EVALUATION OF CONTROLLED FREEZING TO REMOVE TRAPPED RESIDUAL NAPL

by

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ABSTRACT

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Groundwater contamination continues to pose a threat to the drinking water supply. Contaminants, namely non-aqueous phase liquids (NAPLs), seep into the soil from hazardous waste sites and underground storage tanks. Once in the soil, 10 to 50 percent of the contaminant remains trapped in both the saturated and unsaturated soil. This trapped residual contaminant then slowly and continually dissolves, contaminating the groundwater. No current methods for removing this trapped residual contaminant are 100 percent effective and cost effective. Thus, new innovative remedial techniques are needed to effectively address this problem.

The present study focuses on removing trapped residual through controlled freezing. It is also focused on gathering frozen and unfrozen gradient data with and without dodecane, the representative NAPL used in the bench scale study. For the experiments, a cell was developed using glass beads to represent the porous media, thermistors within the cell for temperature measurement, and freeze pipes placed vertically on the exterior of the cell to create the freeze front. The experiments consisted

of setting up a water saturated only cell and also a water-residual NAPL saturated cell. The freeze pipes were turned on, while simultaneously starting a flow of water into the cell to flush any freed residual away from the freeze front. Periodic temperature measurements were taken throughout the cell to obtain gradient values and the amount of trapped residual removed was measured to determine the effectiveness of this procedure.

The data from the gradients revealed two main trends. The two main trends were: 1) the frozen gradient was greater than the unfrozen gradient and 2) the unfrozen to frozen gradient ratio remained fairly constant throughout all of the experimental runs. The results of the removal effectiveness varied greatly, ranging from 76 percent to 26 percent removal effectiveness. The results clearly demonstrate that this method of trapped residual contaminant removal is effective, although not 100 percent efficient. The results from this experimentation indicate that further research using variations of some or all of the parameters used in this study is needed.

ACKNOWLEDGMENTS

I would like to thank Dr. Orlando B. Andersland and Dr. David C. Wiggert for giving me the opportunity to research this topic and for their continued assistance and guidance. I would also like to thank Lizette Chevalier for her help and encouragement and J.C. Brenton for his aid in designing and constructing some of the needed devices for this research as well as taking care of many of the technical problems that occurred during this experimentation.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES

NOMENCLATURE

A	Total Cross Sectional Area	$[L^2]$
g	Acceleration Due to Gravity	$[LT^{-2}]$
l	Length of the Cell	$[L]$
N_b	Bond Number	$[1]$
N_c	Capillary Number	$[1]$
n	Porosity	$[1]$
Q	Flow Rate	$[L^3T^{-1}]$
R	Particle Radius	$[L]$
w	Width of the Cell	$[L]$
μ	Displacing Fluid Viscosity	$[MT^{-1}L^{-1}]$
v	Displacing Fluid Velocity	$[LT^{-1}]$
v_s	Seepage Velocity	$[LT^{-1}]$
$\Delta\rho$	Fluid Density Difference	$[ML^{-3}]$
σ	Interfacial Tension	$[MT^{-2}]$

CHAPTER 1

INTRODUCTION

1.1 Description of the Problem

Leakage that occurs from hazardous waste sites and underground storage tanks continues to pose a threat to the drinking water supply. When these hazardous materials, namely non-aqueous phase liquids (NAPLs), seep into the soil, they migrate down through the porous media, leaving a residual as they progress. When they reach the water table, the NAPLs continue to sink if they are more dense than water (DNAPL), or float on the water table if they are less dense than water (LNAPL) as shown in Figure 1 (Wilson, et al, 1990). In both cases, between 10 and 50 percent of the contaminant is left behind in the form of a residual which continually contaminates the groundwater by dissolving slowly over a long period of time. In the case of LNAPL, a large percentage of the contaminant can easily be removed by saturating the soil and allowing the LNAPL to float to the surface of the water table where it can be disposed. When this saturation occurs, generally by a rise in the water table, 50 to 90 percent of the contaminant is removed. The remaining 10 to 50 percent becomes trapped in the soil by capillary forces present in the porous media. The entrapment within a water wetted saturated soil pore and an air saturated soil pore is illustrated in Figure 2 (Hunt, et al, 1988).

The capillary force, or pressure, is the result of interfacial forces acting between the water, contaminant, and soil pores. Compared to buoyant, viscous, and gravity forces present in the porous media, capillary forces are the strongest and thus prevent the residual contaminant from being released from the soil pore (Corey, 1986). The concept behind residual trapping is discussed in greater detail in Chapter 2.

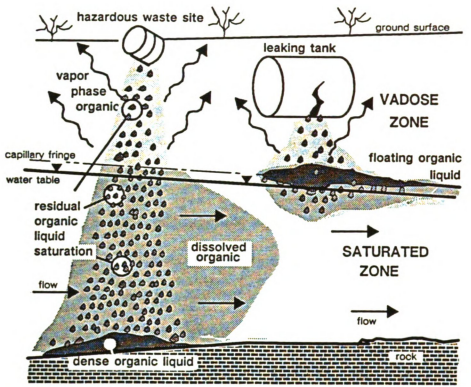

Figure 1: Sources and Processes by Which the Soil Becomes Contaminated

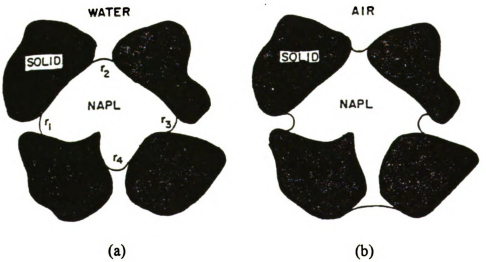

Figure 2: (a) Water wetted saturated and (b) air saturated entrapment within a soil pore

1.2 Current Methods of Treatment

There are several methods currently used to cleanse contaminated soil in both saturated and unsaturated media. However, no method currently used is economical and 100 percent effective in removing residual contamination in either type of media.

Soil washing is the most effective method of treating contaminated soil and can be used in either a saturated or unsaturated instance. This method involves excavating the soil and then cleaning it. Two commonly used cleaning methods are to heat the soil to very high temperatures to burn away the contaminant or to wash the soil. After it has been cleaned, it is then replaced in its previous location, or dumped somewhere else. This method is 100 percent efficient, however, it is very expensive and is therefore usually only used on smaller areas of contamination (Wilson, et al, 1990). In unsaturated soil, vapor extraction is one of the more effective methods used to remove residual contaminants. It involves forcing hot gases down through the soil, which volatize the residual in the soil. The resultant gases are then vacuumed out. This method can reduce the residual contamination by up to 95 percent, however, is again only effective in unsaturated conditions. In saturated soil, surfactant flushing is a method that is currently being examined. This technique attempts to remove the residual contaminant by altering the interfacial tension between the residual contaminant and the porous media, thus allowing residual mobilization to occur easier (Wilson, et al, 1990). Surfactant flushing has proven to be successful in laboratory experiments, however, it has been less successful in the field. This occurs for several reasons. First, in experimental applications it is easier to ensure that the surfactant will come into contact with all the residual contaminant in the soil, thus, optimizing the use of the surfactant. However, in

field applications, this becomes much more diffucult to do, mainly because it is not possible to see down into the soil and determine which portions have been in contact with the surfactant and which areas need to be treated. Another factor to consider when using surfactants is that in experiments the surfactant can be obtained from the soil easily, while In the field, it is difficult to retrieve the surfactant once it has entered the soil (Andersland and Wiggert, 1994; Wilson, et al, 1990). Another method currently used mainly in saturated media is biodegradation, which is the injection of bacteria into the contaminated soil. These bacteria then feed upon the contaminant, while not contaminating the soil or groundwater. However, this method is generally not used alone since the bacteria most often feed only upon the contaminant that is dissolved in the water leaving the undissolved residual (Wilson, et al, 1990).

