, 100-kg, and 1000-kg with the MHP blend time reduced from the reported 20 hours (typical) to 45 minutes. However, the amount of LN2 required was about 0.8 kg/kg MHP. Since on-site recovery or regeneration of LN2 is energy-intensive or logistically prohibitive, the delivery of LN2 in 10,000's-kg to FOL for full-scale operations would be a logistical concern. Therefore, the LN2-based approach would be suitable for MHP production at a fixed-location facility where LN2 can be readily supplied.

These findings point to a direction of utilizing a cooling medium that can be as effective as LN2, and more importantly can be conveniently recovered and reused. These requirements have lead to the consideration of using refrigerants for direct contact cooling in the MHP production process. The most recent effort has focused on a close-loop direct contact refrigerant evaporation method. Experimental efforts and findings of this concept will be presented in a separate report.

LIST OF SYMBOLS AND ABBREVIATIONS

ΔH - the heat of reaction (kcal/gmole or kJ/gmole),
M - the batch weight of MHP (kg)
Q - the heat of mixing (kcal or kJ),
Q_W - heat generation based on weight fractions (kcal),
Q_M - heat generation based on mole concentration (kcal),
T - temperature (K or °C),
S - solubility (g/kg, mole/kg),
U - the overall heat transfer coefficient (BTU/hr-ft^2-°F),
W - weight fraction,
c_p - heat capacity at constant pressure (kJ/kg°C),
ABL - Airborne Laser,
AFRL - Air Force Research Laboratory,
BHP - basic hydrogen peroxide,
COIL - chemical oxygen iodine laser,
CONEMP - Concept-of-Employment,
CONOPS - Concept-of-Operations,
DI - de-ionized water,
FOL - Forward Operating Location,
GN2 - gaseous nitrogen,
GUI - graphical user interface,
LN2 - liquefied nitrogen,
MC - Mission Capability,
MHP - mixed-base hydrogen peroxide,
MMI - man machine interface,
MOH - mixed-hydroxide solution (LiOH/NaOH/KOH),
$O_2(^1\Delta_g)$ - singlet delta oxygen,
PDRR - Program Definition and Risk Reduction,
PFA - perfluoroalkoxy polymer,
PLC - programmable logic controller,
PVC - polyvinyl chloride,
RPM - revolution per minute,
TR - tons of refrigeration (1 TR = 12,000 Btu/hr),
Teflon - polytetrafluoro ethylene,
VLE - vapor-liquid equilibrium.

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APPENDICES

APPENDIX A – MHP FORMULATION AND CALCULATIONS

The strength of an MHP solution is typically characterized by the concentrations of hydroxyl ions and hydrogen peroxide per unit weight of the solution (i.e., moles OH^-/kg MHP and moles of H_2O_2/kg MHP), respectively. The MHP strength may vary, depending on its formulation (or recipe). To achieve best utility results and compensate for peroxide decomposition, MHP formulations require an excess of hydrogen peroxide to hydroxides on the molar basis, with a typical molar ratio of about 1.15. An ideal MHP formulation provides maximum base and peroxide concentrations while maintaining all species in solution during MHP production, storage, and singlet oxygen generation. Three formulations that were used at AFRL/MLQL are given below.

(1) The 4.20 MHP Formulation (Welch and Hurley):

0.2259		H_2O_2 (a)
0.0328	kg_j	$LiOH \bullet H_2O$ (cr)
0.0469	$\longrightarrow$	NaOH (cr)
0.1419	kg_{MHP}	KOH (cr)
0.5526		H_2O

(2) The 4.86 MHP Formulation (Welch and Hurley):

0.2659		H_2O_2 (a)
0.0638	kg_j	$LiOH \bullet H_2O$ (cr)
0.0424	$\longrightarrow$	NaOH (cr)
0.1279	kg_{MHP}	KOH (cr)
0.5000		H_2O

(3) The 4.51 MHP Formulation (Welch and Hurley):

0.3545		H_2O_2 (a)
0.07092	kg_j	$LiOH \bullet H_2O$ (cr)
0.06760	$\longrightarrow$	NaOH (cr)
0.06344	kg_{MHP}	KOH (cr)
0.4436		H_2O

Note: In these MHP formulations, it is assumed that H_2O_2 (a) is 70 wt% of hydrogen peroxide in water, and all three bases (cr) are solids of 100% purity.

APPENDIX B – THERMAL ENERGY REMOVAL REQUIREMENTS FOR MHP PRODUCTION

The heat values associated with mixing base solutions and mixing base solution(s) with hydrogen peroxide are given in Table B-1. The thermal duty (Energy/Time/Weight of MHP) of the MHP production process is based on the heat of reaction and heat losses to environment, and therefore determines the total thermal energy transfer requirement.

Table B-1. Thermal Energy Transfer Requirements for MHP-Related Reactions

Based on 1 kg MHP	Unit	$KOH-H_2O$	H_2O_2-KOH	H_2O_2-MOH
Heat of Reaction (ΔH)*	kcal/mol	13	12	10
Base Concentration	mol/kg MHP	4.50	4.50	4.50
Heat Generation	Kcal/kg MHP	58.5	54	45
Operation Time (t)	s	225	225	225
Average Heat Flow (Q)	kcal/s	0.260	0.240	0.20
where $Q=\Delta H/t$	kW	1.09	1.00	0.84
	BTU/hr	3714	3429	2857
	TR	0.310	0.286	0.238

* Heat of dilution for KOH (Truesdell et al., 1995); NaOH – 10.2 kcal/mol, and $LiOH{\bullet}H_2O$ – 9.6 kcal/mol (Dean, 1992).

Heat of hydrogen peroxide decomposition to O_2 and H_2O (vapor) = 13 kcal/mol.

Since hydrogen peroxide intrinsically decomposes at high pH conditions, reducing MHP temperature is one of the most practical means to minimize the rate of peroxide decomposition in the MHP solution. Typically, MHP is produced, stored, and consumed at temperatures around 0°C and preferably at –15°C as long as the MHP of a given formulation remains as a solution.

APPENDIX C – SUPPLEMENT TO SECTION 2

2-3-1. Forced-Circulation Air-Cooler

Typical forced-circulation air-cooling evaporator capacities as a function of tube/fin heat transfer surface areas are summarized in Table C-1. For example, cooling capacity of 1 TR can be potentially achieved with a temperature difference of 20°F (11°C) between the load and the ambient (see the last row entry in Table C-1). Only a 1/8-hp motor is required to provide air circulation for heat removal. Since 13 TRs are needed (see Table 2-1) to prepare the base solutions for a batch of 1000-kg MHP, a 1.63-hp motor will suffice for cooling the equivalent base solutions.

Table C-1. Forced Circulation Evaporator Capacities (Althouse et al., 1992)

Surface Area (ft^2)			Parallel Paths	Cooling Capacities (Btu/hr)		Motor		Fan	
Tube	**Fin**	**Total**		**15°F TD**	**25°F TD**	**hp**	**Speed (rpm)**	**Diameter (in)**	**Air Flow (cfm)**
2.94	32.4	35	3	2200	4500	1/80	1800	12	620
5.88	63.0	69	5	4100	7200	1/80	1800	12	465
7.94	70.1	78	3	5200	9000	1/10	1140	15.5	1200
13.2	117	130	5	8300	12300	1/10	1140	15.5	1000
14.7	83.3	98	3	6500	10500	1/8	1140	17	2020
17.2	146	163	5	10000	14000	1/8	1140	17	1715

TD – temperature difference between ambient air and process fluid.

2-3-2. Chiller

The use of chillers to provide cooling for MHP production has been widely practiced. The bench-mark system at AFRL/MLQL was based on the conventional design including a chiller and a 500-ml jacketed glass beaker. Typically, it took about one hour to make a 250-g batch of MHP using this setup. Due to limited heat transfer area available in the conventional heat exchanger devices and limited sensible heat in the coolants, the time required for large-scale MHP production is relatively long. Some reports indicate the time for production of 1000 kg MHP to be more than 15 hours. In addition to the heat transfer surface area requirement, the coolant and coolant reservoir add a significant logistical burden to field deployment.

2-3-3. Surface Evaporator

Figures C-1 through C-3 show photos of apparatus configuration for the evaporator system, evaporator, and evaporator with pumps, respectively. The evaporator was a miniature radiator with overall dimensions of 5-inch (length) x 5-inch (width) x 1-inch (thickness). Refrigerant passes through about 24-inch, 3/8" O.D. Stainless Steel tubing interlocked with 114 copper fins. A heat transfer capacity of 1000 Btu/hr was specified for the unit used in this study (Lytron, Model AS04-05G01SB) by the manufacturer. The radiator was Nickel-plated by the electroless coating process at Coatings Technology, Inc. (Phoenix, AZ). This radiator was installed on a bench-scale refrigeration system equipped with a 1/3 HP compressor and air-cooled condenser as shown in Figure C-1.

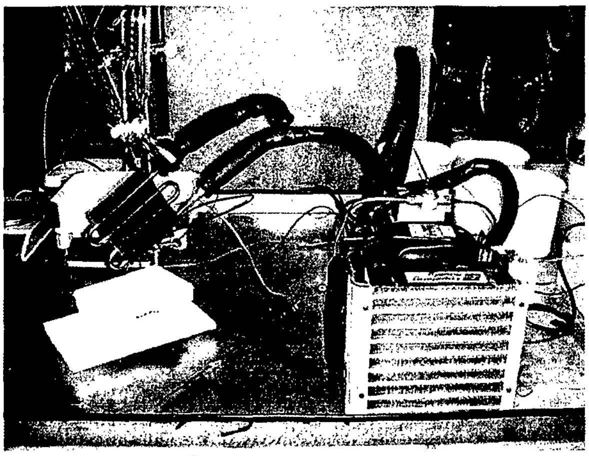


Figure C-1. Surface Evaporator Setup

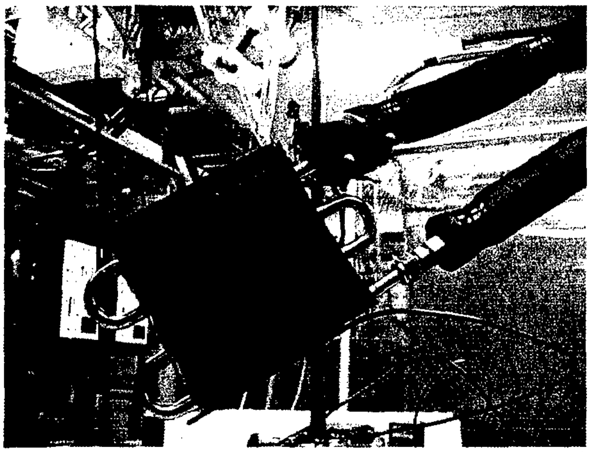


Figure C-2. Electoless Nickel Plated Radiator Coil

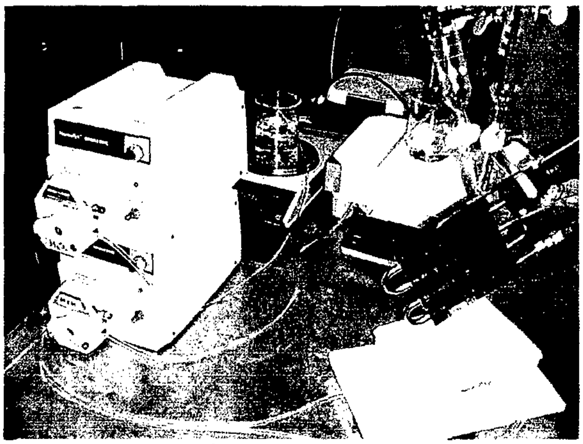


Figure C-3. Feed Delivery System for Surface Evaporator Setup

2-3-4. Vacuum Evaporator

Table C-2 summarizes the boiling points of water at various pressures below atmospheric. Since hydrogen peroxide is present in the fluid mixture, some hydrogen peroxide may evaporate as water does. Table C-3 shows the vapor-liquid equilibrium (VLE) data of the hydrogen peroxide-water binary mixture for two constant temperatures at 30°C (literature value) and 0°C (extrapolated value). The VLE data are presented for both liquid phase and vapor phase compositions in terms of molar and weight fractions of hydrogen peroxide. For the 4.86 MHP formulation, the concentration of hydrogen peroxide in the liquid phase is 19.4 wt%. At 30°C, the vapor concentration of hydrogen peroxide at equilibrium will be 0.21 wt%. At 0°C, the vapor concentration of hydrogen peroxide is dropped to about 0.1 wt%.

Table C-2. Heat of Evaporation of Water as a Function of Pressure

Temperature	**Saturation Pressure**				**Heat of Evaporation**	
(°C)	(mBar)	(MPa)	(mmHg)	(in H_2O)	(kJ/kg)	(kcal/kg)
0	6.11	0.0006109	4.6	2.46	2501	597.8
5	8.72	0.0008721	6.5	3.47	2490	595.0
10	12.3	0.001228	9.2	4.92	2478	592.2
15	17.1	0.001705	12.8	6.84	2466	589.4
20	23.4	0.002339	17.5	9.35	2454	586.5
25	31.7	0.003169	23.8	12.7	2442	583.7
30	42.5	0.004246	31.8	17.0	2431	580.9
35	56.3	0.005628	42.2	22.6	2419	578.1
40	73.8	0.007384	55.4	29.6	2407	575.2
45	95.9	0.009593	71.9	38.4	2395	572.4
50	123	0.01235	92.6	49.5	2383	569.5

Table C-3. Vapor-Liquid Equilibrium for the H_2O_2-H_2O Binary Mixture

H_2O_2 Concentration	**Liquid Phase**		**Vapor Phase**	
	mole fraction	wt%	mole fraction	wt%
T=30°C	0.1	17.3	0.001	0.19
4.86 MHP Formulation	**0.113**	**19.4**	**0.0011**	**0.21**
	0.2	32.1	0.01	1.87
	0.3	44.7	0.025	4.62
	0.4	55.7	0.05	9.04
	0.5	65.4	0.09	15.7
H_2O_2 Feed Stream	**0.553**	**70.0**	**0.12**	**20.5**
	0.6	73.9	0.15	25.0
	0.7	81.5	0.255	39.3
T=0°C (extrapolated)	0.1	17.3	0.0005	0.09
	0.103	17.8	0.0006	0.11
4.86 MHP Formulation	**0.113**	**19.4**	**0.0008**	**0.15**
	0.2	32.1	0.0075	1.41
	0.3	44.7	0.02	3.71
	0.4	55.7	0.035	6.41
	0.5	65.4	0.065	11.6
H_2O_2 Feed Stream	**0.553**	**70.0**	**0.090**	**15.7**
	0.6	73.9	0.12	20.5
	0.7	81.5	0.22	34.8

Note: Data at 30°C are from Scatchard et al. (1952), and data at 0°C are extrapolated.

Based on the water vapor pressure data and the preliminary MHP test results, it is expected that a pressure of about 10 mbar is adequate for the production of MHP at ambient temperatures. For this low vacuum range process, a wide range of vacuum systems may be considered. Some of these systems include air or water aspirators (jet pumps), air or steam ejectors, and single stage rotary (mechanical) vacuum pumps. Further investigation is needed to estimate energy consumption to operate the vacuum pump as compared to other cooling methods as well as the extent of hydrogen peroxide loss due to evaporation.

Apparatus Setup

The concept of MHP production using vacuum evaporation has been proven through preliminary bench-scale tests (250-g batch) using a rotary evaporator system equipped with a vacuum aspirator (Brinkmann Model B-169). A photo of he proof-of-the-concept system is shown in Figure C-4. Since the concentrated hydrogen peroxide feed stream could result in higher vapor concentration of hydrogen peroxide, the injection port of hydrogen peroxide during the blending operation was always submerged below the liquid level.

Typical Results

The mixing of hydrogen peroxide with mixed-base solution typically took about 15 minutes for a 250-g batch, while the temperature of the solution was maintained below 30°C and at a system pressure of about 20 mbar. A close-up photo of the observed MHP boiling at 22.6°C is shown in Figure C-5. According to the data given in Table C-2, water boils at about 17°C at 20 mbar. Figure 2-2 shows that the 4.51 MHP formulation begins boiling at about 21°C. The 4°C boiling point rise was due to the presence of the MHP electrolytic components. Detailed results from the water simulation tests and MHP blending tests are summarized in Table C-4.