1.3 Effect of Soil Freezing on Contaminants

Previous experimentation has been conducted on the effect of freezing on contaminant immobilization. Iskander (1986) showed experimentally that artificial freezing can be used to successfully immobilize contaminants in the soil without any ill effects to the environment (Iskander, Jenkins, 1985). Iskander also showed that creating an artificial freezing front in the soil could separate contaminants and possibly act as an alternative to slurry walls or other types of contaminant barriers. Further research on the effectiveness and integrity of using frozen soil as a contaminant barrier is currently being conducted. It was also noted in Iskander's research that repeated freezing and thawing of a contaminated area of soil tended to consolidate the hazardous waste material (Iskander, 1986). This leads to the concept that controlling the rate at which the soil is frozen could

release the contaminant which is trapped and allow an effective cleanup of the contaminated area.

Based on Iskander's research and other similar experiments, researchers at Michigan State University (MSU) began to examine how and if controlled freezing could remove trapped residual contamination through a series of experiments conducted by Soehnlen (1991). The experiments were run using 1 mm diameter glass beads to simulate the porous media. These beads were placed in a sealed tank 15 cm wide by 25 cm high with a thickness of 1.5 mm. The cell was saturated with water, followed by a NAPL (dodecane), and then resaturated with water, leaving a residual in the porous media. The cell was then lowered into a coolant tank to create a freeze front. Many different lowering rates were attempted until an optimum rate, a rate at which the residual contaminant is most effectively removed from the media, was found. At this optimum rate of 0.8 cm/day, it was noted that as the freeze front "pushed" the residual out in front causing it to build up, the amount of water present at the freeze front would decrease. As a result of the limited water at the frost line, the freeze front could not continue and would then "jump" over the built up residual and continue freezing on the other side (Soehnlen, 1991). The experiment showed that the formation of ice will force residual that is trapped in the porous media out of the pore. This phenomena of exclusion from the ice formation can be explained by the way ice crystals form. Ice crystals form very pure and do not accept any substitute ions into the structure. When ice forms, its formation possesses much stronger forces than the capillary forces which trap the residual and can thus overcome them. Also, when ice forms it increases in volume by approximately 9%. This increase also drives the residual from the soil pore (Pounder,

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1965). The experimentation by Soehnlen (1991) left many unanswered questions, some of which are examined in this research.

1.4 Scope of Investigation

In light of previous research, the present study focused on creating a controlled freeze front to remove trapped residual NAPL from a porous media. In conducting this research, two main objectives were established. The first was to obtain information on temperature gradients at the frost line, and the second was to determine NAPL removal effectiveness by this controlled freezing technique. These goals, equipment design and experimental work are related to the aforementioned research by Soehnlen (1991) conducted at MSU. This experiment was directed toward gaining a more precise and accurate understanding of parameters reported in previous work, while further developing the theories behind this new method of treatment.

To gain a greater understanding of the gradient data and removal effectiveness, extra devices were included in the design of the system. These devices include thermistors, a flushing water system, entrance and exit valves, and a horizontal freezing system.

Thermistors were added uniformly in the cell to obtain temperatures throughout the cell and to ensure that temperature measurements could be taken at and around the frost line regardless of where it was in the cell. There was limited interference in the continuity of the porous media due to the small size of the thermistors. The specifications and accuracy of the thermistors and the data logger, used to read the temperatures, are included in Chapter 3.

A flushing water system was also added to the cell design. This was added to prevent the contaminant from building up at the freeze front as it was released. If the freed contaminant is not flushed away from the frost line the freeze front will "jump" over the buildup of contaminant because of the high concentration of residual and low concentration of water. This was one of the main observations from Soehnlen's (1991) experiments. The flushing water is also provided to flush the freed residual to the top of the cell where it is removed through exit valves.

Finally, the system was designed to represent one that might be used in the field. This included having a horizontal freezing system with the water flushing system previously described. The horizontal freeze front was created by placing two copper tubes, on each side of the cell. These tubes were placed up against the glass of the cell, spaced 10 inches (25.4 cm) apart. More precise details and a schematic showing the freezing system can be found in Section 3.1. This is fairly representative of vertical freeze pipes placed in the ground at a field site. The flushing water is also somewhat representative of a water injection system that would be used in the field. The experimental flushing water enters freely along the bottom of the cell under a screen, migrates horizontally and vertically up through the soil. In the field, the flow would be directed into the media at an upward angle and would progress in the same manner as the current experimentation.

CHAPTER 2

SYSTEM CHARACTERIZATION

2.1 Soil Characterization

In this experiment, glass beads were used to represent soil. They were selected for these experiments primarily due to their homogeneity, known properties, such as porosity, and visualization advantages (Morrow, et al, 1988). These properties aid in setting up a homogeneous residual and allowed the freezing to be performed in a relatively predictable environment. The glass beads used measured between 0.92 and 1.24 mm in diameter. This small size was chosen because of the narrow cell that was selected for the current experimentation (4 mm cell opening). The porosity of the glass beads in the cell was approximately 0.39. This was determined by filling a graduated cylinder to a specified level with glass beads and then compacting them with a small narrow metal rod as they would be compacted in the cell. A measured amount of water was then added until the water was level with the glass beads. The cylinder was examined to ensure that the beads were saturated and there was no air present in the media. The volume of voids was taken as the volume of water poured into the graduated cylinder. The porosity could then be determined by dividing the volume of voids by the total volume. This process was repeated three times with very consistent results. The seepage velocity is calculated once the porosity is known and is given by v_s:

$$v_s = q/An \qquad \text{(Eq. 1)}$$

where q is the flow rate, A is the total cross sectional area, and n is the porosity (Potter, Wiggert, 1991). The seepage velocity was used extensively in calculating the changing

flow rate as the freeze front advanced and was also used in relating these flow rates to the capillary number.

2.2 Contaminant Characterization

To understand more about the contaminant that was selected for this experiment, it is necessary to examine how NAPLs are trapped in a porous media. After the contaminant has seeped into the soil, it has infiltrated the pore spaces of the soil. The capillary forces, which are much stronger than the buoyant, viscous or gravity forces present, then cause entrapment of the contaminant to occur. The capillary number is given by N_c:

$$Nc = \frac{v\mu}{\sigma} \qquad \text{(Eq. 2)}$$

where v is the displacing fluid velocity, μ is the displacing fluid viscosity, and σ is the interfacial tension (in this case between the dodecane and water) (Hunt, et al, 1988). The capillary number is the ratio of viscous to capillary forces. It is when the capillary force becomes larger than the viscous, gravity, or buoyant forces present in the porous media that the residual is trapped.

The initial capillary number was selected based on graphs of residual oil saturation versus capillary number (Figure 3). The capillary number selected was the one which just begins mobilization of the residual. In Figure 3, this is the point on the curve where the slope begins to increase rapidly. Using these graphs in Figure 3, a flow rate can be calculated which will change as the length of the cell changes due to the advancement of the freeze front. It is given as:

$$Q = \frac{Nc\sigma wln}{\mu} \qquad \text{(Eq. 3)}$$

where l is the length of the cell (which will vary depending upon the advancement of the freeze front), w is the width of the cell which is constant, and n is the porosity of the media which also remains constant.