Figure C-4. Vacuum Evaporation Setup

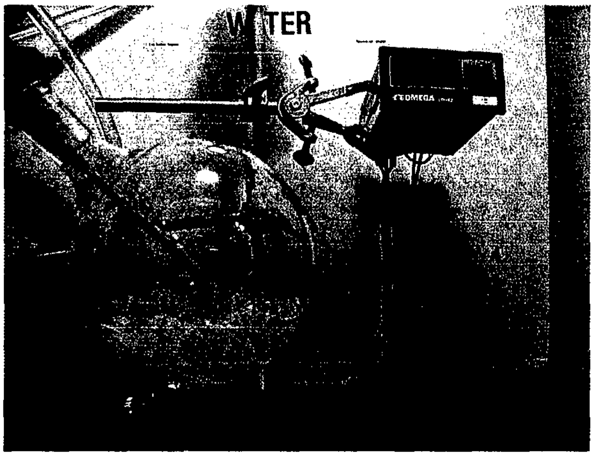


Figure C-5. MHP Boiling under Vacuum

Table C-4. Test Conditions and Results for Bench-Scale MHP Production by Vacuum Evaporation

Based on 1 kg MHP	Unit	H_2O				H_2O_2-MOH				
Test Date		2/15/01	2/16/01	2/20/01	2/22/01	3/16/01	3/23/01	4/26/01	4/30/01	5/4/01
Heat of Reaction (ΔH)*	kcal/mol	0	0	0	0	12	12	12	12	12
Base Concentration	mole	0.00	0.00	0.00	0.00	4.52	4.52	4.52	4.52	4.52
Run Time (t)	s	3600	3600	3600	3600	2100	3600	960	1020	690
Average Heat Flux (Q)	kcal/s	0	0	0	0	0.0258	0.0151	0.0565	0.0532	0.0786
$Q=\Delta H/t$	BTU/h	0	0	0	0	369	215	807	760	1123
	W	0.000	0.000	0.000	0.000	108.1	63.0	236.4	222.5	328.9
Water Bath Temp	°C	40	30	40	35	23	N/A	N/A	N/A	N/A
Solution Temp	°C	N/A	N/A	N/A	N/A	21.5-34	18 - 28	18 - 32	17 - 27	18 - 32
Ambient Temp	°C	25	25	25	25	23	25.0	24.6	26.2	25
Average Temp	°C	15	5	15	10					
Difference (ΔT_m)	°F	27	9	27	18					
Pressure	mBar	50-80	40-60	40-60	45-55	60	30	42	20	20
MOH Feed Solution	g	0	0	0	0	189.0	188.04	189.0	187.5	187.6
Water Added	g	250	250	250	250	30.5	10.70	30.18	36.90	26.80
H2O2 (70%)	g	0	0	0	0	65.67	61.14	60.4	61.2	62.1
Total Load	g	250	250	250	250	285.2	259.9	279.6	285.6	276.5
Final Solution	g	187.4	241.2	170.9	216.0	276.7	231.5	264.4	268.3	258.4
Water Evaporated	g	62.6	8.8	79.1	34.0	8.5	28.4	15.2	17.3	18.1
	gmol	3.5	0.49	4.4	1.9	0.47	1.6	0.84	0.96	1.01
	wt%	25.0	3.5	31.6	13.6	3.0	10.9	5.4	6.1	6.5
Water Evap Rate	%load/s	0.0070	0.0010	0.0088	0.0038	0.0014	0.0030	0.0057	0.0059	0.0095
Heat Removed	kcal	36.0	5.1	45.5	19.7	4.9	16.6	8.8	10.1	10.6
	kcal/kgLoad	144	20.4	182	78.6	17.3	63.7	31.5	35.5	38.4
Est. Reaction Heat	kcal/mol OH						14.33	8.99	7.86	8.49
Ave. Heat Flux (qc)	BTU/h	142.9	20.3	180.6	78.0	33.5	65.7	131.2	142.1	219.7
	kcal/s	0.0100	0.0014	0.0126	0.0055	0.0023	0.0046	0.0092	0.0099	0.0154
	W	41.8	5.9	52.8	22.8	9.8	19.2	38.4	41.6	64.3
Pumping Rate @ Pres	L/min	20.23	3.7	33.2	14.3	3.0	19.9	7.6	18.2	19.0
Pumping Rate @ Amb	L/min	1.30	0.18	1.64	0.71	0.30	0.59	1.18	1.27	1.96
Base Conc. (Target)	mol/kgMHP							4.520	4.520	4.520
Adjusted								4.274	4.212	N/A
Measured								4.048	4.047	N/A
Deviation	%							-5.3	-3.9	N/A
Peroxide Conc (Target)	mol/kgMHP							4.972	4.972	4.972
Adjusted								4.701	4.633	N/A
Measured								4.397	4.345	N/A
Deviation	%							-6.5	-6.2	N/A

* All reactions shown are exothermic, i.e., heat is generated from each of these reactions.

** Heat transfer area (A) is calculated from $q = U A \Delta T_m$,
where U is the overall heat transfer coefficient (BTU/ft^2-^oF-hr)

APPENDIX D – SUPPLEMENT TO SECTION 3

3-2-1. The Jacketed Beaker System

Apparatus Setup

Figure D-1 shows a typical setup for the jacketed beaker apparatus for MHP blending. The cooling was achieved by a chiller (PolyScience, Model 1157) with Syltherm XLT (Dow Chemicals) as the coolant. Either a magnetic stirrer (shown in Figure D-1) or a blender was used to provide agitation during the mixing process.

Figure D-1. MHP Blending in a 500-ml Jacketed Beaker

Operating Procedure

Typical procedures for MHP production using the jacketed beaker apparatus are summarized below:

- Ready chemicals ($LiOH \bullet H_2O$, NaOH, KOH, and 70% H_2O_2) and beakers;
- Add the amount of water (DDI) required by a given formulation into a transfer beaker;
- Dissolve the required amount of $LiOH \bullet H_2O$ in the water while using a magnetic stirrer;
- Add the required amount of NaOH into the LiOH aqueous solution;
- Add the required amount of KOH into the LiOH and NaOH mixed solution;
- Without cooling, this mixed-base solution (MOH) can reach a temperature of about 70°C.
- Transfer this hot MOH solution into the jacketed beaker with a coolant already circulating in the jacket. The coolant temperature is set at about –5°C.
- After the temperature of the MOH solution falls below 0°C, the addition of 70% hydrogen peroxide aqueous solution begins;
- The addition of 70% hydrogen peroxide solution is quite slow to keep the solution temperature from exceeding 280 K. The blending process usually takes about one hour.

3-2-2. The Recirculation Systems

Apparatus Setup

Figures D-2A and D-2B show eight different blending apparatus configurations that were tested. The common feature of these configurations was the recirculation loop. The bulk liquid phase was pumped through either a double pipe (DP) or a concentric-tube (CT) arrangement co-currently or counter-currently relative to the LN2 and feed streams. Configurations involving LN2 sparging and fluid dispersion through nozzle sprays (NZ) were also tested. Most of these configurations were only tested under simulated conditions using water and LN2.

Figure D-2A. LN2 Injection and MHP Blending Test Configurations

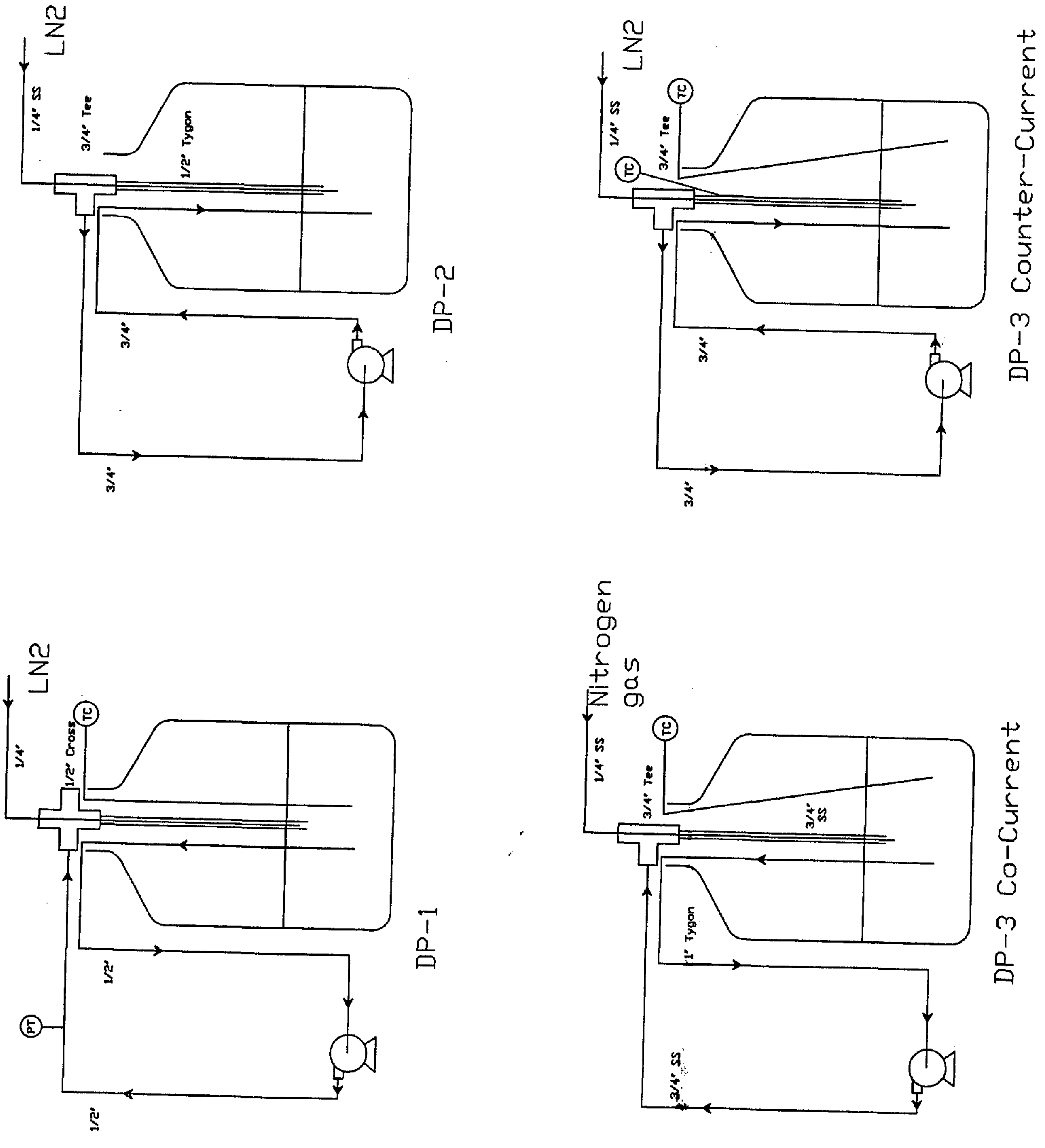
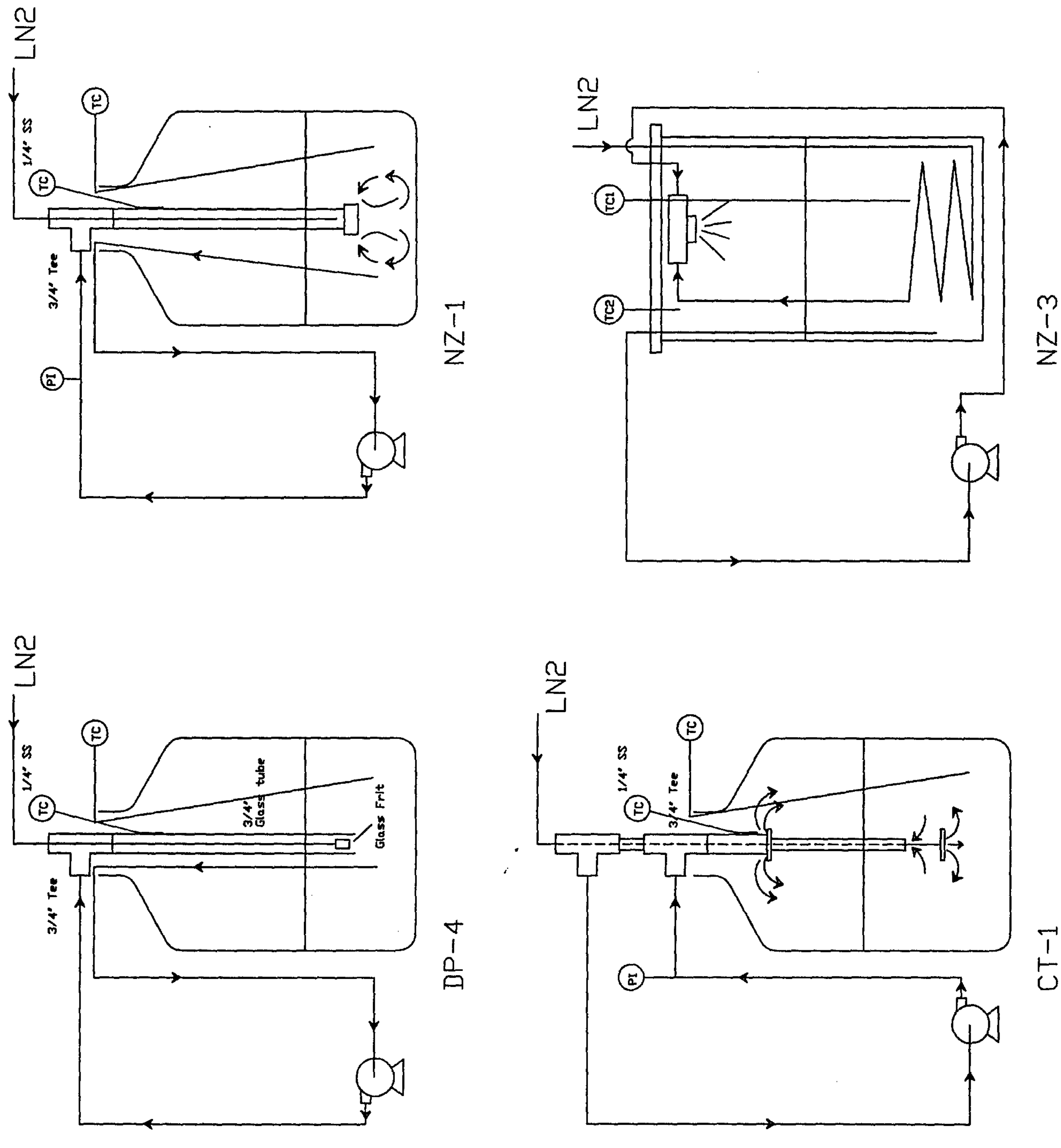


Figure D-2B. LN2 Injection and MHP Blending Test Configurations



Operating Procedures

The procedure for simulation tests using water and LN2 involved

- adding a predetermined amount of water into the blending vessel;
- starting the pump to recirculate water;
- recording the onset temperature of water;
- sparging LN2 into water; and
- recording temperature change until temperature of water drops to about 5°C.

The procedure for blending MHP using LN2 as the cooling source typically involved

- preparing an MOH solution;
- transferring the MOH solution into the blending vessel;
- starting the pump to recirculate the solution;
- sparging LN2 into the MOH to precool the solution;
- beginning peroxide addition using a peristaltic pump when temperature of the solution drops below 0°C; and
- adjusting the pumping rate of hydrogen peroxide to maintain the temperature of MHP solution below 5°C.

Test Results

Different fluid recirculation and dispersing configurations and results from testing these systems using water as the simulant and LN2 as the cooling source are summarized in Tables D-1 and D-2, respectively. Based on the data obtained from these simulation tests, the DP-3 co-current configuration was selected for MHP blending test.

3-2-3. The LN2 Spinner System

Apparatus Setup

As shown in Figure D-3, the LN2 spinner system became much simpler as compared to the recirculation systems. The system consisted of a glass blending vessel (14-liter capacity), a plastic cover, a spinner made of PFA (perfluoroalkoxy) tubing fitted through a Teflon male connector (Swagelok), and a PFA shaft connecting to the LN2 supply dewar.

Operating Procedures

Typical procedures for blending MHP using the LN2 spinner system involved

- preparing an MOH solution;
- transferring the MOH solution into the blending vessel;
- sparging LN2 into the MOH solution to precool the solution;
- adding slowly hydrogen peroxide to the MOH from the top cover near the stationary shaft using a peristaltic pump when temperature of the solution drops below 0°C,; and
- adjusting the pumping rate of hydrogen peroxide to maintain the temperature of MHP solution below 5°C.

Test Results

Initially, simulation tests were conducted using compressed air as the motive fluid and water as the liquid medium. Figures D-4A and D-4B show the static and dynamic conditions of the system setup, respectively. The mixer rotating speed and pressure head, respectively, were correlated with motive air flow rate, as shown in Figure D-5. Subsequent MHP blending tests were conducted using this blending configuration.

Table D-1. Liquid Nitrogen Injector Designs: Dimensions and Flow Characteristics

Injector	Description	Mixing		Outer Tube					Inner Tube				Annular	Equiv.	H2O	H2O	Reynolds No.	
ID#		TEE	Material	O.D.	W.T.	I.D.	L	Material	O.D.	W.T.	I.D.	l	Area	Dia.	Flowrate	Velocity		
		(in)		(in)	(in)	(in)	(in)		(in)	(in)	(in)	(in)	(in2)	(in)	(gpm)	(f/s)	(20 C)	(5 C)
DP-1		0.5	Pyrex	0.5	0.0645	0.37	15	316 SS	0.25	0.065	0.12	14.25	0.0590	0.121	0.33	1.78	1669	1192
DP-2		0.75	Pyrex	0.5	0.0645	0.37	21	316 SS	0.25	0.065	0.12	21.5	0.0590	0.121	0.74	4.02	3769	2692
DP-3		0.75	316 SS	0.75	0.065	0.62	21	316 SS	0.25	0.065	0.12	21.5	0.253	0.370	3.2	4.03	11531	8236
DP-4		0.75	Pyrex	0.75	0.065	0.62	21	316 SS	0.25	0.065	0.12	21.5	0.253	0.370	3.2	4.03	11531	8236
DP-5		0.75	316 SS	0.75	0.065	0.62	21	316 SS	0.25	0.065	0.12	21.5	0.253	0.370	3.2	4.03	11531	8236

Injector	Description	Mixing		Outer Tube					Inner Tube				Annular	Equiv.	H2O	H2O	Reynolds No.	
ID#		TEE	Material	O.D.	W.T.	I.D.	L	Material	O.D.	W.T.	I.D.	l	Area	Dia.	Flowrate	Velocity		
		(in)		(in)	(in)	(in)	(in)		(in)	(in)	(in)	(in)	(in2)	(in)	(gpm)	(f/s)	(20 C)	(5 C)
CT-1		0.75	316 SS	0.75	0.065	0.62	23	316 SS	0.25	0.065	0.12	25.75	0.253	0.370	3.2	4.03	11531	8236
		1	316 SS	1	0.065	0.87	6	316 SS	0.75	0.065	0.62	23	0.153	0.120	3.2	6.67	6192	4423
CT-1A		0.75	316 SS	0.75	0.065	0.62	23	316 SS	0.25	0.065	0.12	25.75	0.253	0.370	3.2	4.03	11531	8236
		1	316 SS	1	0.065	0.87	6	316 SS	0.75	0.065	0.62	23	0.153	0.120	3.2	6.67	6192	4423
CT-1B		0.75	316 SS	0.75	0.065	0.62	23	316 SS	0.25	0.065	0.12	24.5	0.253	0.370	3.2	4.03	11531	8236
		1	316 SS	1	0.065	0.87	6	316 SS	0.75	0.065	0.62	23	0.153	0.120	3.2	6.67	6192	4423

Injector	Description	Mixing		Outer Tube					Inner Tube				Annular	Equiv.	H2O	H2O	Reynolds No.	
ID#		TEE	Material	O.D.	W.T.	I.D.	L	Material	O.D.	W.T.	I.D.	l	Area	Dia.	Flowrate	Velocity		
		(in)		(in)	(in)	(in)	(in)		(in)	(in)	(in)	(in)	(in2)	(in)	(gpm)	(f/s)	(20 C)	(5 C)
NZ-1	Y33180-PP	0.75	Pyrex	0.75	0.065	0.62	21	316 SS	0.25	0.065	0.12	21.5	0.253	0.370	3.2	4.03	11531	8236
NZ-2	Y33180-PP	0.75	316 SS	0.75	0.065	0.62	21	316 SS	0.25	0.065	0.12	21.5	0.253	0.370	3.2	4.03	11531	8236
NZ-3	SU5	none		0.5	0.065	0.37		316 SS	0.25	0.065	0.12	21.5	0.058	0.120	0.3	1.37	1276	911

Water properties: density = 1 g/cc, viscosity = 1 cP (20 C), 1.4 cP (5 C), heat capacity = 1 cal/g C.

Table D-2. Simulation Tests of Different Blender/Injector Configurations and Sizes for Cooling Water by Liquid Nitrogen

Test	Blender	Injector	Temperature			H2O	Heat	H2O2	Heat	LN2	Cooling	Thermal	Run	Cooling	LN2	LN2/	Recirc.	Blender
Date	Configuration	ID#	Begin	End	Diff.	Load	Burden	Load	Mixing	Input	Capacity*	Eff.**	Time	Rate	Rate	H2O	Rate	Capacity
			(°C)	(°C)	(°C)	(kg)	(kJ)	(kg)	(kJ)	(kg)	(kJ/kgN2)	(%)	(min)	(°C/min)	(kg/m)	(kg/kg)	(kg/m)	(min/°C)
	Co-Current^	DP-1	15	10	5	10	209	0	0	1.05	428.8	**48.7**	7	0.71	0.15	0.105	1.3	**7.5**
	Co-Current	DP-2	20	6	14	10	585.2	0	0	2.58	1053.6	**55.5**	19	0.74	0.14	0.258	2.8	**15.6**
	Counter-Current	DP-2	20	12	8	10	334.4	0	0	1.44	588.1	**56.9**	11	0.73	0.13	0.144	2.8	**8.5**
	Co-Current	DP-3	21	5	16	10	668.8	0	0	2.56	1045.5	**64.0**	22	0.73	0.12	0.256	12	**12.7**
	Counter-Current	DP-3	19	5	14	10	585.2	0	0	2.04	833.1	**70.2**	15	0.93	0.14	0.204	12	**6.5**
	Co-Current	DP-4	21	8	13	10	543.4	0	0	2.5	1021.0	**53.2**	29	0.45	0.09	0.25	12	**26.1**
	Counter-Current	CT-1	22	5	17	10	710.6	0	0	3.4	1388.5	**51.2**	25	0.68	0.14	0.34	12	**24.4**
	Counter-Current	CT-1A	21	5	16	10	668.8	0	0	2.74	1119.0	**59.8**	14	1.14	0.20	0.274	12	**9.6**
	Counter-Current	CT-1B	23	8	15	10	627	0	0	2.64	1078.1	**58.2**	19	0.79	0.14	0.264	12	**14.0**
	Co-Current	NZ-1	22	5	17	10	710.6	0	0	2.86	1168.0	**60.8**	23	0.74	0.12	0.286	12	**15.2**
	Co-Current	NZ-2	21	9	12	10	501.6	0	0	2.24	914.8	**54.8**	20	0.60	0.11	0.224	12	**16.9**
	Parallel^	NZ-3	20	5	15	7	438.9	0	0	1.98	808.6	**54.3**	15	1.00	0.13	0.283	~1	**12.9**
	Co-Current^^	DP-3	19	-9	28	10	1170.4	1.582	1653	9.16	3740.8	**75.5**	50	0.56	0.18	0.916	12	**40.1**
7/8/99	Direct Mix	10-kg	8	4	4	10	167.2	1.582	1653	8	3267.1	**55.7**	67	0.06	0.12	0.8	0	**593.4**
7/7/99	Direct Mix	10-kg	24	4	20	7	585.2	0	0	2.5	1021.0	**57.3**	6	3.33	0.42	0.357	0	**4.6**
11/2/99	Direct Mix	100-kg	21	6	15	58.7	3678.5	0	0	11.5	4696.4	**78.3**	35	0.43	0.33	1.643	0	**83.1**
2/28/00	Rotary Mixer	1-kg	22	-3.7	26	0.55	59.084	0	0	2.3	939.3	**6.3**	23	1.12	0.10	0.329	0	**27.6**

* Cooling Capacity = Weight LN2 x Unit Cooling Capacity of LN2

Unit Cooling Capacity of LN2 = Heat of Evaporation + Heat Capacity x 200C = 408 kJ/kg LN2

** Thermal Efficiency = 100 x (Heat Released by Water+Heat of Mixing)/Cooling Capacity of LN2

Blender Capacity = (kgLN2/kgH2O)x(100-Thermal Eff.(%))/Cooling Rate (Note: Smaller BC's = Better Blenders)

^ Vanton pump was used for recirculating water; Moyno pump (Model 332) was used for all other tests.

^^ The glass bottle (Pyrex) was submerged in ice bath, piping and pump were not insulated

In all other tests, the glass bottle, piping, and pump were not insulated (water condensation on these surfaces was visible during tests).

1. Cp (water) = 1 cal/g C, Cp (N2 gas) = 0.25 cal/g C, heat of evaporation of N2 = 47.7 cal/g, density of LN2 (1 atm, 70K) = 0.841 g/cc

DP - double pipe; CT - concentric-tube (multiple tubes); NZ - nozzle

Co-/counter-current - LN2 is vaporized by recirclating water; Parallel - LN2 is vaporized thru a coil in the tank; LN2 line - 1/4"O.D.x0.065 316SS tubing

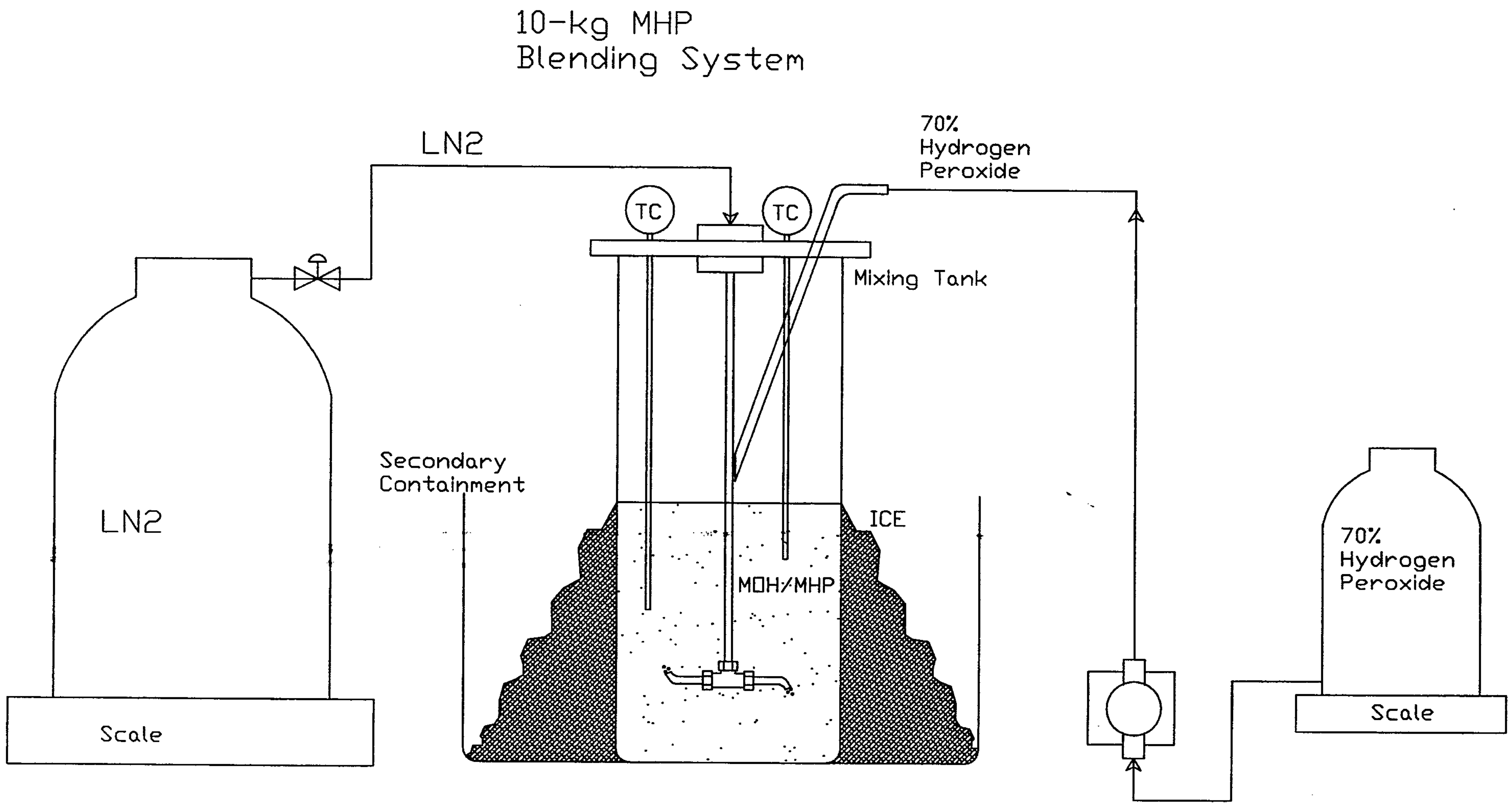


Figure D-3. LN2 Spinner System Schemtic

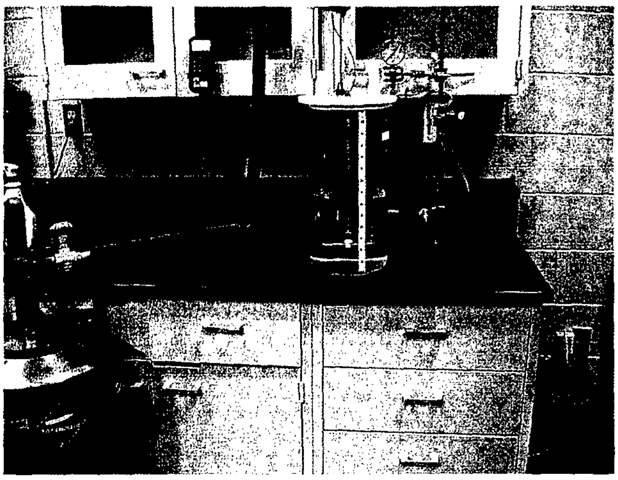


Figure D-4A. LN2 Spinner Test Setup

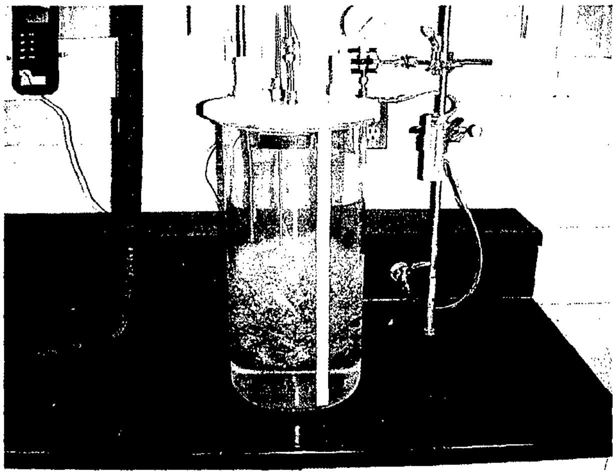


Figure D-4B. LN2 Spinner in Motion

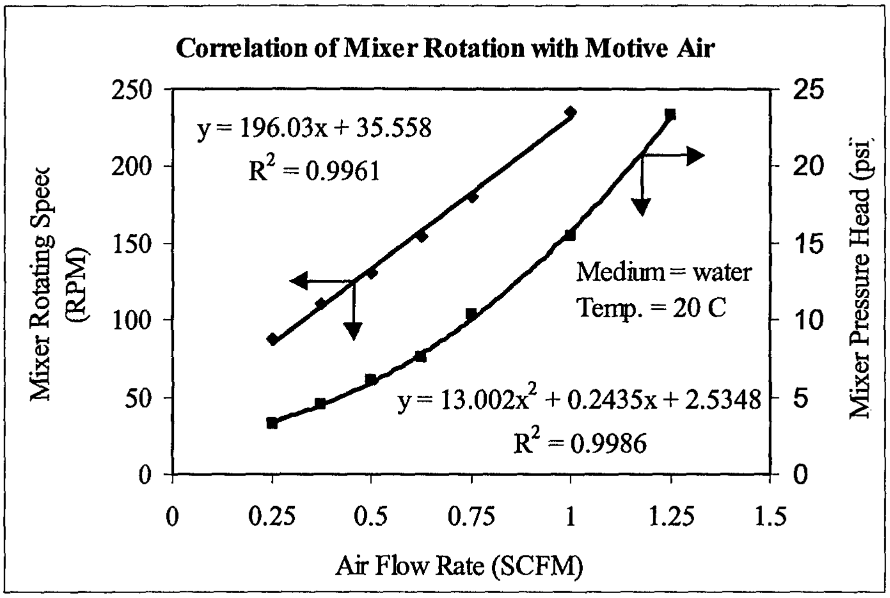


Figure D-5. Correlation of Spinner Rotation with Motive Air Flow Rate

3-2-4. The Rotary System

<u>Apparatus Setup</u>

The idea behind this system was to enhance mixing by the rotary movement of the vessel in addition to the turbulence created by the boiling LN2. The rotary system was designed to accommodate a 1000-ml flask or a 14-Liter glass vessel as the MHP blending vessel. The blending vessel was mounted on a holder connected to a slow-speed motor (about 30 RPM). The rotating shaft was 45° above the horizontal. The tip of a stationary bundle consisting of a feed line for hydrogen peroxide, a feed line for LN2, and a thermocouple was extended into the blending vessel. Typical procedures of using this system involved:

- loading an MOH solution;
- starting the motor to rotate the blending vessel;
- injecting LN2 to pre-cool the MOH solution; and
- adding H_2O_2 solution.

IR Imaging Demonstration Tests

On 14 April 2000, a demonstration test was conducted to evaluate the feasibility of using an IR camera to study temperature distribution and imaging of the solution during the MHP blending process. A 5-kg batch of MHP was made while the IR imaging of the top surface of the solution was recorded by a camera pointed through the open top of the blending vessel. The setup for a 1-kg batch test is shown in Figure D-6. The setup for a 10-kg batch test equipped with an IR camera is shown in Figure D-7.

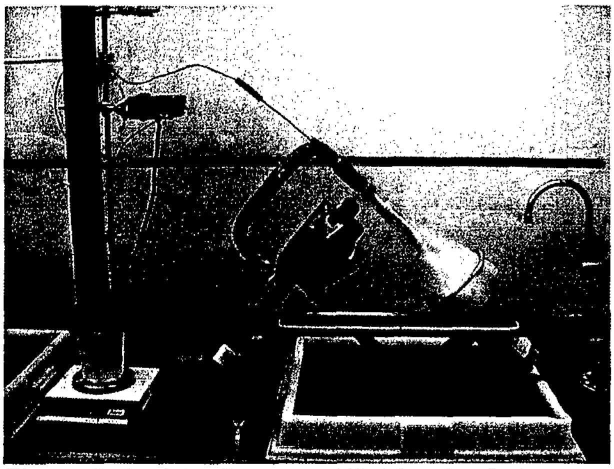


Figure D-6. 1-kg Rotary MHP Blender Setup

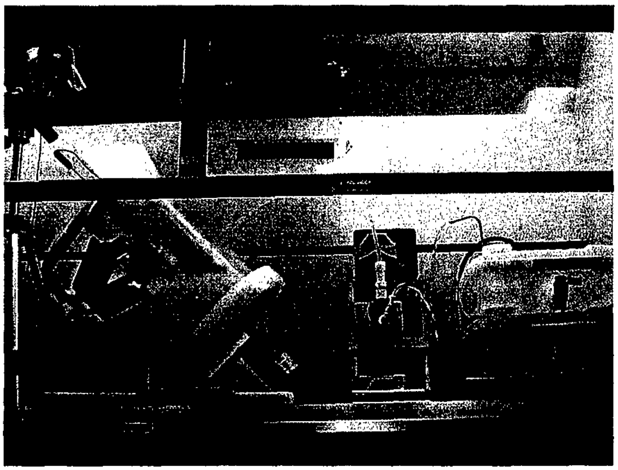


Figure D-7. 10-kg Rotary MHP Blender Setup Equipped with an IR Camera

APPENDIX E – 1ST GENERATION OF 100-KG BATCH LN2 SYSTEM

A system for making 100-kg of MHP was the next step in the incremental scale up of rapid MHP production systems. Prior to making this system, the capability of making 1-kg and 10-kg batches had already been demonstrated in the lab. The previous systems were based on spinning the mixing vessel while adding the ingredients to water and bubbling in liquid nitrogen to cool the mixture. Previous work had shown that dissolving the solid bases prior to adding peroxide was an important step in the mixing process and using liquid nitrogen as the cooling media significantly reduced the mixing time. Cooling the base solution was not necessary at the 1-kg and 10-kg scale since the rate of liquid nitrogen addition to the mixing vessel, relative to the size of the batch, was fast. The cooling time for the base solution was just a few minutes. Another reason this step was not done was the amount of liquid nitrogen used relative to the amount of liquid nitrogen available was small.