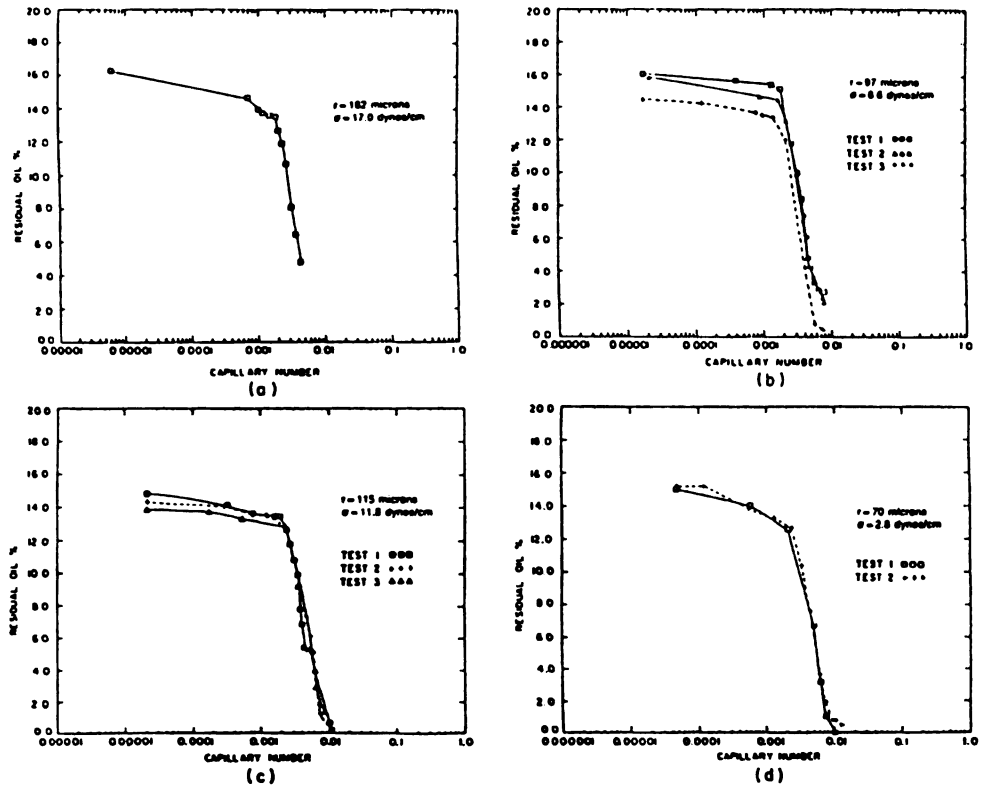

Figure 3: Residual Oil Saturation Versus Capillary Number

One way the contaminant can become trapped is by a large variation in the size of the pore space through which the contaminant and water travel, due to the flow from an aquifer. When this occurs, the smaller pores drastically reduce the capillary pressure between the NAPL and water causing the NAPL to snap off (Wilson et al, 1990). This is referred to as singlet blob trapping and is illustrated in Figure 4a. If the pore space that the NAPL and water travel through is relatively constant in size, then the capillary force does not change significantly and the oil and water each remain continuous. This is

shown in Figure 4b. The NAPL can also be trapped when a pore is bypassed. This simply means there is more than one path through which the contaminant and water can travel. The contaminant and water enter the smaller pore path first due to capillary forces (Corey, 1986)(Hunt, et al, 1988). The fluids may then follow the same path, or enter through another pore path. After the NAPL and water have entered both paths, the larger path becomes less resistant to the fluids and thus, the smaller pore path is bypassed leaving the residual trapped in the pore. This is shown in Figure 4c. The two different types of trapping can also occur together. The bypassing could take place in the larger path with the pore size varying, snapping off the NAPL (Wilson, et al, 1990)(Hunt, et al, 1988). It is important to understand that the percentage of residual that will be trapped is determined by these two trapping mechanisms and the variability of soil from place to place. Thus, by using uniform, spherical glass beads, the variability in soil from place to place is practically eliminated and a more accurate estimate of the percentage of trapped residual contaminant can be made.

The contaminant used in the experiment was normal dodecane. This was used due to its low solubility, its relative safety compared to other types of LNAPL, and its low volatility. The dodecane was dyed red with Oil Red O, biological stain. Glass beads were soaked in this oil-dye mixture for three days and then visually examined to ensure that the dye would not color the beads red; it did not. The interfacial tension between the dodecane and water is 52.8 mN/m at 25 °C. This number will vary some at a temperature of 0 °C (next to the freeze front), however, will not change significantly. This value is used in the equation for capillary number (Eq. 2) to gain an estimate of the velocity required for the residual to begin mobilization.

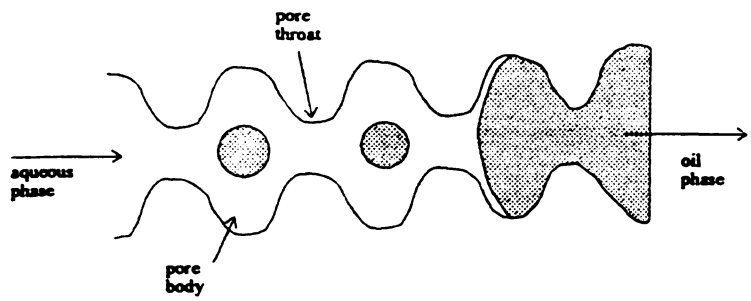

Figure 4a: Singlet Blob Trapping

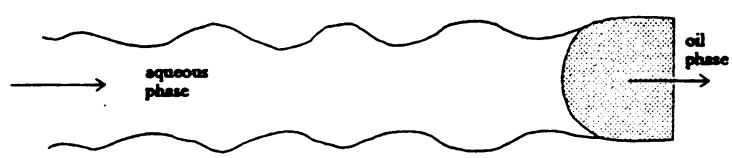

Figure 4b: Constant Size Pore Space

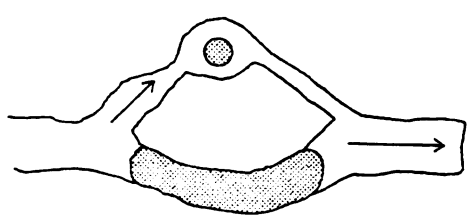

Figure 4c: Bypass Trapping

CHAPTER 3

EXPERIMENTAL SETUP

To determine how the experimental system would be set up and what would be included in it's design, the objectives stated in Section 1.4 were examined closely. In addition to the objectives, there were physical features that were also desirable. These objectives include designing the cell so that pictures could be taken to show the exclusion process of the ice on the residual dodecane, and creating a horizontal freeze front similar to that applied in the field. Ideal components for the system were then investigated to determine their feasibility of using them. Limitations on these components resulted mainly from excessive cost. In these cases alternatives had to be created and/or found and used. Specifics are explained in the following sections.