Equipment

As shown in Figure E-1 (schematic) and Figure E-2 (photo), the 100-kg MHP Blending System consisted of four subsystems:

- MHP blending tank;
- liquefied nitrogen (LN2) supply;
- 70% hydrogen peroxide supply; and
- dry air or nitrogen supply.

The MHP blending tank is a 55-gallon, high-density polyethylene (HDPE) tank installed in horizontal position. The tank has a 12-in by 20-in rectangular opening at the top to interface with the supply manifold, which is equipped with six rotating mixers driven by evaporating nitrogen.

The LN2 is supplied by a LN2 dewar, which is linked to the MHP blending tank by a piece of ¼-in O.D. x 0.049-in Stainless Steel tubing with polyurethane tube insulation. The weight of the LN2 dewar is monitored by an electronic scale. At the supply manifold, LN2 is distributed into the six rotating mixers.

The 70% hydrogen peroxide aqueous solution is delivered from the H_2O_2 tank to the MHP blending tank by an electronically controlled, diaphragm pump. The H_2O_2 supply is distributed to six unrestraint outlets, one for each rotating mixer. The outlets are individually attached to the rotating mixers. The weight of the H_2O_2 tank is monitored by an electronic scale to calculate the flow rate of H_2O_2.

The control of LN2 flow is achieved by injecting a stream of dry air/nitrogen into the LN2 line at the inlet of the supply manifold. The compressed air (60 psi) passes through a water filter, a carbon dioxide filter, an electronic control valve, a pressure transducer, a flow meter, and a check valve prior to connecting to the LN2 line.

Control System

The 100-kg MHP Production System is equipped with a PC computer for process control, monitoring and data logging. Lookout™ control software and Fieldpoint interface hardware, manufactured by National Instruments (Austin, TX), were used. The Fieldpoint interface had the following capabilities: 8 analog input channels; 8 analog output channels; 8 discrete input channels; 8 discrete output channels; and 8 thermocouple channels.

The computer readable devices include: LN2 Tank Scale; thermocouples; and air flow rate.

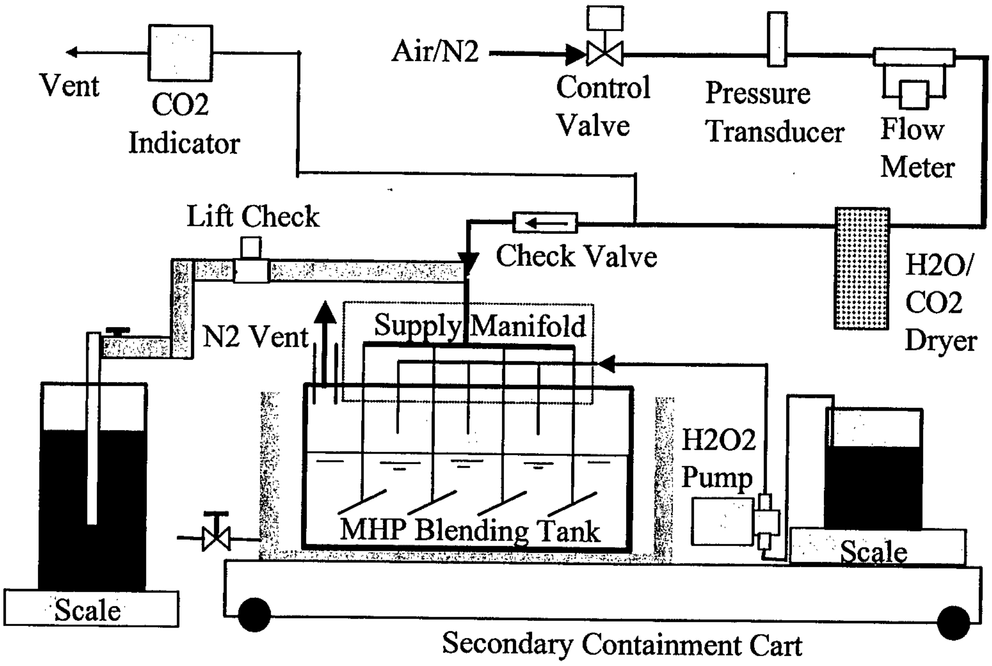


Figure E-1. 1^{st} Generation 100-kg MHP Production System Schematic

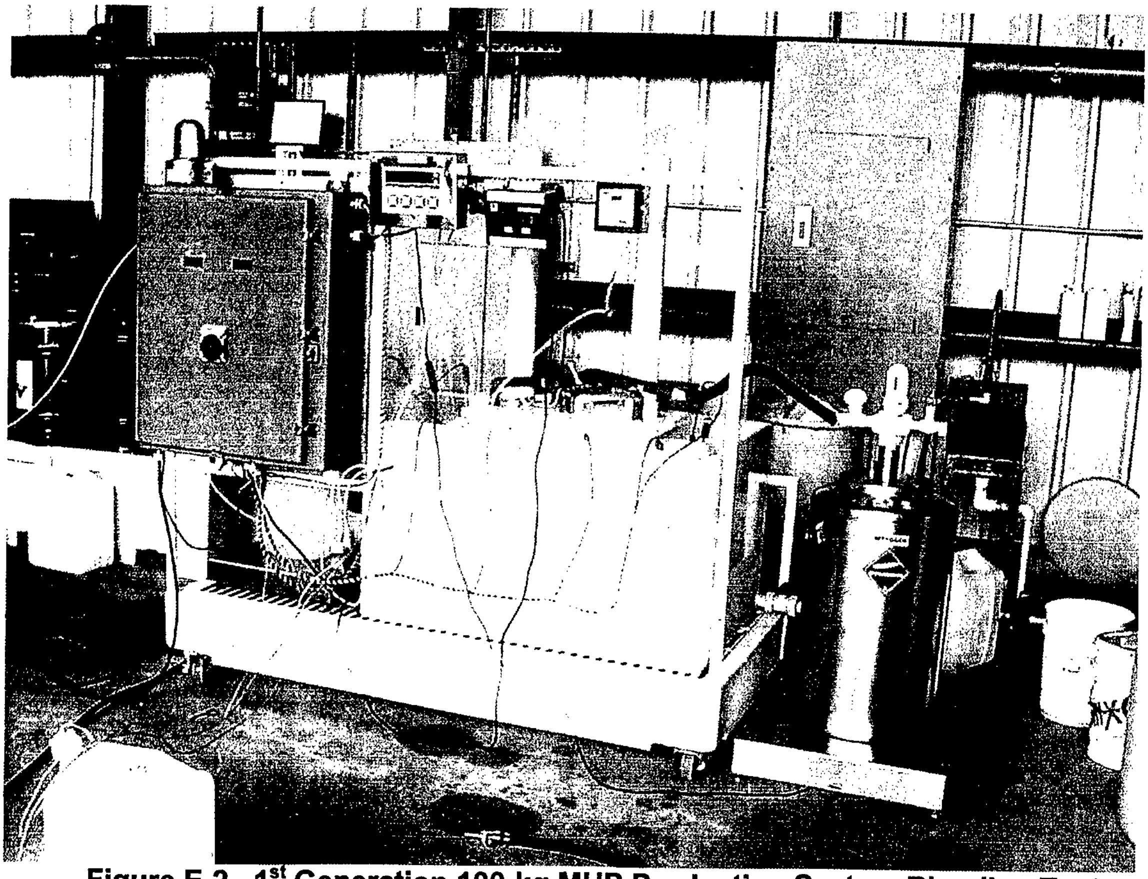


Figure E-2. 1^{st} Generation 100-kg MHP Production System Blending Test

The computer controllable devices include: air flow control valve; and hydrogen peroxide pump on/off and flow rate adjustment.

The minimum required features for a PC computer to utilize the control package are as follows: 486-DX; PCI bus; Window 95, 98, or NT operating system; 90 MHz; 32 MB ram memory; and 120 MB hard disk drive.

The process diagram, displayed on the computer screen (Figure E-3), allows the operator to perform real time process control and monitoring. Key process parameters, such as temperature, flow rate, batch weight are displayed and logged. The computer also signals alarm conditions.

Operating Procedure

Procedure for Operating the 1st Generation 100-kg MHP Blending System is highlighted below:

1. Prepare MOH solution in the blending tank
2. Load H_2O_2 solution (70 wt%) in the feed tank
3. Fill the LN2 dewar
4. Connect electrical power supply (plug the cord into 120VAC 60Hz power source)
5. Connect compressed air supply
6. Connect communication cables
7. Turn on the main power switch at the local control panel
   Note: The red light on top of the local control panel should begin to flash
8. Press the power button on the H_2O_2 scale to power up the display
   Note: The display for LN2 dewar will be on as soon as the main power switch is on.
9. Verify the both LN2 and H_2O_2 scales display <u>kg</u> units.
10. Zero-out both scales with <u>nothing</u> on them.
11. Place the H_2O_2 solution on the H_2O_2 scale and the LN2 container on the LN2 scale. Attach the appropriate hoses/fittings.
12. Verify the switch on the front of the H_2O_2 pump is on and in the <u>clockwise</u> rotation direction. The switch on the back of the pump should be in <u>external</u> control mode.
13. Verify both scales are reading full product weight (non-zeroed).
14. Turn on the computer
15. Launch Lookout
16. Open the program file: mhp-203.lkp
17. Make sure the main switch (at upper left corner of the screen) indicates "STOP"
18. Verify the thermocouples in the blending tank all read approximately the same temperature and that these readings agree with the temperature indicators on the local control panel.
19. Press "Initialize - scales" a couple of times.
    Note: This establishes communication with the two scales, i.e., receiving weight data from the scales. This procedure stores these initial weights so that they may be totalized later and also resets key internal parameters.
20. Enter the H_2O_2 concentration (the assay value for the specific batch).
21. Make sure there is enough H_2O_2 and LN2 to complete the blending test.
22. Decide on manual or automatic control of the air valve and the H_2O_2 pump.
    Note: Manual mode gives complete control to the user through the use of the slider bars. Automatic mode attempts to control everything with built in algorithms. Move the two switches to the appropriate positions: Manual-Off-Auto.

23. Make sure the LN2 E-Stop switch is (off) down.
    Note: When this switch is activated in automatic mode while running, the air valve will fully open, effectively shutting off the LN2 flow.
24. Fully open the LN2 hand valve to introduce the LN2 into the blending tank.
25. Move the main switch of the control panel to "START".
    Note: The control system is now activated. If in automatic mode: A regulated flow of LN2 cools the blending mixture. When the temperature of the mixture becomes -1°C H_2O_2 will start to be added. (The H_2O_2 pump will need to be placed in manual mode and primed before this point. Immediately put pump back in automatic mode. Pump speed will continuously be optimized to reduce the amount of LN2 used. When the correct mass of H_2O_2 has been added (determined from H_2O_2 concentration) the H_2O_2 pump will stop. The LN2 will continue with its cooling and stirring until the hand valve at the LN2 dewar is shut off. If the mixture gets colder than -5°C the air valve will be turned on, reducing the LN2 flow. If at any time the mixture gets warmer than 4°C the H_2O_2 pump will cut off until the mixture cools back down.
26. After the H_2O_2 has been successfully added to the mixture, the LN2 hand valve should be closed. **Note**: To continue stirring without the use of the LN2, Flip the LN2 E-Stop switch up while in automatic mode.
27. To shut the air off (flip the LN2 E-Stop switch down).
28. Turn the air valve and H_2O_2 pump mode selector switches to "Off".
29. Flip the main switch of the control panel to "STOP".
30. Data have been saved to c:\lookout\day\100-kg MHP Batch.csv

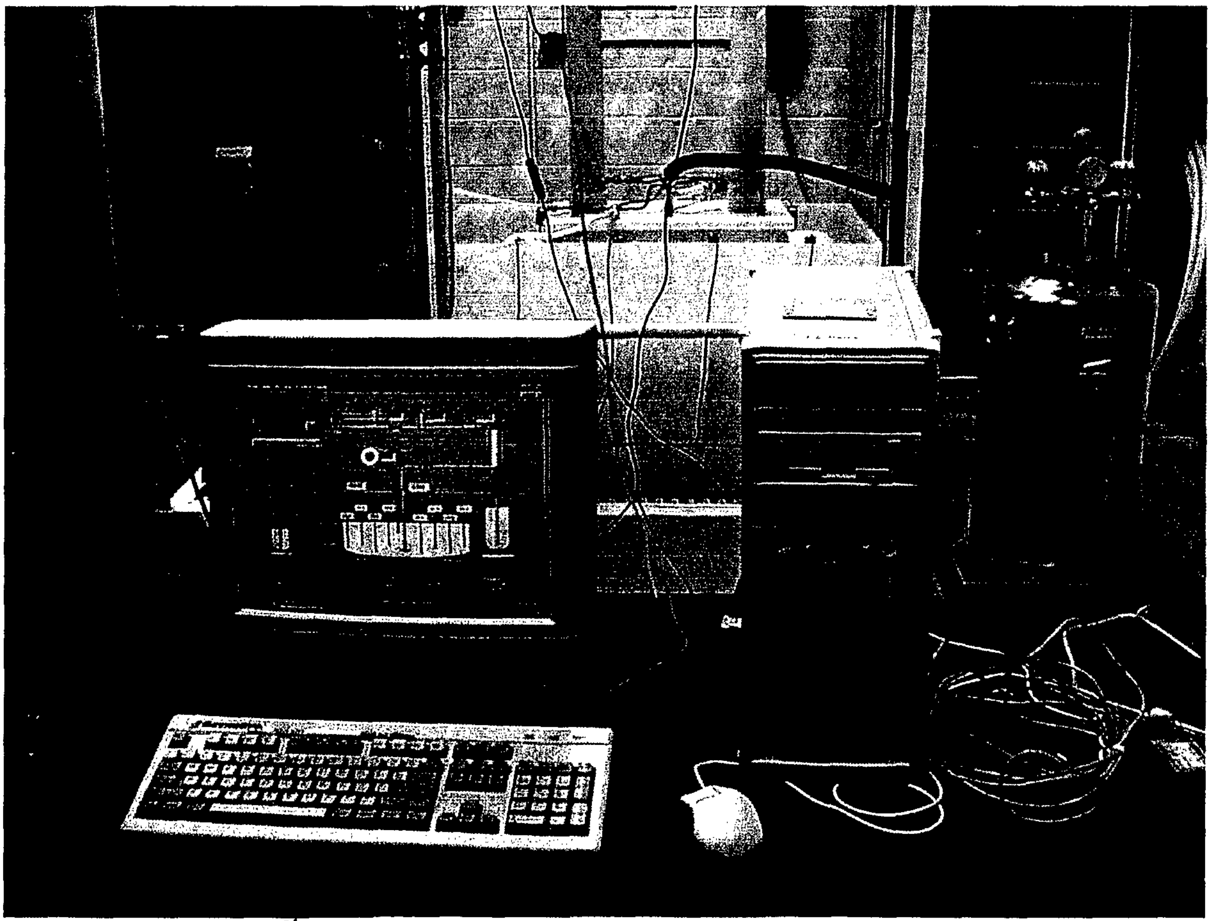


Figure E-3. 1st Generation 100-kg MHP Production System Control Panel

APPENDIX F – 2ND GENERATION OF 100-KG BATCH LN2 SYSTEM

Introduction:

To meet the process requirement of producing a 100-kg batch of MHP in less than an hour while maintaining MHP temperature below 0°C during and after the peroxide addition, several major changes in hardware design were made in the 2nd-generation 100-kg batch system to improve the processing capabilities in terms of LN2 flow rate control, base solution flow rate control, hydrogen peroxide flow rate control, and temperature control (mixing mechanism). These features were also needed to explore the effect of ingredient addition sequence on MHP production. The reactor vessel was made of a vertical stainless steel dewar fitted with a 0.5 mm-thick food-grade PVC liner. The vessel was placed on a platform scale, and the weight change of the vessel due to the addition of feed solution was monitored by a computer. A mechanical stirrer was used and mounted on a steel frame not in touch with the reactor vessel. LN2 was introduced through a sparger ring placed at the bottom of the vessel. The feed system consisted of three diaphragm pumps (one for hydrogen peroxide and two for base solutions) whose flow rates were controlled by the computer.

The system was used to evaluate effective means to control the MHP production process. Experimental data indicated that one of the most important process control parameters for the LN2-based system was the LN2 injection rate. If the flow rate of LN2 was too slow, the cooling rate would be limited, whereas if the flow rate of LN2 was too fast, there may not be sufficient time to achieve adequate mixing and LN2 could blow the MHP out of the mixing tank. Since the MHP production time can be decreased by (1) increasing the rate of coolant input, and (2) increasing the rate of ingredient input, a cascade control scheme using the flow rate of LN2 to control the peroxide/base flow rate and therefore the temperature of MHP was adopted.

During and after the addition of peroxide these two things are connected, but before the peroxide enters the mixture the rate of ingredient addition is a function of pumping speed. Setting the order of addition of ingredients can help increase the rate of pumping. Knowing the addition order allows the designer to size the pumps and piping to achieve maximum flow rate. Adding more than one chemical at a time would also decrease the overall MHP production time. This would require the independent measurement of each ingredient using separate scales. The temperature control scheme could use the flow rate of LN2 and the flow rate of the ingredient being added to queue the pump for an additional ingredient stream. Once the LN2 flow and batch temperature has reached some minimal value and the ingredient being added has reached some maximum flow rate, the next ingredient could be initiated. At this point the temperature control would primarily go to the LN2 flow then to the flow rate of the new ingredient addition. The flow rate of the ingredient that was being added would remain at the maximum level until that the addition had been completed. This would allow more than one ingredient to be added at a time and decrease the amount of time required to mix the MHP.

General Process Description:

The general concept for the process is to dissolve the solid caustics in water. The caustic solutions can then be dispensed into the mixing tank based on mass. The peroxide is also dispensed by mass into the mixing tank. A computer, to keep the temperature of the mixture from climbing above zero, controls the flows of the ingredients. The computer also controls the amount of each ingredient added. The ingredients are mixed in a tank that is continuously being sparged with liquid nitrogen and mixed with an agitator. Figure F-1 shows the process and instrumentation diagram (P&ID) of this system. Table F-1 provides the description, materials of construction and comments for each piece of the equipment in this system.

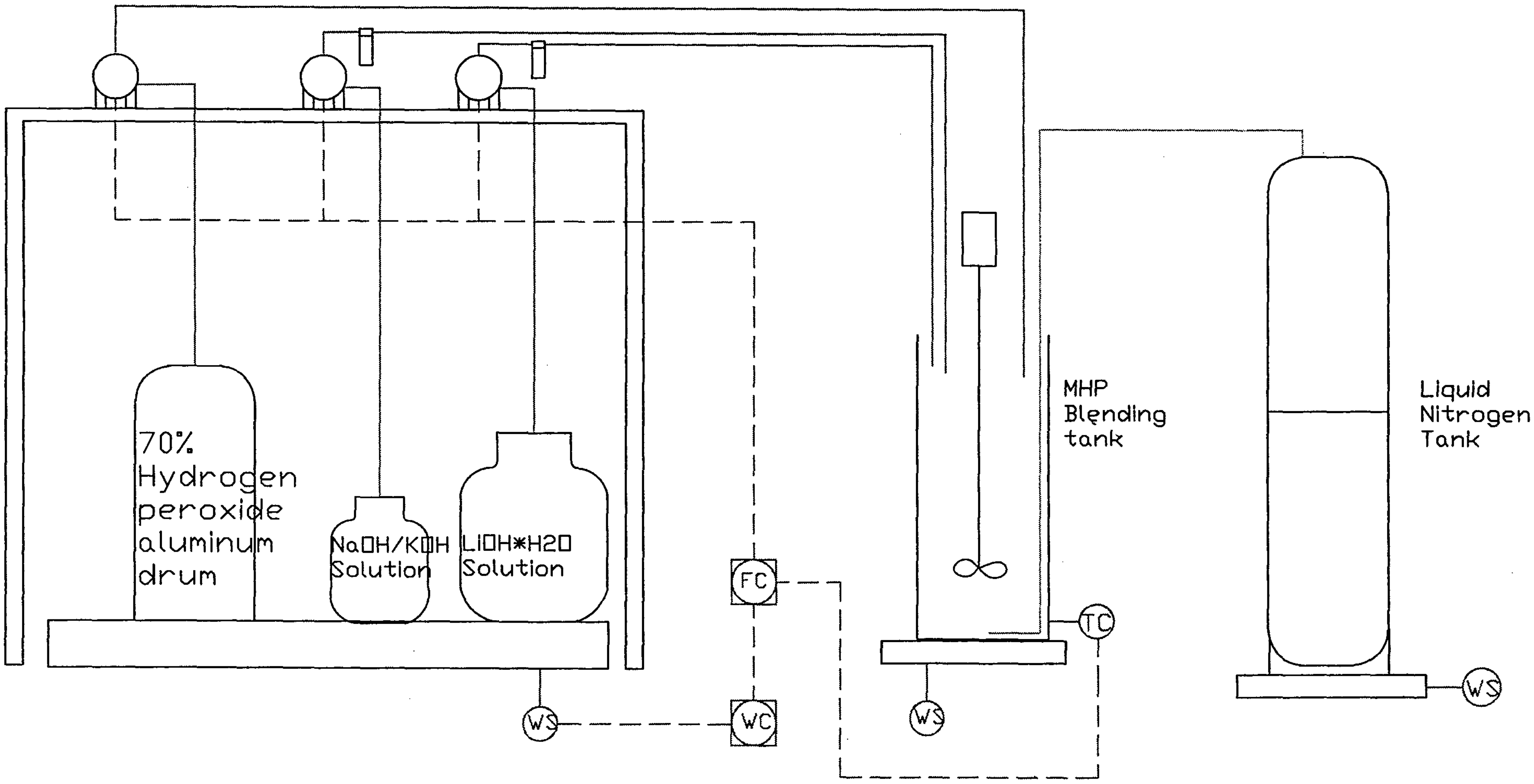


Figure F-1. 2^{nd} Generation 100-kg MHP Production System P&ID

Table F-1. List of Component Materials for 2nd Generation 100-kg MHP System

100-kg MHP production system			
Equipment	**Description**	**Material of Construction**	**Comment**
Caustic and Peroxide scale	36" X 36" Platform scale with a 1000 lb capacity	Stainless steel	This scale was purchased based on price and availability
Peroxide Drum	30-gallon drum	Aluminum 1060	These drums are specially designed for Concentrated peroxide storage.
Lithium hydroxide solution container	12 gallon Carboy container	Polypropylene	The volume of solution needed depends on the recipe being used.
Sodium/Potassium Hydroxide solution container	5 gallon Carboy container	Polypropylene	The volume of solution needed depends on the recipe being used.
Caustic tubing	1/2" OD	Extruded Polypropylene	This tubing was specially made for the caustic metering pumps.
Peroxide Tubing	1/2" OD	Extruded PFA	Material was specifically chosen for use with concentrated peroxide.
Caustic Metering pumps	LMI Milton Roy diaphragm pump	PVC and Teflon	Pumps about 25 gph, materials of construction based on chemical compatibility and price
Peroxide metering pump	LMI Milton Roy diaphragm pump	Stainless steel and Teflon	Pumps about 25 gph, materials of construction based on chemical compatibility with 70% H_2O_2
Caustic filters	Standard water filters	Polypropylene / Buna N Seals	Filter cartridges are sub micron rated for removing particles from drinking water
Tank Lid	In house fabrication	Polyethylene	Purchased in sheets and cut to fit
MHP tank	50 Gallon Pope Cryogenic Dewar	Stainless steel	Purchased for insulation and high height to diameter ratio.
Agitator	~1hp, 10-30 rpm, 6 inch Diameter Impeller	Shaft and Impeller Teflon coated Stainless Steel	Sized to provide the best top to bottom mixing in a tank with no baffles.
MHP Tank Liner	Bag that fit into the tank	PVC	This was purchased to protect the MHP from contamination from the stainless steel.
Liquid Nitrogen sparger	In house fabrication	PFA	Design to evenly distribute liquid nitrogen in the bottom of the tank
Thermal couples	E Type	Teflon coated	Material chosen for chemical compatibility

Equipment:

The equipment for the process can be grouped into several systems. These systems include: a caustic dilution system, a caustic and peroxide delivery system, a mixing system, a liquid nitrogen delivery system, and a computer control system.

Caustic Dilution System:

The system was setup based on dissolving the solid caustic in water prior making the MHP. The solid caustics were dissolved into two separate solutions. One solution was an 18.5% $LiOH \bullet H_2O$ (10.6% LiOH). This concentration was chosen because it is close to the solubility limit of LiOH in water. The second caustic solution was a mixture of NaOH and KOH. The amount of water in the second solution was determined by taking the total amount of water in the formulation and subtracting out the amount of water in the LiOH solution, the 70% hydrogen peroxide and the water in the solid KOH (usually contains 10% water). The KOH and NaOH was dissolved in this amount of water. The size of the containers for the caustic solutions was determined by the MHP recipe to be made. The particular formulation used for making the 100-kg batches of MHP required about 12 gallons of the LiOH solution. The NaOH/KOH solution to be used was around 5 gallons.

Caustic and Peroxide Delivery System:

In order to dispense each of the caustic solutions and the peroxide, each solution container was placed on a scale and the suction line for the pump for that solution entered the container through the top and just reached the bottom of the container. The discharge from the base pumps pass through a filter and then into the MHP mixing tank. The peroxide pump does not have a filter on it for safety reasons. Filters in peroxide lines have a tendency to concentrate impurities. This increases the possibility of the peroxide decomposing rapidly and causing the filter housing to rapidly disassemble.

The pumps used in the process are diaphragm metering pumps. These pumps were designed to have a variable flow rate. The max flow rate of each pump is reported by the manufacturer to be ½ gal/min. However, independent tests on each pump showed that the real max flow rate was closer to 1 gal/min. The ½ gal/min flow rate was set as a design criteria for the 100-kg system in order to be able to satisfy the requirements for the system. The pumps for the base solutions are identical. The wetted material for these pumps is PVC and Teflon®. These materials were chosen for their inertness with all caustic solutions. The peroxide pump is constructed primarily of stainless steel and ceramic. This set of materials was what the pump manufacturer recommended for use with 70% H_2O_2. Before this pump could be used to pump H_2O_2, the metal parts had to be passivated. The passivation procedure followed was from the Solvay Interox brochure on safe hydrogen peroxide handling (www.ee.surrey.ac.uk/SSC/H2O2CONF/mjeff.htm).

The filters used in the system where selected based on the size of the filter, cost, and availability. The size the filter needed to be was based on the desired flow through the filter and the size of the tubing to be connected to the filter. There was no other specification for choosing the filters.

The tubing used was ½ O.D.. The tubing for the base solutions was a special type distributed by the pump manufacturer. This is the only tubing that will work with the fittings on the pumps. The tubing for the peroxide line is made of PFA.

Mixing System:

The MHP mixing tank purchased for this system is 21" in diameter and around 48" tall. The tank is a right circular cylinder made of stainless steel and open at one end. For insulation the tank is double walled with vacuum and aluminum insulation in the space between the walls. The tank is a large cryogenic dewar. The tank is much larger than needed to make 21 gallons of MHP and the height is over twice as large as the diameter. This shape was chosen because the original design for the system was to rotate this tank while it set at an angle. The actual dimensions for the tank are not important except it needs to hold 100-kg of MHP and not splash out MHP when the liquid nitrogen is supplied. Even this tall tank requires a lid to keep MHP from splashing out of the tank. To ensure that the stainless steel did not contaminate the MHP without passivating, a PVC bag was put in the tank. This bag acts as a coating over the stainless steel. No batches were made without a coating on the stainless steel.

The lid for the mixing tank is constructed of thick polyethylene plates cut to fit the top of the tank. The lid was made circular with a quarter section cut out (see Figure F-2).

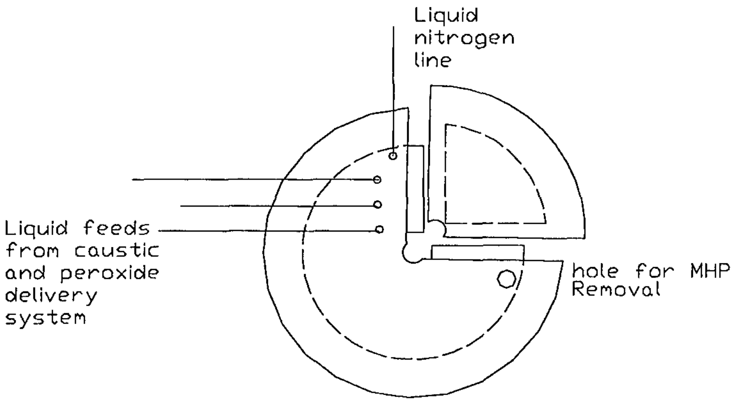


Figure F-2. 2nd Generation 100-kg MHP Production Vessel Cover

The quarter section was made to be removable so that the operator can access the inside of the tank. In the large section (the stationary section) there are holes for each of the base solutions, the peroxide line, the liquid nitrogen feed, a hole for inserting a pipe to suck the MHP out of the tank, and a hole in the center for the agitator shaft. The holes cut for the caustic and peroxide where drilled so that the ½" tubing just fit through the holes. This was enough to secure the tubing and keep it from coming out during the addition of the caustics and peroxide. The hole for the liquid nitrogen line was made for a bulkhead fitting for ½" tubing. The hole for the agitator was made about twice the diameter of the agitator shaft so the shaft could move while turning and not interfere with the lid.

The agitator for the 100-kg system was picked based on the tank that was already chosen. The impeller used was chosen to induce as much top to bottom flow within the fluid as possible. This required a small diameter (about 6") paddle type impeller since the tank has no baffles. The speed of the agitator was also set to maximize top to bottom flow in a tank without creating a vortex in a tank with no baffles. To meet these criteria the agitator speed was set to be 10-30 rpm. The slow speed increased the possibility of top to bottom flow without creating a vortex in the liquid. The motor for this agitator was sized based on the impeller size and speed. The diameter of the agitator shaft had to be abnormally large due to the length of shaft that was required to reach the desired depth of liquid in the given tank. The manufacturer of the shaft determined its diameter. The shaft and impeller are coated with Teflon.

The agitator is supported over the tank by a custom-built agitator stand. This stand is constructed of 2-inch tubular steel and can be bolted to the ground when the system is in operation. The agitator stand also is a base for the metering pumps that feed caustic and peroxide to the mixing tank.

Liquid Nitrogen Delivery System:

The liquid nitrogen was supplied from a 120 liter dewar. This was rented from a local gas supplier. On the dewar there are two valves, one valve is for getting nitrogen gas out of the dewar and the other valve is for getting liquid nitrogen. Insulated flexible 5/8" stainless steel tubing was connected the liquid nitrogen valve on the dewar. The other end of the tubing was secured to the bulkhead fitting installed in the lid of the MHP tank.

To deliver liquid nitrogen to the bottom of the MHP tank a pipe with a sparge ring attached was built to fit the tank. One end of the pipe was attached to the bulkhead fitting that was put in the lid. At the other end of the pipe a piece of ½" tubing was attached that made a circle that had an outside diameter that was just smaller than the inside diameter of the MHP tank. The length of pipe this tubing was attached to was long enough so that the tubing ring rested on the bottom of the tank. Small holes were drilled in this tubing so that the liquid nitrogen would be directed up and towards the center of the tank. The holes in the tubing were 0.100" in diameter. Holes smaller than this tended to create too much resistance to liquid nitrogen flow. When holes smaller than this were tested the liquid nitrogen flow was much to slow to meet the mixing requirements for the system. With holes larger than 0.100" the liquid nitrogen flow could be controlled manually from the liquid nitrogen supply. About 2 kg/min of liquid nitrogen is needed to counter the heat generated from mixing the peroxide and base together in the 100-kg system. To control the liquid nitrogen flow the valve on the liquid nitrogen dewar was manually adjusted.

Computer Control System

The computer control system has several components to it. These components can be split into three categories: (1) computer software, (2) computer hardware, and (3) control instruments.

The computer software in this case is Lookout™. National instruments produces and distributes this software. This software can be used to perform process control from the computer or can be used as a man machine interface (MMI) between the operator and a programmable logic controller (PLC). For the 100-kg system this software was used to perform the process control from a desktop computer (a laptop could be used as well). A graphical user interface (GUI) was made on the operators' screen of the software. This screen had a graphical depiction of the 100-kg equipment and text boxes to display information being reported to the computer from the monitoring instruments (thermocouples and scales) and the information the computer was sending to the control equipment (the metering pumps). This combination of graphics and information allows the operator monitor the system, where it is in the mixing process, what the temperature is and if the system is adding in the correct amounts of each ingredient. Through the GUI the operator can monitor the process or interact with it to stop, start, or change pump speeds. The operator can also run the process in automatic or manual modes.

The computer hardware consists of a desktop computer, or laptop, and distributed input/output (I/O) hardware. The specification for the computer was determined by the software being used on it. The distributed I/O equipment chosen was FieldPoint, also a product of National Instruments. FieldPoint consist of a communication module, and tract that other modules can be connected to it. The modules used with FieldPoint depend on the type of inputs and outputs that will be needed to control and monitor the field instruments. In the system being described an analog input, an analog output, and a thermocouple module was used.

The control instruments consisted of thermocouples, pumps and scales. Two thermocouples monitored the temperature in the mixing tank. One thermocouple was made to reach the bottom of the mixing tank and the other was made long enough to reach to a level that would be the middle of a finished batch of MHP. The caustic and peroxide pumps have the option of being controlled manually or with a 4-20 mA output signal from the FieldPoint analog output module. A switch on the back of the pumps allowed the control mechanism to be switched. Two scales where used in this system. One scale monitored the weights of the caustic and peroxide, the other scale was used to monitor the weight of the LN2 dewar.

The monitoring and control scheme used in this system was to add the proper weights of each ingredient (one at a time), while monitoring the temperature of the mixture. If the temperature approached a set temperature the flow of the ingredient would be decreased incrementally until the temperature began to fall or the pumping stopped. The liquid nitrogen flow was constant so if the pumping stopped the temperature would drop relatively fast, and the pumping would resume. Once the predetermined weight of the ingredient had been added the pump would stop and the next pump would come on. The same process would repeat until all ingredients where added. The agitator for the system is manually operated.