3.1 Description of Apparatus and Instrumentation

The entire system consisted of a cooling process, a temperature measurement system, the cell itself, and a water flushing system. A schematic of the experimental system is shown in Figure 5. The cooling system consisted of a coolant tank and four 2 inch diameter copper tubes with valves. The coolant tank held 48 gallons of a 50/50 mixture of antifreeze and water and was maintained at a temperature of -24.5 °C (+/- 2 °C). A pump was included on the coolant tank to pump the coolant mixture through the copper tubing. The copper tubing was flattened, providing a width of 3 1/8 inches (7.9 cm) of copper to be in direct contact with the glass of the cell. This tubing couuld not be flattened perfectly, thus, allowing only 50 percent of the copper (1.56 in or 3.95 cm) to be in direct contact with the glass. This is the reason that such a large diameter tube

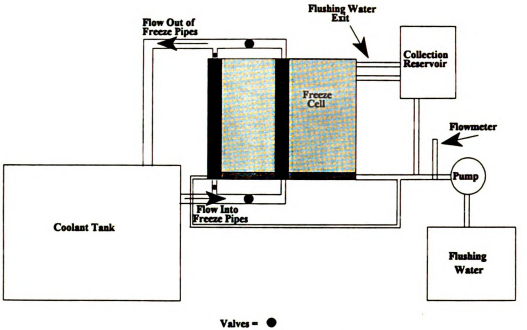

Figure 5: Schematic of Experimental System

was chosen. The ends of the tubing were kept round to allow a fitting to be placed on them easier. The tubing was placed on both sides of the cell with two tubes per side and each tube directly opposite another as shown in Figure 6. The copper tubes were bent out at the ends because the cell was so narrow that the tubes could not be placed up against the glass without hitting the one directly opposite. Valves were included in the copper tubing system to allow coolant to be flushed through either the first set of tubes, the second set, or both. The entire cooling system was insulated with therma-cel insulation, 0.5 inches (1.27 cm) thick, which fit snugly around all the copper piping and Tygon™ tubing. The temperature measurement system consisted of 20 YSI precision thermistors (44033 with resistance of 2252 OHMS at 25 °C). The thermistors were obtained from Newark Electronics in Grand Rapids, Michigan. Three conductor thermistor wire was used with the thermistors. It was obtained from S.W. Controls in

Plymouth, Michigan. The wire was cut into 20-6.5 foot (2.2 m) pieces, the ends stripped, the wires ohmed to determine which two of the three wires would be used, and then the ends soldered to the thermistors. A heat sink was used when soldering the wire to the

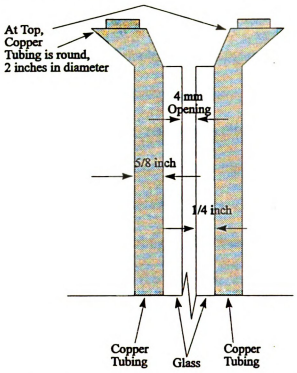

Figure 6: Profile of the Copper Tubing Placement

thermistors so that the thermistors would not be damaged. A water proof shrink tube was then placed over the wires to aid in protecting them from the water and ice. An oil resistant silicon sealant was then used to ensure the thermistor and wire would remain waterproof. The thermistors were calibrated using a 0 °C ice bath. Because the resistance measured by the thermistors was linear, only this calibration was required. To ensure this linearity, a thermistor reading, with the calibration from the 0° C ice bath already applied, was taken at room temperature and was then compared with two different thermometers. The three temperatures read to within 0.2 °C of each other, supporting that this linearity was indeed correct. During the experimentation, a logging

multimeter was used to read the thermistors. This machine read to the nearest 0.1 °C and was accurate to plus or minus 0.3 °C for temperature ranges of -80 °C to + 80 °C.

The cell consisted of two glass sides 1/4 inch thick, two plexiglass ends variable in thickness, and a plexiglass bottom also variable in thickness. Two plexiglass sides that fit around the copper tubing were then placed against the glass on each side to help support it. An inflow valve was provided on each side of the cell, while two outflow valves were included on one side of the cell. Along the bottom of the cell, a wire screen was placed (Figure 7a and b) to allow the water entering the cell to pass freely into the cell. This wire mesh was fine enough to keep the glass beads from penetrating through it, but still allowed water to pass freely through. This free flow of water into the cell allowed for an even distribution across the cell. This, in turn, allowed a relatively homogeneous residual to be set up as well as consistent flushing from one experiment to the next.

Three different sealants were used to try and seal the cell. The first was a silicon sealant (aquarium sealant) which appeared to seal the cell until the NAPL was added. Since the NAPL was oil based, it deteriorated the adhesiveness of the sealant to the glass and plexiglass. The second sealant used was Leak Lock™. This was chosen due to its resistance to oil, however, it did not adhere well to the glass or plexiglass. Finally, a third sealant, Ultra Blue Silicon Sealant, was used. This sealant is used primarily in the automotive industry, is readily available, adheres to most anything, and can withstand temperatures of -80 to 500 °F. This last sealant effectively sealed the cell.

The water flushing system used for this cell was designed with three primary needs in mind. The first was to provide an effective way to saturate the cell with water, dodecane,

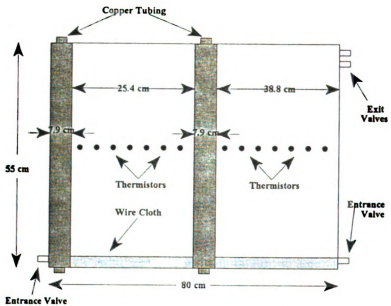

Figure 7a: Schematic of the Cell with Thermistors and Wire Screen

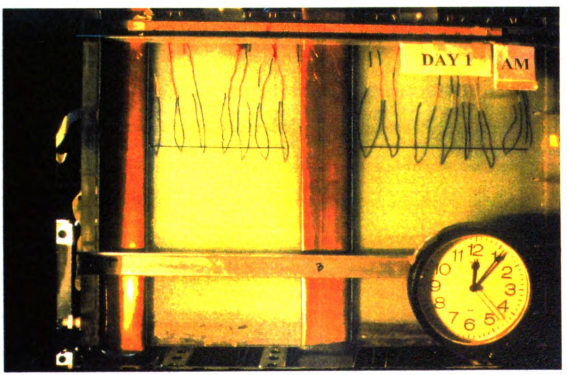

Figure 7b: Photo of Cell with Thermistors and Wire Screen

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and then again with water. The second was to flush the dodecane away from the freeze front as it advanced, and to provide enough water for the freeze front to remain continuous. The third need was to allow drainage of the cell if required. The final system, as used in the experimentation, can be seen in Figure 5. This system which was created pumped deionized water (using a Cole-Parmer variable speed drive with pressure loaded pump head, model number G-07144-05) into a direct reading flowmeter (Cole Parmer, model number G-32012-33), through a three-way valve, and finally through a T-valve which led to both cell entrances. The water was pumped through the three-way valve and allowed to flow either into the cell or into a collection reservoir by simply turning the valve. This three-way valve also allowed for drainage of the cell when setting up the residual and when completing the experiment and emptying the cell.

Deionized water was used in the experiments because of results from previous experiments. In the experiment conducted by Soehnlen (1991), regular tap water was used and the minerals in the water were expelled along with the residual contaminant as the freeze front advanced. In effect, this created two contaminants in the experiment. To simplify the problem and concentrate on removal of the NAPL, deionized water was employed. The water was pre-cooled in a cold room and then moved back and forth between a cooler with ice and a freezer to maintain the temperature. The temperature of the water was maintained at 10.5 °C (+/- 1.5 °C). This temperature range was selected because it is close to the temperature of ground water which would be the most preferable water source in a field situation because it is the most inexpensive. The last experimental run was performed with a water temperature of 0 °C to examine the effect of a colder flushing water temperature on the effectiveness of removing the trapped residual NAPL.

3.2 Experimental Procedure

To accomplish the stated objectives, contaminant and non-contaminant experiments were run using seven different capillary numbers and corresponding flushing rates as shown in Table 1. Contaminant and non-contaminant runs were used for several different reasons. The main reason was to compare the frozen and unfrozen gradients in both cases and determine if they were the same or if the presence of a NAPL affected them. Another reason for using both cases was to gain gradient data more quickly. In the case without NAPLs present, it was easy to run the experiments quickly because no clean up was necessary after each experimental run. The only time necessary between experiments was the time it took the porous media to thaw. However, in the case of a contaminant run, the cell and the glass beads had to be emptied and cleaned in between each experimental run. It was also beneficial to run the non-contaminant experiments first to get the "bugs"' out of the system before introducing the NAPL, which would cause a greater amount of time to be spent not only fixing the problem, but, also cleaning it up.