Procedure for MHP Production

Prior to making a batch of MHP all equipment was cleaned thoroughly with De-ionized water. Particular care was taken in cleaning the pump and tubing for transfering 70% peroxide. The tank and the liquid nitrogen line inside the tank were also cleaned very well. The caustic lines and pumps were rinsed and the filters where taken apart and washed thoroughly.

The day before a batch was to be made, the caustic solutions were made. When making the sodium hydroxide/ potassium hydroxide solution a great deal of heat is released. The final temperature of the solution is dependent on the final concentration of the mixture. Making the caustic solutions up the day before allowed the sodium hydroxide/potassium hydroxide solution to cool back to near room temperature overnight. This practice reduces the total amount of liquid nitrogen needed by around 25%. Once the lithium hydroxide solution was made it was transferred into the lithium hydroxide feed container. After the sodium hydroxide/potassium hydroxide set overnight and cooled to room temperature it was transferred to the sodium hydroxide/potassium hydroxide feed container for the system. After the caustic solutions were put into their containers they were put in position on the scale under their respective pump. At this time the hydrogen peroxide drum was also moved into place on the scale. The dip tubes from the suction side of each pump were placed in the appropriate container and connected to the suction side of the pumps. Great care is taken not to get any dirt or other contamination in the 70% peroxide drum.

The liquid nitrogen dewar was moved onto the scale for monitoring its weight. The stainless steel flexible tubing was attached to the liquid withdrawal valve on the nitrogen dewar and to the bulkhead fitting in the top of the mixing tank. Once all of the connections into the mixing tank are made, the quarter piece of the lid can be put into place.

A communication line from the I/O communication module to the computer is connected and the first chemical addition can begin. Some testing has been done on the order of ingredient addition. However, no data exist supporting one particular addition sequence over another. One factor that should be a concern in this area is that when sodium hydroxide is added before the peroxide the solution tends to turn into a thick viscous fluid with needle shaped particles. This effect goes away after a certain amount of peroxide has been added. How much peroxide needs to be added is unknown.

One method to prevent this is to add the peroxide before the NaOH solution is added. This can be done two ways, one is to add the H_2O_2 first the other is to add the LiOH solution first and then add the H_2O_2. The problem with adding the H_2O_2 first is that it has to be cooled with the LN2. If the LN2 is turned on with 5 gallons of 70% H_2O_2 in the tank the vapor that comes out of the tank will contain drops of 70% H_2O_2. Additionally if any thing splashes out of the tank then it is 70% H_2O_2 and this can be a safety hazard. The best method, in this circumstance, is to add the LiOH solution first. In most recipes used to date the amount of 18.5% lithium hydroxide monohydrate needed is around half of the total batch weight. When the lithium solution is added and then the peroxide, the highest concentration of H_2O_2 that can splash out is less than 25%, not entirely safe, but much safer than 70% H_2O_2.

The sequence of addition for most of the tests was to add the LiOH solution first. Once all of the LiOH solution is added then the LN2 and the agitator are turned on. When the temperature of the LiOH solution has dropped below 0°C, then the H_2O_2 addition can begin. The flow of H_2O_2 can be controlled by the computer to make sure the bulk temperature of the solution stays at 0°C or below. The 100-kg batch test results indicated that where the temperature in the batch was measured was not important. Even with very slow agitation the peroxide and lithium hydroxide reacted and mixed so quickly that no observable temperature gradient could be seen. This indicates that the reaction and mixing of the two chemicals takes place instantaneously.

During the addition of H_2O_2 the heat of reaction decreases with the amount of H_2O_2 added. As more H_2O_2 is added, the H_2O_2 pump can add H_2O_2 at a faster rate. Since the flow of LN2 is constant, this reduction in the amount of heat released is translated to the H_2O_2 pump speed increasing. Once the amount of H_2O_2, on a molar basis, has reached the amount of base in the solution, the heat of reaction decreases significantly to around one forth of the original rate. As a result of this effect the H_2O_2 pump will reach max speed and the temperature of the solution will continue to decrease. By the time all of the H_2O_2 is added the temperature of the solution is below 0°C.

The LiOH solution and peroxide have been added to the mixing tank and the resulting mixture is below 0°C. This mixture is about 75% of the total batch weight (depending on the recipe). As soon as the computer detects that all of the peroxide has been added the computer will turn off the peroxide pump and turn on the sodium hydroxide/potassium hydroxide pump. Once the mixture of sodium hydroxide/potassium hydroxide is mixed with the solution of lithium hydroxide and peroxide that is in the mixing tank, the temperature begins to rise very rapidly. This is due to the fact that now the excess peroxide in the batch has base to react with. During this addition the computer will also slow the pump speed as the temperature increases. When the temperature starts to decrease then the computer will begin to increase the pump speed. If the mixture temperature stays near 0°C then the computer will hold the pump speed constant.

Once all of the NaOH/KOH solution has been added the MHP mixing is complete. The NaOH/KOH pump will shut off automatically when the proper weight has been added. The agitator and LN2 continue to run. At this point the batch of MHP can be cooled to lower temperatures by leaving the LN2 on until the desired temperature is reached and then the liquid nitrogen can be turned off. The agitator can be turned off at this stage also. Excess agitation tends to cause the amount of bubbles in the MHP to increase, but no test have been performed to determine if the increase in agitation causes increased decomposition of peroxide in MHP.

Test Results

A total of seven 100-kg batches of MHP were made with this system. Figure F-3 shows typical profiles of MHP temperature, LN2 storage tank weight, and MHP batch weight exhibited by all of the seven MHP production tests. The results illustrated the capabilities of this 100-kg system in controlling and monitoring ingredient addition weight, LN2 injection rate, and MHP temperature during the MHP production.

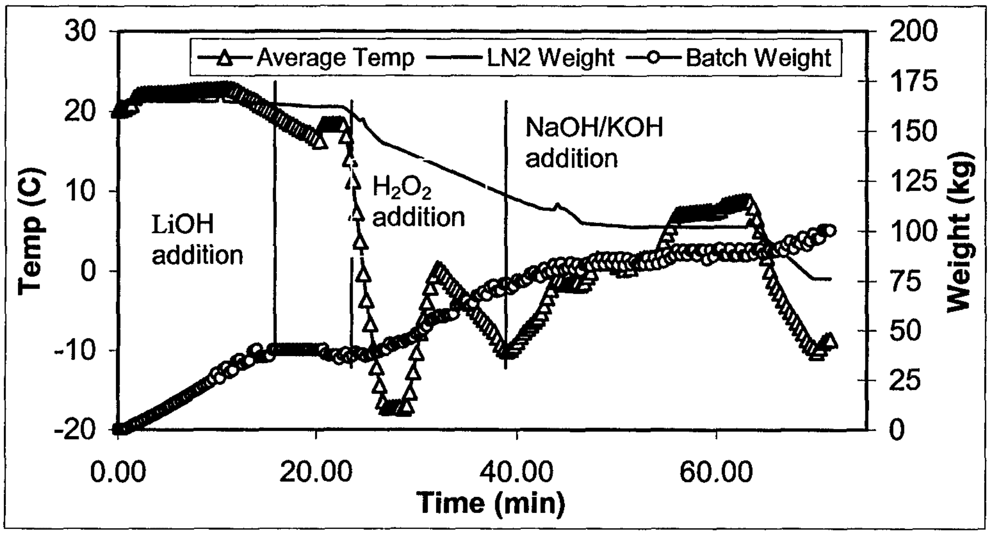


Figure F-3. MHP Weight and Temperature Profiles of a Typical 100-kg MHP Test

Based on the success of the 1st and 2nd generation of 100-kg batch systems, the next incremental step in MHP production scale-up was a system capable of making 1000-kg in one hour. Making 100-kg batches of MHP encountered challenges unforeseeable in the previous small lab-scale tests. Some of the challenges included control of liquid nitrogen flow rate and temperature, caustic solution cleanliness, and addition sequence of ingredients. Solutions to these challenges paved the way to an improved process at the 1000-kg scale level.

APPENDIX G – 1000-KG BATCH LN2 SYSTEM

Introduction

The basis for scaling the direct-contact cooling MHP production process up to a batch size of 1,000 kilograms is as follows:

1. A full-scale magazine for the Airborne Laser system is estimated at between 6,000 and 10,000 kilograms.
2. The largest batch of MHP produced to-date is approximately 1,000 kilograms.
3. A batch size of 1,000 kg allows direct comparison to other MHP production processes.
4. A batch size of 1,000 kg increases the development process by a factor of ten from the previous size of 100 kg. The scale-up of chemical processes typically should not exceed a factor of ten.
5. A batch size of 1,000 will answer the essential engineering questions of process scaling factors, MHP producibility, system reliability, and demonstrate the actual reduction of blend time from MHP production processes developed and operated by others.
6. The information and experience gained from previous scale (1 kg, 10 kg, and 100 kg) systems indicate a high probability of success in scaling the system up to the 1,000 kg size.

General Process Description

The general approach is the same as the 2nd generation 100-kg system. The solid caustics are dissolved in water. The caustic solutions can then be dispensed into the mixing tank based on mass. The peroxide is also dispensed by mass into the mixing tank. The operator of the system can change the order of ingredient addition. The flows of the ingredients are controlled by a computer to keep the temperature of the mixture from climbing above 0°C. The computer also controls the amount of each ingredient added. The ingredients are mixed in a tank that is continuously being sparged with liquid nitrogen and mixed with an agitator. The liquid nitrogen flow is controlled manually. The process flow and instrumentation diagram is shown in Figure G-1.

Equipment

The equipment used in this system can be grouped into several key components. These key components are: a caustic dilution system, a caustic delivery system, a peroxide delivery system, an MHP mixing system, a liquid nitrogen delivery system, a DI water system, and a computer control system.

Caustic Dilution System:

The system was setup based on the idea of dissolving the solid caustic in water prior making the MHP. Three tanks were put into place to store each caustic solution. A tank was installed to dilute each caustic in water. This tank was placed under the weigh hopper for the bulk solids handling system.

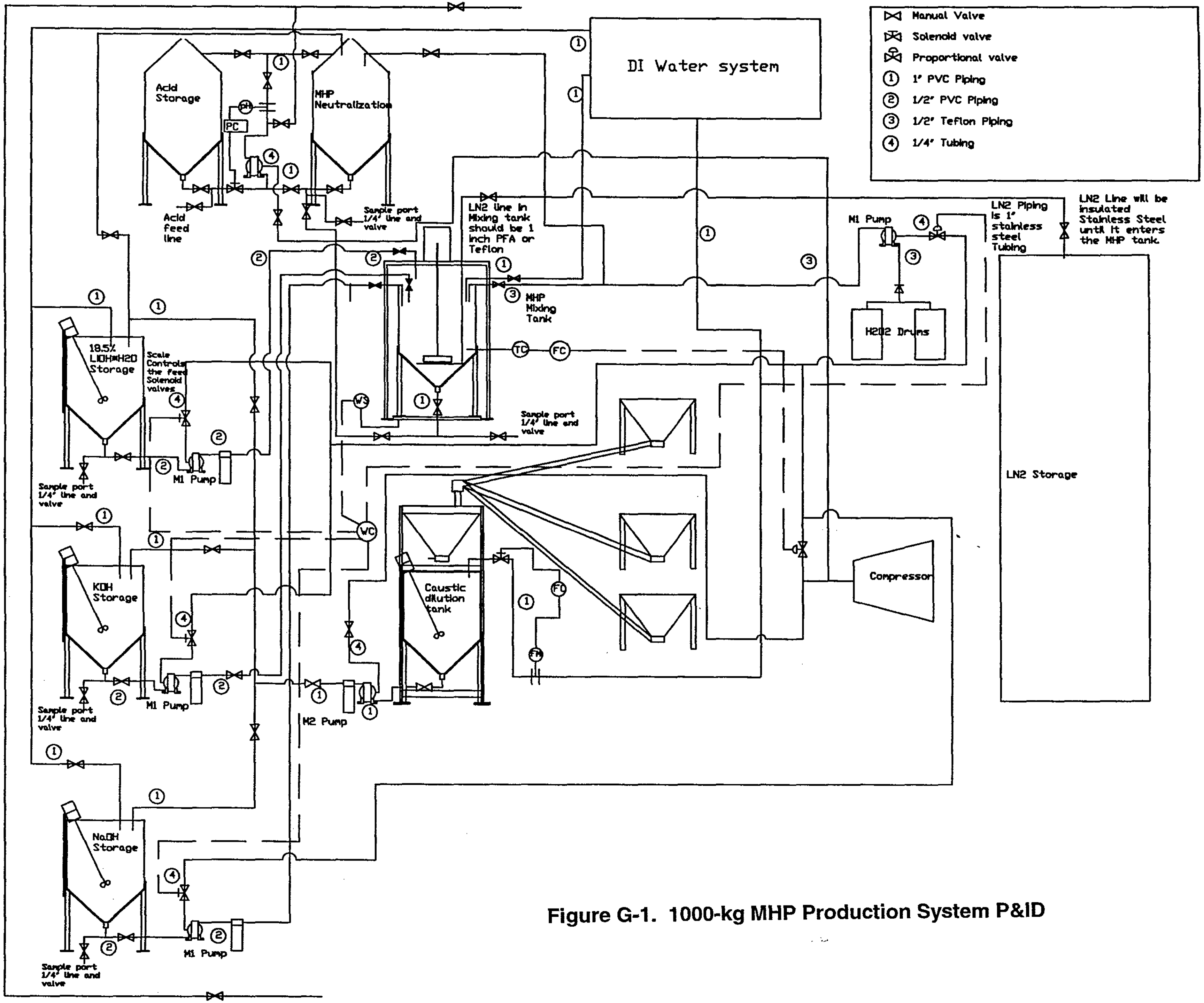


Figure G-1. 1000-kg MHP Production System P&ID

In the 100-kg system the sodium hydroxide and potassium hydroxide were put into one solution. This was convenient when making small scale MHP production, such as 100-kg batches. For larger scale operations, it was decided that the 1000-kg system should be setup to allow the preparation and storage of each caustic solution separately.

To move and weigh the solid caustic a Flexicon® bulk solid conveying system was purchased and installed. The bulk solid handling system consists of 3 feed hoppers that are at ground level. These hoppers are made so that drums of caustic can be dumped into them through a small hole in the top of the hopper. A Flexicon® conveyor is attached to the bottom of each hopper. The conveyor when on will move the solid material from the hopper to a weigh bin. The weigh bin stands about 6 feet off the ground and has load cells to measure how much caustic is in the bin. The bulk handling system has an internal computer control system that monitors the weight of solids in the weigh bin. When the pre-entered set point is reached the conveyor automatically shuts off. Once the proper amount of weight has been put in the weigh bin the solid material in the weigh bin can be discharged through a butterfly valve located at the bottom of the bin. The system was to convey the exact weight of each caustic into the weigh bin and then dump that weight into a dilution tank located underneath the weigh bin. Once in the dilution tank, the solid caustic would be dissolved in water using a portable mixer. From this dilution tank each caustic solution could be pumped to the MHP tank or to one of three caustic storage tanks.

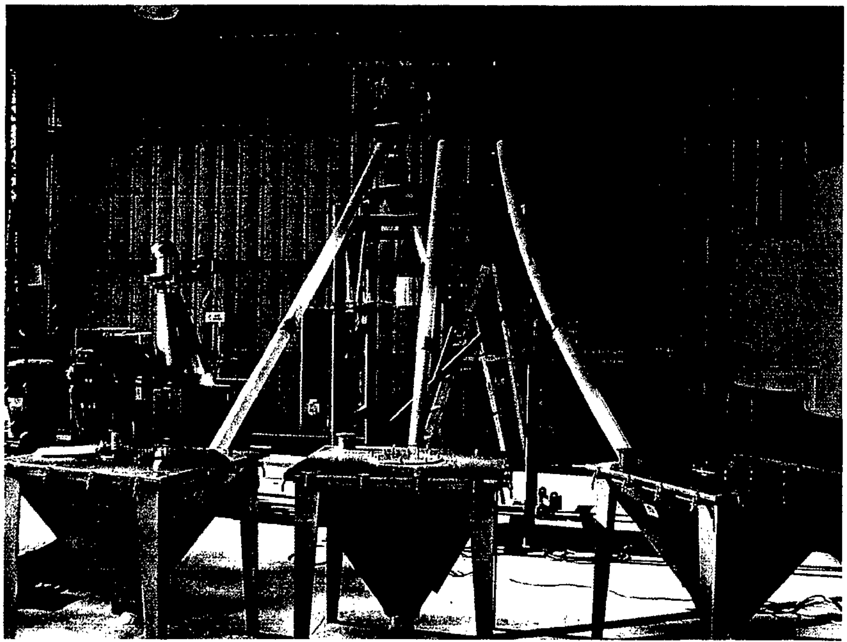


Figure G-2. Flexicon® Solids Conveying System

Two fundamental problems emerged when using the Flexicon bulk solids handling system. The first problem was that the solid caustic did not distribute evenly in the weigh bin. This caused the dry caustic material to build up rapidly and reach the top of the weigh bin before the weight set point was reached. There is no instrument, on the bin, to determine if the volume limit had been exceeded. So the conveyor would keep running when there was no room for additional material. This resulted in material coming out the top of the conveyor and spilling on the ground. The other problem was that due to the hollow Flexicon auger the conveyor had to be full all the time for it to move material and a certain amount of weight was required in the feed hopper for the conveyor to move material. This made it so that about 200 lbs of dry caustic was needed before any caustic could be moved to the weigh bin. When all the caustic needed was moved, this 200 lbs had to be removed from the system before the system could be cleaned. If the solid caustic had been left in the conveyor, it would have turned to one solid piece due to the hydroscopic nature of the caustic material. If MHP was being made continuously then this solids handling system could work well, it would not need to be emptied and cleaned until the system was shutdown for an extended period of time. However, if one batch is being made at a time, as is the case here, this system wastes time and material.