Capillary Number	0.00000	0.00011	0.00020	0.00028	0.00030	0.00037	0.00045
Flow Rate (ml/min)	0	19	35	49	53	65	79

Table 1: Capillary Numbers and Corresponding Flushing Rates

The first step in running a non-contaminant experiment was to place 18 thermistors in the cell, 1 in the antifreeze, and 1 in the flushing water. These thermistors were uniformly spaced 1 to 1 1/2 inches (2.5 to 3.75 cm) apart in the cell. The glass beads

were then poured into the cell around the thermistors. Once the cell was full of dry glass beads, the cell was saturated using the pump and flushing water system and prodded with a narrow metal rod to eliminate any air pockets. Glass beads were then added as needed to fill the cell to the first exit valve. Once the media was set up in the cell, initial thermistor readings were taken, including the temperature of the antifreeze and the flushing water. Next, styrofoam insulation (1 1/2 inches, 3.81 cm, thick) was placed completely around the cell in two layers, including over the top and bottom of the cell. Finally, the pumping of the coolant and the flushing water were started simultaneously. Thermistor and flowmeter readings were taken more frequently at the beginning of the experiment and less frequently as the freeze front advanced. This was done because the freeze front advanced very quickly at first and then continually slowed down. To maintain a constant flow rate, the flow was reduced proportionally as the freeze front advanced and reduced the area over which the flow could enter the cell. This reduction was based on determining the seepage velocity from a capillary number. The readings were stopped when either the freeze front advanced the entire length of the cell, or until the freeze front reached a point where it could not advance any further, i.e. the point of equilibrium. In the initial experiments, the flow rate was decreased once this point of equilibrium was reached in order to gain an understanding of the speed of the freeze front and how much variations in the flow rate would affect it. At each different flow, readings were taken for a minimum of two days to ensure equilibrium had indeed been met.

For a contaminant run, the thermistors and glass beads were placed in the cell as the cell was saturated as in the non-contaminant run, and the locations of the thermistors

were again measured. The dodecane was then evenly applied along the top of the cell as the water table was slowly lowered. Once the cell was saturated with dodecane, the water table was slowly raised. The rate at which the water table was decreased and raised were monitored. The free oil was removed by raising the water table allowing the oil to float to the surface of the water and then collecting it so that a percent of residual could be found. This value was then compared with tabulated values of percent residual remaining depending on the speed of the water acting as the water table. Again thermistor readings were taken periodically depending on the rate of freeze front advancement. Figure 8a shows the initial saturation of the cell with dodecane. The water table is being lowered and the residual is being added from the top of the cell. The residual is less dense than water, and thus, will only travel as far down in the cell as the water has gone. Figure 8b shows the cell completely saturated with dodecane while Figure 8c shows the residual being left behind as water is pumped back into the cell removing the free dodecane. Next, in the contaminant experiment, the freeze pipes and flushing water were then started simultaneously. Again, the rate of flushing water was determined based on the capillary number and the initial capillary number value was based on the graphs in Figure 3. The capillary number values were then varied to allow different flow rates to be attempted. These values were the same ones used for the non-contaminant runs (Table 1).

Figure 8a: Water Saturated Cell with Initial Introduction of Contaminant

Figure 8b: Dodecane Saturated Cell

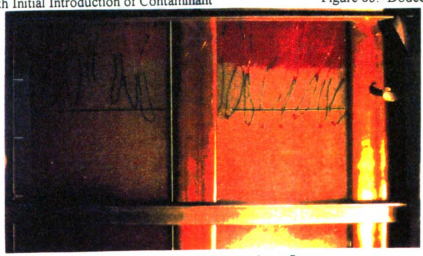

Figure 8c: Residual Contaminant Setup

CHAPTER 4

DISCUSSION OF RESULTS

The two main objectives of this project, as stated in the scope of the investigation, were to gain an understanding of the frozen and unfrozen gradients in the media with and without residual, and to determine how effective the controlled freezing process is at removing residual contaminant.

4.1 The Frozen and Unfrozen Gradient

The gradient data gathered for all experimental runs is presented in Table 2. This table lists the capillary number (used to determine the flow rate and seepage velocity of the flushing water), whether dodecane residual was set up for the experimental run, and the measured frozen and unfrozen gradients for the "Close-up" and "Entire" graphs in °C/in and °C/cm. The range of capillary numbers used was based upon data from Figure 3 as explained in Chapter 3. The capillary number of 0.00030 was used primarily because this is the average value calculated from the graphs in Figure 3. The specifics of obtaining this number are discussed in greater detail in Chapter 3.

Obtaining frozen and unfrozen gradient data is an important aspect of this research. Gradient data can be used in a controlled freezing remediation field application to aid in replicating a successful experimental cleansing process. If accurate gradient values can be obtained through experimentation, the speed at which the freeze front should propagate to successfully remove the contaminant can be reproduced. Also, it is necessary to understand the seepage velocity of water required to flush the freed residual contaminant to the ground surface. This seepage velocity also affects the freezing rate. Therefore, many different factors are occurring which all interact and ultimately define

the gradients. Thus, to effectively use the gradient in a field application, a common correlation is needed that relates the parameters to each other and to the gradient. These successful gradient parameters become essential in a field application because the entire process will be done completely under the ground and out of view. For example, it is desirable to not only determine at what freezing rate residual contaminant is successfully removed, but, also to understand whether this rate should be maintained by a very cold freeze pipe with a very high flushing water seepage velocity or with a freeze pipe that is not as cold with flushing water that has a lower seepage velocity, or some other optimum combination.

The gradient values were determined by graphing the temperature measurements of each thermistor versus the thermistor locations in the cell. The readings taken were read from a data logger which read to within +/- 0.3°C. The thermistors themselves had a negligible error, while the thermistor wire was not long enough to affect the data. Therefore, the uncertainty for the gradient values was based on only one factor. Thus, the uncertainty is small for the gradient data portion of the experiment. In Figures 9 and 10, the thermistor locations are represented by the individual marks (i.e., circles, squares, x's, etc.). These values were then plotted over time as shown by each line in Figures 9 and 10. The headings "Close-up" and "Entire" listed in Table 2 refer to two separate graphs that were plotted for each experimental run. Figure 9 shows the experimental data plotted over the entire cell length for a particular run, while Figure 10 shows only data close to the 0°C isotherm (i.e. data over a smaller range of cell length) plotted for a particular run. Examples of this are shown in Figure 9 which shows the experimental data over the entire cell length (30 in., 76 cm) plotted for a run with no dodecane and no

Capillary Number	Dodecane (Y or N)	Frozen (dT/dx) in (deg C/in) Close-up	Frozen (dT/dx) in (deg C/in) Entire	Frozen (dT/dx) in (deg C/cm) Close-up	Frozen (dT/dx) in (deg C/cm) Entire	Unfrozen (dT/dx) in (deg C/in) Close-up	Unfrozen (dT/dx) in (deg C/in) Entire	Unfrozen (dT/dx) in (deg C/cm) Close-up	Unfrozen (dT/dx) in (deg C/cm) Entire
0.00045	Y	8.16	8.40	3.21	3.31	5.90	5.53	2.32	2.18
0.00037	N	7.85	8.00	3.09	3.15	5.85	5.82	2.30	2.29
0.00037	Y	6.16	6.41	2.43	2.52	4.67	4.47	1.84	1.76
0.00037	Y	7.74	7.83	3.05	3.08	6.25	4.27	2.46	1.68
0.00030	N	3.43	4.33	1.35	1.70	2.62	3.16	1.03	1.24
0.00030	N	5.71	5.44	2.25	2.14	4.13	4.08	1.63	1.61
0.00030	Y	7.14	7.14	2.81	2.81	4.79	4.33	1.89	1.70
0.00030	Y	4.44	4.40	1.75	1.73	3.64	3.30	1.43	1.30
0.00030	Y	4.64	5.00	1.83	1.97	2.32	3.08	0.91	1.21
0.00030*	Y	3.09	2.71	1.22	1.07	2.19	2.11	0.86	0.83
0.00028	N	3.76	4.44	1.48	1.75	3.26	3.12	1.28	1.23
0.00028	Y	7.22	7.29	2.84	2.87	6.29	5.93	2.48	2.33
0.00020	N	2.91	2.91	1.15	1.15	2.17	2.17	0.85	0.85
0.00011	N	2.32	2.32	0.91	0.91	1.21	1.21	0.48	0.48

* Indicates flushing water temperature used in experiment was 0° C
Table 2: Frozen and Unfrozen Gradients, With and Without Dodecane

seepage velocity ($N_c = 0$), and Figure 10 which uses the same data from the same experimental run, however, only experimental data around the 0° C isotherm (12 in, 30.5 cm) is plotted. These two graphs were plotted to gain a more accurate estimate of the gradient. As the freeze front reached equilibrium, the coolant temperature fluctuated as discussed in Chapter 3, thus, the last reading was not necessarily the furthest distance the

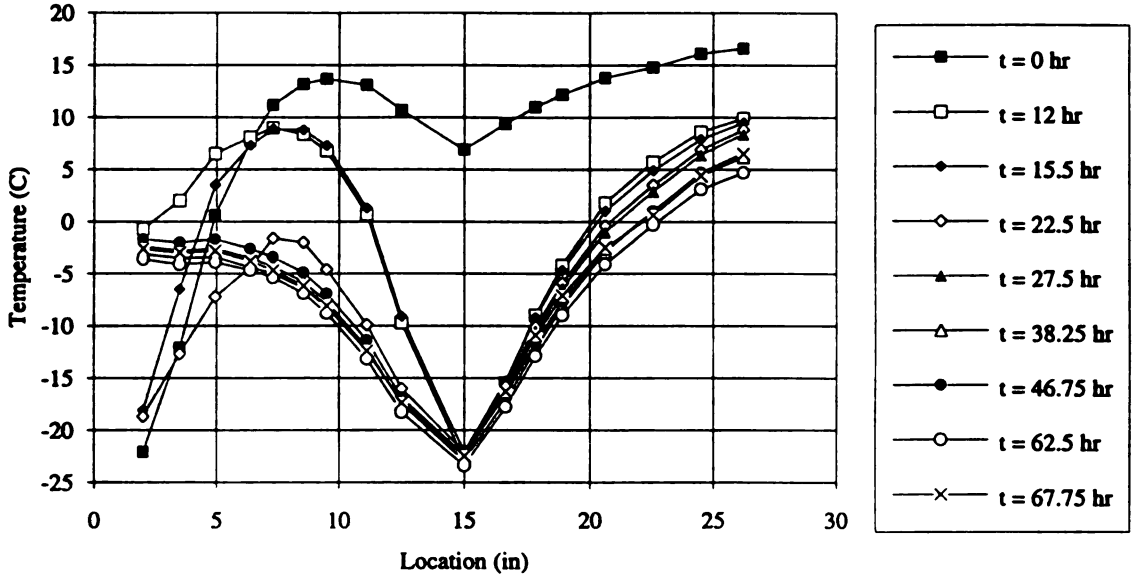

Figure 9: Temperature vs Location for Flow = 0 ml/min with Dodecane

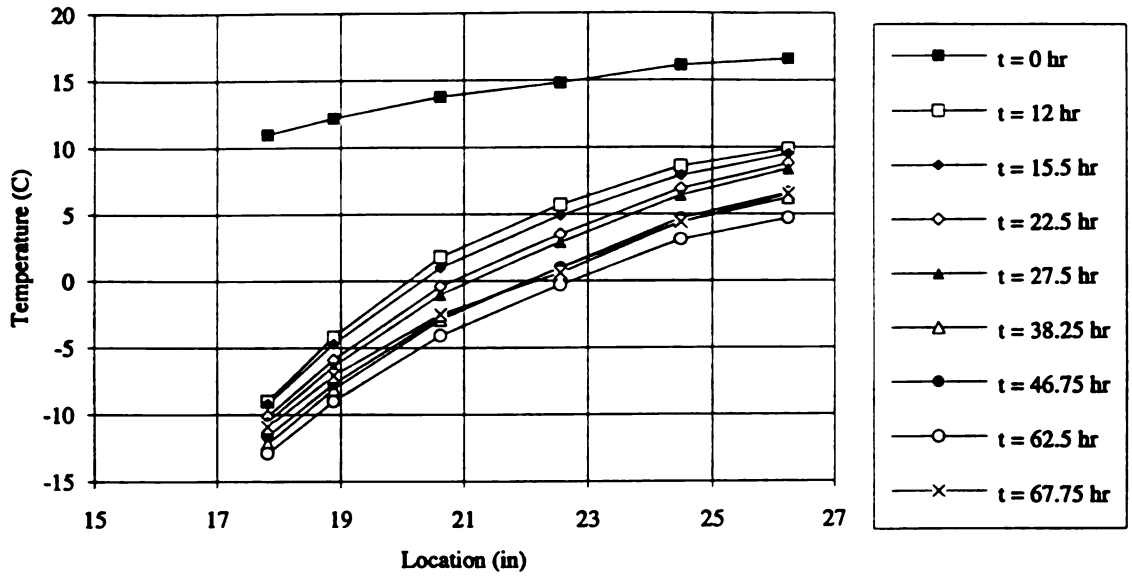

Figure 10: Temperature vs Location for Flow = 0 ml/min with Dodecane

freeze front had reached. For example in Figure 10, the line for t=62.5 hours crossed the 0°C mark at the furthest distance from the freeze pipe (22.7 in., 57.7 cm), however, the last reading taken was at t = 67.75 hours and crosses 0°C closer to the freeze pipes (22.2 in., 56.4 cm). Therefore, the two gradient values for a "Close-up" and "Entire" graph were averaged for each experimental run and both sets of graphs and the tabulated data are included in Appendix A.

The "Entire" and "Close-up" results from Table 2 were averaged and are shown in Table 3 along with a frozen to unfrozen gradient ratio and the capillary numbers. Many interesting trends can be seen in this table. The most obvious and consistent trend is that the frozen gradient is larger than the unfrozen gradient. This trend supports the fact that ice has a greater thermal conductivity than water, and therefore, the temperature change over a distance, x, should be greater in ice than the temperature change through water over the same distance, x. The ratio of unfrozen gradient to frozen gradient on average is 0.72, as shown in Table 3. This ratio remains fairly consistent throughout the data

indicating the change in capillary number does not effect the ratio between the two gradients. This relatively constant ratio can also be seen in Figures 11 and 12. The data for the frozen and unfrozen gradients is scattered over approximately the same total length only shifted over about 1 inch. Also, the distance between each individual point is similar for the frozen and unfrozen data.