The process for making caustic solutions that worked best was to dump the drums of dry caustic straight into the caustic storage tanks, with water already in them. Weighing the drums before and after dumping controlled the weight of solid caustic being put into the tanks. If a certain amount of solid caustic was needed, only the amount needed was put into the drum before dumping. This method for diluting the solid caustic completely bypassed the Flexicon bulk solids handling system and the dilution tank.

The water added to the caustic storage tanks was measured by volume. The volume was determined by the flow meter on the DI water system. The size of all the caustic storage tanks was based on the volume of enough lithium hydroxide solution to make 2 batches of MHP. The amount of 18.5% lithium hydroxide monohydrate (10.6% lithium hydroxide, this concentration is close to the solubility limit of lithium hydroxide) to make 2 batches of MHP is approximately 200 gallons (this depends on recipe, but the worst case was used in determining demand). The caustic dilution tank (the tank under the Flexicon system) and the three caustic storage tanks have a 250-gallon capacity. The construction of these tanks is Polypropylene. This material was chosen for its chemical compatibility with strong caustic solutions and cost. Polypropylene also has a higher maximum operating temperature than polyethylene. Polypropylene has an upper limit on operating temperature of 115°C. Dissolving sodium hydroxide or potassium hydroxide in water can produce temperatures in excess of this. This caused alterations in the caustic dilution procedure. Due to this temperature constraint the sodium hydroxide and potassium hydroxide solutions had to be made in increments.

The concentrations of the sodium hydroxide and potassium hydroxide solutions were not set for this process. These concentrations were allowed to vary depending upon the recipe being made. However, only a very small portion of the 250-gallon capacity of each tank was used. This made shaft length for the portable mixers very long. Normal shaft lengths, on portable mixers are 36 inches; the shafts used in this system are 52 inches. Smaller tanks would have been more practical, but would have limited the flexibility of the system.

The portable mixers used in this system were not purchased for this system. The mixers used were left over from previous work. To use them new shafts and impellers had to be purchased. The combination of increased shaft length and increased impeller diameter lead to premature failure of the motors on these mixers.

Caustic Delivery System:

When MHP is made, the proper amount of each caustic solution and peroxide are transferred into the MHP mixing tank. The caustic storage tanks were described in the previous section. A computer monitors the weight of each caustic added to the MHP tank. Through programming, the software keeps track of the amount of each ingredient in the MHP tank. When all of one ingredient has been added, the computer diverts the air from that pump to the pump for the next ingredient.

The caustic solutions are transferred from their storage tanks to the MHP tank by small air operated diaphragm pumps (Wilden M-1 pumps). The transfer lines, for the caustic solutions, are made of PVC piping. This piping connects the storage tanks, through a pump and filter, to the MHP mixing tank. A scale that the MHP mixing tank is mounted to monitors the amount of each caustic solution being added to the mixture. As with the 100-kg system only one ingredient can be added to the mixing tank at a time.

The caustic pumps are located near the discharge of each of the caustic storage tanks. These pumps pull material from the tanks and pump it through the filter and into the MHP tank. The transfer line for each caustic storage tank, and the dilution tank, has a filter on the discharge side of the pump. This removes any solid contamination from the caustic solutions before they reach the MHP mixing tank. The filters that are inline are the same filters that were used in the 100-kg system. The filters were selected based on availability, cost and compatibility.

The pumps used in the process are air-driven Wilden (Model M1) diaphragm pumps. These pumps were chosen based on flow rate, cost, and availability. The flow rate of each pump, on the caustic storage tanks, is reported by the manufacturer to be 5 gallon per minute, but is dependent on the air pressure being used to drive the diaphragm and on the resistance to flow on the discharge side of the pump. If the pump is getting 60-psi air pressure and the resistance to flow on the discharge side is 15 psi, then the net pumping pressure is 45 psi. The 5-gallon per minute flow rate was set as a design criteria for the 1000-kg system in order to be able to satisfy the requirements for the system. The pumps for the base solutions are identical. The material of construction for these pumps is polypropylene and Teflon®. These materials were chosen for their inertness with all caustic solutions.

The pump that is used for transferring caustic solution out of the dilution tank under the Flexicon® weigh hopper is a bigger pump than the other pumps. The manufacturer of this pump claims the max flow rate is 20 gallons per minute. However, the flow rate is dependent on the air pressure being used to drive the diaphragm and on the resistance to flow on the discharge side of the pump.

The piping used to transfer caustic solutions from the storage tanks to the MHP tank are ½" pipes. At the discharge of the tanks, a sample port is attached. This sample port consist of ½" PVC pipe with a valve on it for taking samples. The piping from the caustic dilution tank to the caustic storage and MHP mixing tank is 1" pipe. This line also has a sample port that is identical to the sample ports on the caustic storage tanks.

Peroxide Delivery System

The peroxide is stored and transferred from 30-gallon aluminum drums into the MHP mixing tank. These drums are made of high purity aluminum and are made for storing semi-conductor grade of 70% hydrogen peroxide. These drums where also used as the peroxide feed tank in the 100-kg system. However, in the 100-kg system approximately 5 gallons of peroxide was used to make a batch of MHP. In the 1000-kg system around 50 gallons is needed per batch.

Two drums of peroxide are needed to make a batch of MHP. During the mixing of MHP when the first drum became empty the tube from the suction side of the peroxide pump was manually taken out of the empty drum and placed into a new drum. In order to minimize the possibility of contaminating the aluminum drums, polyethylene lids were made. These lids screwed onto the top of the peroxide drums and had bulkhead fittings for the suction tube to connect to. On the other side of the bulkhead fitting a dip tube that was long enough to reach the bottom of the drum was connected.

The peroxide pump does not have a filter on it for safety reasons. Filters in peroxide lines have a tendency to concentrate impurities. This increases the possibility of the peroxide decomposing rapidly and causing the filter housing to rapidly disassemble.

The peroxide pump is identical to the caustic pumps. The peroxide pump is mounted to the agitator support frame of the MHP tank. This minimizes the amount of piping used to deliver the 70% peroxide into the mixing tank. More piping increases the chances for contamination and leaking.

To transfer the 70% peroxide ½" PFA piping and ½" PFA tubing are used. The peroxide line enters the MHP mixing tank through a bulkhead fitting in the side of the tank just below the lid. After entering the tank tubing directs the peroxide to near the impeller of the agitation system. The suction line for the peroxide pump has a check valve located before the lid in the drum to keep any MHP or water from being siphoned from the mixing tank into the peroxide drum.

MHP Mixing System:

The MHP mixing tank purchased for this system is a 500-gallon polyethylene tank. This tank is a standard conical bottom tank made by several different manufacturers. This tank is attached to a stand painted with epoxy paint. Covering the tank and the stand is 2 inches of fiberglass insulation held in place by a PVC cover that is held in place and sealed with silicone caulking. A circular piece of polyethylene plate is welded into the cone of the tank about 2/3 of the way up from the apex of the cone. This piece of polyethylene has large holes cut in it so that MHP can flow through it easily. This piece of polyethylene is what the liquid nitrogen sparger attaches to. The tank also has 4 baffles spaced evenly around the inside circumference of the tank. The baffles are 1" thick, 4" wide and run the length of the right circular cylinder portion of the tank. The baffles help induce top to bottom mixing from the agitator.

A polyethylene lid has also been constructed, of polyethylene, and welded into place to minimize the amount of MHP splashing out of the tank. In the lid several holes have been cut. There are 3 holes cut for the ½" pipes from the caustic storage tanks. There are two holes for 1" pipe. One hole is for the transfer line from the caustic dilution tank. The other is for a DI water line. There is also a bulkhead fitting in the lid for the liquid nitrogen line. The hole cut into the center of the lid accommodates the agitator shaft. There is also a hole cut for an 8-inch piece of duct to exhaust the nitrogen gas from the tank to outside the building. A section of the lid has also been cut away, and can be moved in and out of place, so the operator can look into the tank while cleaning. The section of lid is secured back into place during MHP mixing. A Sketch of the lid is shown in Figure G-3.

The agitator for the 1000-kg system was picked to provide intense agitation. This agitation is to induce good distribution of liquid nitrogen, in the MHP, and improve the heat transfer between the nitrogen and the MHP. To get a good distribution of liquid nitrogen in the tank a Smith impeller was used (Figure G-4). This impeller is designed to disperse gases into liquids. When the liquid nitrogen enters the tank it starts boiling. To keep the nitrogen in the solution as long as possible the smith impeller was placed just above the nitrogen sparger. The blades of the smith impeller are designed to break the nitrogen into small pockets in the MHP. The more intense the agitation the more dispersed the liquid nitrogen is.

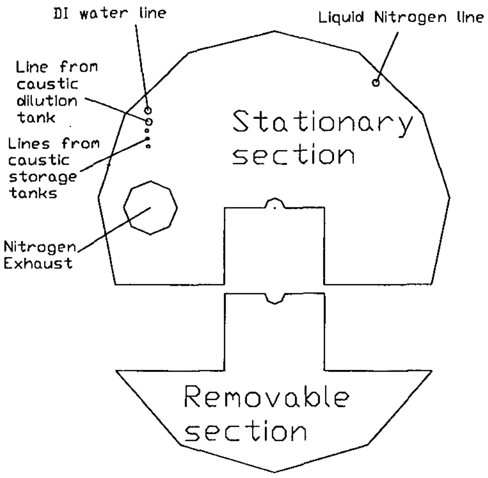


Figure G-3. Sketch of MHP Reactor Tank Lid.

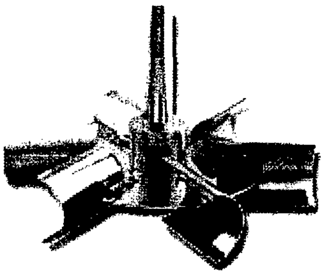


Figure G-4. Smith Impeller Used in the MHP Reactor

To get intense agitation in the tank a motor, given the smith impeller was to be used, was sized to get a torque to volume ratio (in-lb/1000 gallons) greater than 2500 (actual max value of system was 4000). The agitator shaft was made long enough so that the impeller would spin just above the liquid nitrogen dispersion pipe. The motor was purchased with a variable speed drive attached. The agitator RPM could be changed from around 50 to 150 revolutions per minute. The impeller diameter was set to be 18 inches to get the desired agitation intensity. The shaft and the impeller are made as one piece and are made of stainless steel coated with Teflon.

The agitator is supported over the tank by a custom-built agitator stand. This stand is constructed of 3-inch tubular steel and is bolted to the ground. The stand also has a floating top. The top of the stand was made movable so that if the position of the impeller needed to be change (to get the it closer or further from the nitrogen dispersion ring) it could be moved without removing the motor and gear box or cutting the agitator shaft. To move the agitator vertically 8 bolts can be removed and the platform that the motor and gear box is attached, can be moved up or down in increments of 2 inches.

The discharge from the MHP tank is at the apex of the conical bottom. The piping used on the discharge is 1" PVC. This discharge line also has a sample port on it. This sample port consist of ½" PVC pipe with a valve on it for taking samples. To empty the tank an additional pump is used. This pump feeds two 2500-gallon tanks. These were used to store, dilute, and neutralize MHP after it was made. These tanks were not purchased for this purpose. The size of the appropriate tank to perform this function would be approximately 1000 gallons. A 1000-gallon tank would easily accommodate 220 gallons of MHP, an equal amount of dilution water, and the amount of 15% HCL required to neutralize the caustic in the MHP (usually 250-300 gallons).

Liquid Nitrogen Delivery System:

The liquid nitrogen was supplied from a 400-gallon liquid nitrogen tank. This tank was specifically designed to dispense liquid nitrogen. This tank is skid mounted and can be moved with a forklift. This tank also has a flexible metal hose for delivering liquid nitrogen. When in use this hose is attached to 1" insulated stainless steel tubing. This tubing connects to 1" Teflon pipe that enters the MHP tank through the lid.

To control the liquid nitrogen flow rate to the MHP tank there are two valves on the liquid nitrogen tank. One of these valves allows liquid nitrogen to flow around the outside of the tank to make it boil. This builds pressure inside the tank. The other valve controls the flow rate of the liquid nitrogen leaving the tank. Two gauges on the tank allow the operator to know the status of the liquid nitrogen in the tank. One gauge indicates the internal pressure of the tank the other gauge indicates the volume of the liquid in the tank. The liquid nitrogen tank also sets on a scale to keep track how much liquid nitrogen has been used.

To deliver liquid nitrogen to the bottom of the MHP tank, a 1" Teflon pipe is used. This pipe is connected to the stainless steel tube through a bulkhead fitting in the tank lid. This pipe extends down inside the tank along wall next to a baffle. The pipe is secured to the baffle so it does not move in the tank. This pipe makes a loop on the polyethylene plate welded in the bottom of the MHP tank. In this loop, 1/8" holes where drilled. These holes are uniformly distributed around the loop. The sum of the cross sectional area of these holes are 150% the cross sectional area of the 1" Teflon pipe. This increase in surface area and diameter of the holes allows the liquid nitrogen to flow at a fast enough flow rate to meet the requirements of the system. This design was inspired by the results from testing different sparger configurations (hole size and number of holes) in the 100-kg system. While most of the holes are pointing up into the agitator impeller, some point down to get liquid nitrogen into all parts of the tank and to make sure the liquid in the bottom of tank is also agitated. The piping loop in the bottom of the tank is secured in place by being attached to the polyethylene plate that is welded into the tank.

De-ionized Water System:

Water purity is an important part of making good quality MHP. When making MHP in the 100-kg system, the amount of good quality water needed was very small. For the 1000-kg system significantly more water is needed. To ensure a sufficient supply of quality water was available, a DI water system was purchased from US Filters. This device consists of a pre-filter to remove most solids, a water meter, and three DI Resin bed filters to remove most ions from the water supplied. This system produces a little more than 5 gallons a minute when fed from the bases potable water system.

Computer Control System:

The computer control system is essentially the same system used for the 100-kg system. Most of the same hardware and software used on the 100 –kg system is used in the 1000-kg system. One difference between the controls of the two systems is that in the 1000-kg system computer monitors the weight of the MHP tank to determine how much of each ingredient has been added instead of the weight of the ingredients. Another difference is that to control which pump is being used the computer changes the airflow from pump to pump. To change the flow rate of the ingredient being pumped the air pressure driving the pump is changed. The computer now also controls turning on and off the agitator, speed of the agitator is controlled manually.

The computer software used is Lookout™. National instruments produces and distributes this software. This software can be used to perform process control from the computer or can be used as a man-machine-interface (MMI) between the operator and a programmable logic controller (PLC). For the 1000-kg system this software is used to perform the process control from a desktop computer (a laptop could be used as well). A graphical-user-interface (GUI) was made for the operators' screen of the software. This screen had a graphical depiction of the 1000-kg equipment and text boxes to display information being reported to the computer from the monitoring instruments (thermocouples, air pressure, and scales) and the information being sent to the equipment the computer could control (which pump is on and how much air is being supplied). This combination of graphics and information allows the user know how the process is running, where it is in the mixing process, and if the system is adding in the correct amounts of ingredients. Through the GUI the operator can monitor the process or interact with it to stop, start, or change pump speeds. The operator can run the process automatically or manually.

The computer hardware consists of a desktop computer, or laptop, and distributed input/output (I/O) hardware. The specification for the computer was determined by the software being used on it. The distributed I/O equipment chosen was FieldPoint, also a product of National Instruments. FieldPoint consist of a communication module, and tract that other modules can be connected to it. The modules used with FieldPoint depend on the type of inputs and outputs that will be needed to control and monitor the field instruments. In the system being described an analog input, an analog output, a relay output, and a thermocouple module was used.

The control instruments used in this system consisted of thermocouples, solenoid valves, agitator drive and scales. Two thermocouples monitor the temperature in the mixing tank. One thermocouple was made to reach near the bottom of the mixing tank and the other was made long enough to reach to a level that would be the middle of a finished batch of MHP. The caustic and peroxide pumps are air-driven. The pumps are controlled by solenoid valves that regulate the instrumentation air to activate the air-driven pumps. More than one pump can be turned on at a time, but since there is only one scale weighing how much of each ingredient has been added, this feature is only used for cleaning. To control the pumping rate, an automated air regulator changes the air pressure available to the pump.

The monitoring and control scheme used in this system was to add the proper weights of each ingredient (one at a time), while monitoring the temperature of the mixture. If the temperature approached a set temperature, entered by the operator, the flow of the ingredient would be decreased incrementally until the temperature began to fall or the pumping stopped. The liquid nitrogen flow was constant so if the pumping stopped the temperature would drop relatively fast, and the pumping would resume. Once the predetermined weight of the ingredient had been added the pump would stop and the next pump would come on. This process would repeat until all ingredients where added. A list of materials that are used in the 1000-kg system and in contact with MHP and/or its component streams is shown in Table G-1.