The next consistent trend that can be seen from Table 2 and Figures 11 and 12, is that a higher capillary number gives a higher gradient value for both the frozen and unfrozen gradient. This can be explained because as the capillary number increases, the seepage velocity of the water entering the cell to flush the freed residual increases, thus, introducing more heat into the system. Therefore, the temperature will vary more over a distance, x. It would be logical to assume that the unfrozen gradient would vary more than the frozen gradient because of the flushing water entering only on the unfrozen side. However, this is not the case, possibly due to the fact that although the flushing water introduces more heat into the system, it was introduced fairly uniformly over entire the length of the unfrozen side. Therefore, each location on this side was affected in a similar manner. The flushing water process and design is explained in detail in Chapter 3.

Frozen Gradient (dT/dx) (deg C/in)	Frozen Gradient (dT/dx) (deg C/cm)	Unfrozen Gradient (dT/dx) (deg C/in)	Unfrozen Gradient (dT/dx) (deg C/cm)	Capillary Number	Ratio of Unfrozen to Frozen Gradient
8.28	3.26	5.72	2.25	0.00045	0.69
7.93	3.12	5.84	2.30	0.00037	0.74
6.29	2.47	4.57	1.80	0.00037	0.73
7.79	3.06	5.26	2.07	0.00037	0.68
3.88	1.53	2.89	1.14	0.00030	0.74
5.58	2.19	4.11	1.62	0.00030	0.74
7.14	2.81	4.56	1.80	0.00030	0.64
4.42	1.74	3.47	1.37	0.00030	0.79
4.82	1.90	2.70	1.06	0.00030	0.56
2.90	1.14	2.15	0.85	0.00030	0.74
4.10	1.61	3.19	1.26	0.00028	0.78
7.26	2.86	6.11	2.41	0.00028	0.84
2.91	1.15	2.17	0.85	0.00020	0.75
2.32	0.91	1.21	0.48	0.00011	0.52

Table 3: Capillary Number, Average Gradients, and Ratio between Gradients

Capillary Number

Capillary Number

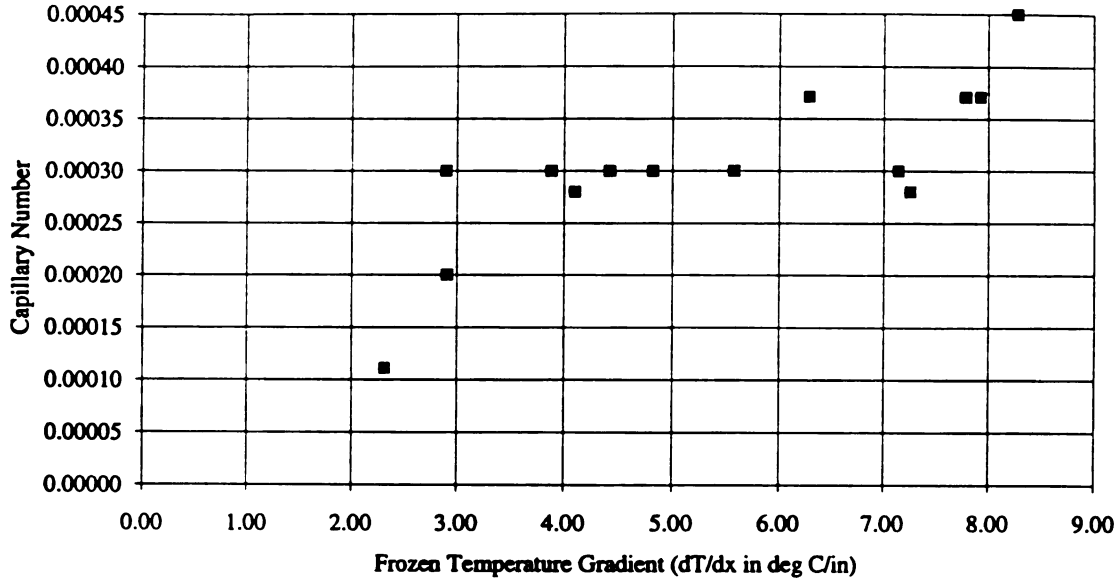

Figure 11: Capillary Number vs Frozen Temperature Gradient

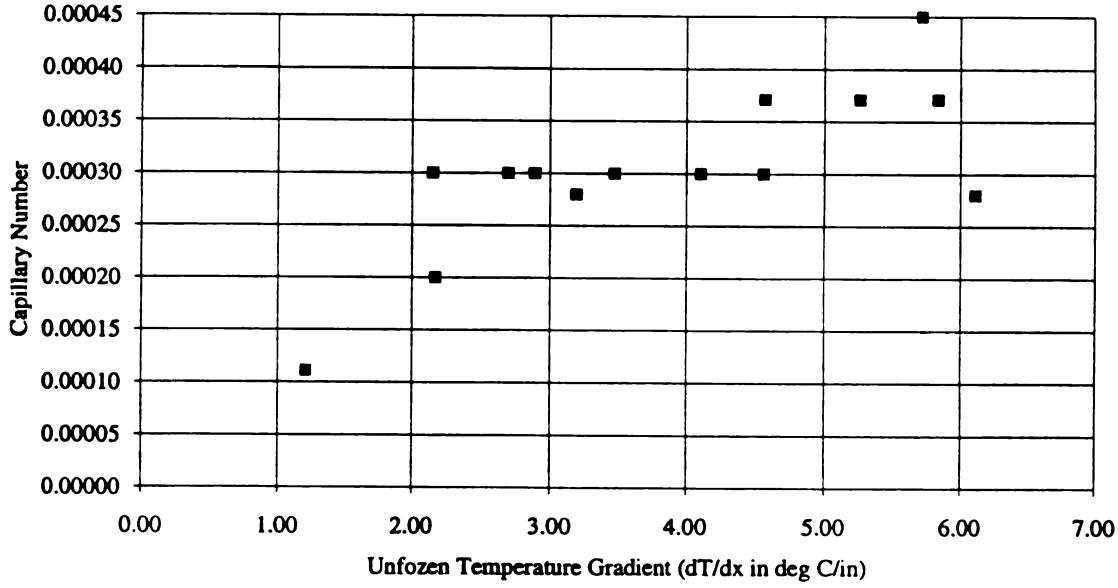

Figure 12: Capillary Number vs Unfrozen Temperature Gradient

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Now that the basic trends have been examined and established, it is desirable to examine the different variations in the experimental procedure that may have affected either the frozen or unfrozen gradient. The first of these variations is whether the presence of dodecane residual had any effect on the frozen or unfrozen gradients. This can be examined by looking at Table 2, which indicates which experiments used dodecane. Comparing the experimental runs with and without dodecane for the same capillary number, no distinct difference can be seen. There is some difference, however not substantial or consistent enough to conclude that its presence affects the gradient values. For the most part, the differences appear to be minor and could easily be caused by the minor variances which make exact reproduction of the experimental runs extremely difficult to achieve. Also, the presence of dodecane residual in the system is small when compared to the volume of water and glass beads used, and would not be expected to noticeably affect the gradient. The results seem to support this.

Another variation in the experimental procedure was to use flushing water at 0°C. Although a temperature of 9 to 12 °C is much more reasonable to use in this experiment, because this is closer to the temperature of ground water which would most likely be used in a field situation involving this process, it is still desirable to examine how other flushing water temperatures effect the results of this experiment. Only one experimental run, shown in Table 2, was performed using a flushing water of 0°C. The frozen gradient values (in °C/cm) are 1.22 for the "Close up" and 1.07 for the "Entire", while the unfrozen values are 0.86 and 0.83 respectively for this particular run. The values are substantially below the other frozen and unfrozen gradient values obtained for this

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capillary number. This occurs because a colder flushing water temperature is introduced into the system and is closer to the freezing temperatures that are ultimately achieved.