Table G-1. List of Component Materials for 1000-kg MHP System

1000-kg MHP production system			
Equipment	**Description**	**Material of Construction**	**Comment**
MHP scale	60" X 60" Platform scale with a 5000 lb capacity	Stainless steel	This scale was purchased based on price and availability
Peroxide Drum	30-gallon drum	Aluminum 1060	These drums are specially designed for Concentrated peroxide storage.
Flexicon Bulk solids Conveyor	Equipment to move and meter large quantities of dry caustic material	Stainless Steel and polypropylene	This system was used very little due to amount of caustic material wasted and operational difficulties.
Caustic dilution tank/caustic storage tanks	300 gallon conical bottom tanks	Polypropylene	Polypropylene chosen for chemical compatibility and better thermal stability than polyethylene
Caustic piping	1" Sch 40- from caustic dilution tank to storage tanks 1/2" pipe from storage tanks to MHP tank	PVC	PVC chosen for chemical compatibility, price and availability
Peroxide Tubing	1/2" OD- From peroxide drums to pump and from top of the tank to near the impeller	Extruded PFA	Material was specifically chosen for use with concentrated peroxide.
Liquid Nitrogen Tubing	1" OD tubing covered in 2 inch insulation	Tubing is Stainless steel and Insulation is polyurethane foam	Tubing was designed to travel 100 feet with little pressure drop and little heat gain
Peroxide Pipe	1/2" sch 40- From pump to the top of MHP tank	Extruded PFA	Material was specifically chosen for use with concentrated peroxide. This tubing included a PFA check valve
Caustic Transfer pump	Wilden M-2 Pump	Polypropylene and Teflon	Pumps about 20 gpm, Pump chosen due to chemical compatibility availability
Caustic Metering pumps	Wilden M-1 Pump	Polypropylene and Teflon	Pumps about 5 gpm, Pump chosen due to chemical compatibility availability
Peroxide metering pump	Wilden M-1 Pump	Polypropylene and Teflon	Pumps about 5 gpm, Pump chosen due to chemical compatibility availability
Caustic filters	Standard water filters	Polypropylene / Buna N Seals	Filter cartridges are sub micron rated for removing particles from drinking water
Tank Lid	In house fabrication	Polyethylene	Purchased in sheets and cut to fit welded into place
MHP tank	500 Gallon conical bottom tank	Polyethylene	Purchased with 2" of fiberglass insulation held in place with PVC wrap, and four 4 inch baffles.
Agitator	5hp, 50-175 rpm, 18 inch Diameter smith Impeller	Shaft and Impeller Teflon coated Stainless Steel	Sized to provide intense agitation and to increase liquid nitrogen dispersion through out the liquid..
Liquid Nitrogen Tank	400 gallon horizontal insulated tank	Stainless steel	The vessel is movable and was designed for storing and delivering liquid nitrogen.
Liquid Nitrogen sparger	1" shc 40 pipe made into a loop and attached to PE plate welded into the bottom of the tank	PFA	Design to evenly distribute liquid nitrogen into the impeller of the agitator.
Thermal couples	E Type	Teflon coated	Material chosen for chemical compatibility

Procedure for MHP Production

Prior to making a batch of MHP all equipment was cleaned thoroughly with de-ionized water. Particular care was taken in cleaning the pump and tubing for transporting 70% peroxide. The tank and the liquid nitrogen line inside the tank were also cleaned very well. The caustic lines and pumps were rinsed and the filters where taken apart and washed thoroughly.

When the system was design it was set up to make large batches of each caustic solution and only use these solutions as needed. When MHP was not being made the caustic solutions would remain in the tanks until it was needed again. However, for most batches the caustic solutions needed would be made the day before the batch was to be made. These solutions were sampled and tested, for hydroxide concentration, the day they were to be used. The reasoning for not storing the caustic solutions was a fear that carbonates would form in the caustic solutions and make them unusable. There has been no testing done determine what effect long term storage has on the caustic solutions or on the MHP made from these solutions. The longest these solutions were stored before being used was one week. There was no noticeable effect in the resulting batch of MHP.

The day before a batch was to be made, the caustic solutions were made. When diluting NaOH and KOH, a large amount of heat is released. The temperature of the final solution is dependent on the final concentration of the mixture. Making the caustic solutions up the day before allowed the NaOH and KOH solutions to cool down overnight. Due to the mass of each solution needed this would cool the solutions down to 30-40°C. The amount of time required to make large batches of caustic solutions was about 3-4 hours. The amount of caustic solution that needed to be made had little impact on this time. The amount of time to make the NaOH and KOH took the longest. These solutions had to be made in increments due to the amount of heat released due to diluting them in water. The normal procedure was to dissolve about 2/3 of the solid caustic mass needed. This solution was allowed to set and cool for a couple of hours and then the rest was added. This procedure was followed to keep the temperature in these tanks from exceeding the maximum operating temperature.

Each caustic solution was made in a similar way. From the recipe to be made, the amount of 18.5% lithium hydroxide monohydrate needed was calculated. The remaining water, dictated by the batch size and the recipe, available was determined. This is the amount of water available to dilute the sodium and potassium hydroxides. Based on the amount of water available and the amount of each caustic needed, the concentration of the sodium hydroxide and potassium hydroxide solutions was decided. The proper amount of water needed in each tank was added before any caustic was put in. The volume of water added to each tank was measured using the flow meter on the DI water system. Once the amount of water was in the tank a working portable mixing was put in the tank and turned on. Once the potable mixer was stirring the water in the tank the caustic could be added. This was done by weighing out the amount of caustic needed into a 55-gallon drum. The drum dumper was then used to dump the caustic directly into the tank of mixing water. Care was taken to try to add the caustic slowly. However, potassium hydroxide came out of the drum very fast, too fast to control the rate. The sodium hydroxide was very hard to get to flow out of the drum and required the operator of the drum dumper to make several dumping attempts and the assistance of a hammer to get all of the sodium hydroxide out of the drum. The portable mixers that were used had a tendency to burn out when used to mix the sodium hydroxide solution. This could be due to the high viscosity of this solution. The impeller of these mixers had been increased from 3" to 6" for the purpose of making caustic dilutions. The combination of high viscosity and the increased diameter could have made the motors fail prematurely.

After the caustic solutions were made the storage tanks were covered. Samples of each solution are taken to determine the concentration of each solution. Each caustic storage tank has a sample port on the bottom of the tank. However, due to the heat generated during the dilution process the PVC piping on the bottom of the tank became deformed. This deformation occurred at lower temperatures than the max operating temperature of the tank. This deformation made the sample ports on the sodium hydroxide and potassium hydroxide storage tanks unusable. The best way of collecting a sample was to pump a small amount of the solution to the MHP tank and take a sample of that. This procedure resulted in a sample that was filter. The filtered caustic is what was used to make MHP.

The liquid nitrogen tank was always filled a day or two before the MHP was to be made. This had to be coordinated with the supplier of liquid nitrogen. The liquid nitrogen supplier needed at least 72 hours notice for a delivery. When a delivery was scheduled the tank had to be moved so that the truck could fill it. Once full the tank had to be moved back on to the liquid nitrogen scale. The flexible hose on the liquid nitrogen tank was then attached to the insulated transfer tubing discussed earlier.

On the day a batch was to be made, the MHP mixing tank is washed again with DI water and emptied. Two 30-gallon aluminum drums of 70% hydrogen peroxide were moved into place near the peroxide pump. The suction line for the peroxide pump is always stored in DI water when not in the peroxide drum. Great care is taken not to get any dirt or other contamination in the 70% peroxide drum.

With all of the equipment and chemicals ready, a communication line from the I/O communication module to the computer is connected. This communication line is used for the operator to communicate with the equipment that is in place. The operator tells the computer what recipe is being made, how much, and the concentrations of the caustic solutions. From this information the computer will determine how much of each ingredient to add. The computer can control how much of each caustic solution and peroxide is added, but any water that needs to be added has to be added manually.

The first addition can begin. Making the MOH solution first and then adding the peroxide is the procedure that has been followed for making every 1000-kg batch of MHP, which has been made at Tyndall AFB. This procedure is to add each of the caustic solutions, one at a time, and any water that is needed into the MHP mixing tank first. The MOH solution is then cooled with liquid nitrogen to near –10°C. Once the solution has reached the desired temperature the peroxide addition can begin. The computer uses proportional-integral (PI) control to control the flow rate of peroxide so that the temperature in the mixing tank remains below 0°C.

During the addition of peroxide the heat of reaction decreases with the amount of peroxide added. As more peroxide is added, the peroxide pump can add peroxide at a faster rate. Since the flow of liquid nitrogen is constant through out, this reduction in the amount of heat released is translated to the peroxide pump speed increasing. As a result of this effect the peroxide pump will reach max speed and the temperature of the solution will fall relatively quickly. When this occurs the operator must manually slow the flow of liquid nitrogen. By the time all of the peroxide is added the temperature of the solution is usually below 0°C.

Summary of Findings

The amount of time required to make 1000-kg of MHP is around 1.5 hours. The process had three phases. The first phase was making the MOH. This phase took approximately 40 minutes. The next phase was cooling the MOH. This phase took about 20 minutes. The third phase was the addition of peroxide, which took around 35 minutes to complete. MHP weight and temperature profiles of a typical MHP production test are shown in Figure G-5.

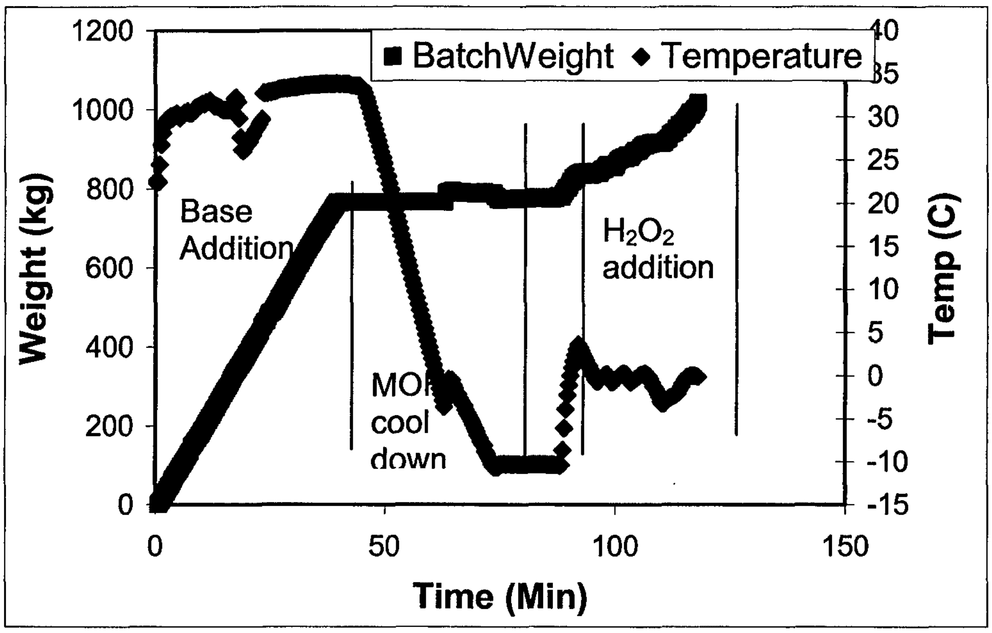


Figure G-5. MHP Weight and Temperature Profiles of Typical 1000-kg Test

During the addition of the caustic solutions and any water that is needed the agitator and liquid nitrogen are left off. The reason for this is that movement of the liquid in the tank affects the reading of the measured weight in the MHP tank. This effect has been observed to be around 6 kg. When adding 50% sodium hydroxide solution, 6 kg can affect the final hydroxide concentration by 0.075 moles of OH/kg of MHP. If a value of 4.2 moles of OH/kg of MHP is the targeted base concentration, the resulting concentration would be 4.125 moles of OH/kg of MHP. In early runs of the system, 3-5% error was the average deviation from the target concentrations. Once the agitator and the liquid nitrogen was left off until all the caustic and water was added to the MHP tank and the amount of peroxide to be added was increased by 10% this error was reduced significantly to less than 1% on average. Table G-2 illustrates this observation.

One way of decreasing mixing time of MHP is to minimize the time to make MOH, and cool the MOH at the same time. The time to make the MOH solution could be decreased significantly if all three caustic solutions could be added at once. When making 1000-kg batches, of MHP, the MOH was always made first. The caustic solutions had to be added one a time since there was only one scale measuring how much of each solution was added. The time that was required to make the MOH this way was around 40 minutes. The amount of time to cool the MOH is around 25 minutes. Both of these phases could occur at the same time and the time to do both could be reduced to less than 25 minutes. To do this the amount of each caustic solution would need a measurement system that is independent of the MHP mixing tank weight and independent of the measurement of the other caustic solutions. With these changes, the MOH could be made by adding all of the caustic solutions at once and the mixture could be cooled at the same time.

Table G-2. Summary of 1000-kg LN2-Based MHP Production Test Results

	Date	Recipe	Actual Moles of OH^-/kg In MHP	Targeted Moles of OH^-/kg in MHP	% error	Actual Moles of H_2O_2/kg in MHP	Targeted Moles of H_2O_2/kg in MHP	% error
Tests without procedural changes	29-Sep-00	4.20	4.298	4.2	2.33%	4.534	4.65	2.49%
	13-Dec-00	4.20	4.613	4.2	9.83%	4.143	4.65	10.9%
	02-Mar-01	4.51TRW	4.645	4.52	2.77%	5.271	5.115	3.05%
	07-Mar-01	4.51TRW	4.391	4.52	2.85%	5.353	5.115	4.65%
	13-Mar-01	4.51USAF	4.378	4.52	3.14%	4.856	4.972	2.33%
	19-Jun-01	4.20	4.08	4.2	2.86%	4.97	4.65	6.88%
Tests with procedural changes	27-Jun-01	4.20	4.248	4.2	1.14%	4.693	4.65	0.92%
	31-Aug-01	4.20	4.176	4.2	0.57%	4.647	4.65	0.06%

A way to reduce the peroxide addition time is to control the bulk temperature, of the MHP, with the liquid nitrogen flow rate. The flow rate of liquid nitrogen could be used to control the flow of peroxide. This would allow the fastest addition of peroxide. The flow of peroxide would never be slowed down until the liquid nitrogen reached a maximum flow rate.

The ventilation, for the MHP tank, was through an 8" PVC coated duct. This duct directed the nitrogen gas, given off in the mixing process, outside the building. The first vent design was using a blower that reportedly could move over 900 cfm. However, when using this blower the pressure in the tank would build up and make the tank lid vibrate and make a lot of noise. When the liquid nitrogen was turned off and the flexible hose for the blower was taken out of the tank it was full of water. Once the blower was removed from the vent line, the flexible hose remained, the vent worked fine. The flexible hose was then replaced with the 8" PVC coated metal duct.

Another observation made from these experimental runs was the temperature rise due to decomposition of the peroxide in stored MHP. After most of the batches were made the temperature of the MHP was lowered to –15°C. An increase in temperature can be attributed to heat exchange with the surroundings, and the decomposition of peroxide. Measured profiles of temperature rise against time for the MOH and the MHP, respectively, give an indication of the how much of heat rise is due to heat exchange (heat loss to ambient) and how much is due to decomposition. Figure G-6 illustrates the difference in the rates of temperature increase near 0°C for MHP and MOH, which is typical of observations from several different trials. This graph indicates that MHP temperature rises at 1.5°C per hour where as the MOH temperature only changes at a rate of 0.4°C per hour. The extra heat given off in the MHP is due to the decomposition of the peroxide. Lab test have shown that the warmer the MHP the faster the peroxide decomposes. The temperature to decomposition rate of peroxide is an exponential relationship (small increases in temperature increase the decomposition rate exponentially). So in order to store MHP at 0°C for long periods of time heat needs to be removed at a rate that is equivalent to changing the temperature of MHP by 1.5°C per hour. The amount of continuous cooling required to store MHP at lower temperatures is much less.

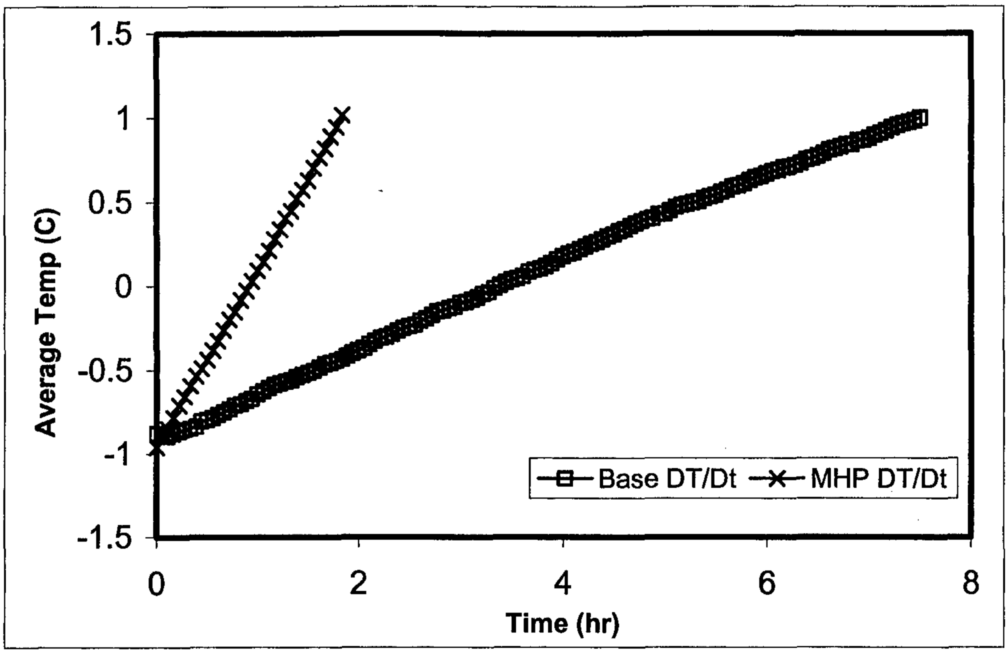


Figure G-6. Temperature Rise of MOH and MHP in 1000-kg Tests