4.2 Rate of Freeze Front Advancement

From previous research by Soehnlen (1991), an optimum rate of freeze front advancement was obtained. The cell in Soehnlen's experiments was slowly lowered into the freeze tank at different rates. The optimum rate was determined by visually observing how much residual was pushed out in front of the freeze front and how much was left behind in the frozen media. The setup and process of Soehnlen's experiment is explained in greater detail in Section 1.2. The optimum rate from his research was determined to be 0.8 cm/day (0.033 mm/hr). In the current experimentation, the freezing system was set up to freeze horizontally across the cell, instead of vertically up it as in the past research. This difference in freezing technique, and the introduction of a flushing water system, did not allow for precise control of the freeze front rate. When the freezing system was first turned on, up to 5 cm of the media on each side of the copper freeze pipe would freeze very quickly. However, over time, the freeze rate would decrease until equilibrium was met, meaning all of the heat possible was being extracted from the media with the freezing system and therefore, the freeze front could not progress any further. It would have been theoretically possible to control the rate at which the media froze simply by controlling the flushing water entering the system. By increasing the flow, which means an increase in seepage velocity and capillary number, more heat can be introduced into the system and thus balance the heat being extracted by the freeze pipes. This seepage velocity could then slowly, at any desirable rate, be reduced, thus

allowing the freeze front to advance. However, to equalize the heat extraction energy of the freeze pipes at the beginning of the experiment, a large flow would be required. The pump chosen for the experiment could not supply the flow required. The pump variable speed is explained in the experimental setup in Chapter 3. Its range was chosen based on what capillary numbers would most effectively aid in removing the residual contaminant, not for controlling the rate of freezing. There were no pumps available that covered the broad range that would be required and that were also within the budget of this research. Rates of freeze front advancement were determined for this experiment anyway so that a comparison with the results of Soehnlen could be made. These rates are shown in Tables 4, 5, and 6 both in cm/hr and in/hr for all of the experimental runs and one run is shown graphically in Figure 13. The data in Tables 4, 5, and 6 is all graphed and included in Appendix B. These freeze rates were obtained by looking at the net movement of the frost line for each timed reading. The exact location of the frost line at the time each temperature reading was taken was determined by interpolation from the thermistor readings. The rate of freeze front advancement varied over each experimental run. The advancement rates were fast at first and then slowed down. It is not until the rates slow down substantially, i.e. towards the end of the experiments, that they approach the 0.8 cm/day rate that Soehnlen, determined to be the most effective. Figures 9, 10, all of the figures in Appendix A, and all of the figures in Appendix B also show this in different ways. In figures from Appendix A, the lines that indicate each time temperature readings were taken start further apart and slowly become grouped together. Therefore, it is still desirable to create a freeze front traveling horizontally at around 0.8 cm/day with a system that will flush the freed residual. This should be examined to determine whether

Freeze Front Advancement with CN = 0

* With Dodecane Run #1					** Without Dodecane Run #1					* Without Dodecane Run #2				
Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Mvment (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)
0	0	0			0	0	0			0	0	0		
3.03	7.70	12.00	0.253	0.641	0.0800	0.203	3.50	0.0229	0.0581	3.12	7.92	8.67	0.360	0.914
1.28	3.25	3.50	0.366	0.929	2.68	6.81	16.00	0.168	0.425	0.520	1.32	7.83	0.0664	0.169
0.500	1.27	7.00	0.0714	0.181						0.310	0.787	4.50	0.0689	0.175
0.300	0.762	5.00	0.0600	0.152						0.180	0.457	4.17	0.0432	0.110
0.950	2.41	10.75	0.0884	0.224						0.150	0.381	4.00	0.0375	0.0953
										0.290	0.737	6.83	0.0425	0.108
										0.520	1.32	17.75	0.0293	0.0744

Freeze Front Advancement for CN = 0.00028

* With Dodecane					** Without Dodecane				
Net Mvment (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)
0	0	0			0	0	0		
2.84	7.21	3.25	0.874	2.22	0.880	2.24	5.50	0.160	0.406
0.571	1.45	8.33	0.0685	0.174	0.390	0.991	5.75	0.0678	0.172
-0.100	-0.254	7.92	-0.0126	-0.0321	0.100	0.254	7.25	0.0138	0.0350
0.200	0.508	7.00	0.0286	0.0726					
0.160	0.406	12.00	0.0133	0.0339					

* = Began readings at second freeze pipe

** = Began readings after first freeze pipe was already turned on

Table 4: Freeze Front Advancement for Capillary Numbers of 0 and 0.00028 With and Without Dodecane

Freeze Front Advancement for CN = 0.00030 with Dodecane

Run #1					Run #2				
Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)
0	0	0			0	0	0		
1.84	4.67	1.42	1.30	3.29	2.31	5.87	1.00	2.31	5.87
0.510	1.30	1.58	0.323	0.820	0.440	1.12	1.00	0.440	1.12
0.510	1.30	3.67	0.139	0.353	1.89	4.80	7.25	0.261	0.662
0.234	0.594	5.50	0.0425	0.108	0.400	1.02	1.75	0.229	0.581
0.240	0.610	5.33	0.0450	0.114	0.200	0.508	5.50	0.0364	0.0924
-0.0400	-0.102	3.33	-0.0120	-0.0305					

Run #3					Run #4				
Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)
0	0	0			0	0	0		
1.95	4.95	2.00	0.975	2.48	3.59	9.12	5.00	0.718	1.82
1.51	3.84	7.00	0.216	0.548	0.760	1.93	6.00	0.127	0.322
-0.120	-0.305	3.50	-0.0343	-0.0871	0.610	1.55	7.50	0.0813	0.207
					0.640	1.63	4.75	0.135	0.342
					0.0900	0.229	6.25	0.0144	0.0366

Freeze Front Advancement for CN of 0.00030 Without Dodecane

Run #1					Run #2				
Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)
0	0	0			0	0	0		
2.15	5.46	2.83	0.760	1.93	3.77	9.58	6.50	0.580	1.47
0.580	1.47	2.92	0.199	0.505	0.360	0.914	5.17	0.0696	0.177
0.590	1.50	3.92	0.151	0.382	-0.0300	-0.0762	4.50	-0.00667	-0.0169
0.930	2.36	5.33	0.174	0.443					
0.880	2.24	5.58	0.158	0.401					
0.390	0.991	5.67	0.0688	0.175					
0.100	0.254	7.33	0.0136	0.035					

* = Began readings at second freeze pipe

** = Began readings after first freeze pipe was already turned on

Table 5: Freeze Front Advancement for Capillary Number of 0.00030 With and Without Dodecane

Freeze Front Advancement for CN = 0.00037

* With Dodecane Run #1					* With Dodecane Run #2					* Without Dodecane Run #1				
Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)
0	0	0			0	0	0			0	0	0		
2.24	5.69	6.00	0.373	0.948	2.25	57.15	4.00	0.563	14.29	2.34	5.94	8.67	0.270	0.686
0.940	2.39	8.75	0.107	0.273	1.26	32.00	8.50	0.148	3.77	-0.0700	-0.178	7.83	-0.00894	-0.023
					-0.120	-3.05	4.50	-0.0267	-0.677					

Freeze Front Advancement for CN = 0.00045

* With Dodecane				
Net Mvment (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)
0	0	0		
1.82	4.62	2.50	0.728	1.85
0.530	1.35	5.50	0.0964	0.245
0.780	1.98	9.00	0.0867	0.220

* = Began readings at second freeze pipe

** = Began readings after first freeze pipe was already turned on

Table 6: Freeze Front Advancement for Capillary Numbers of 0.00037 and 0.00045 With and Without Dodecane

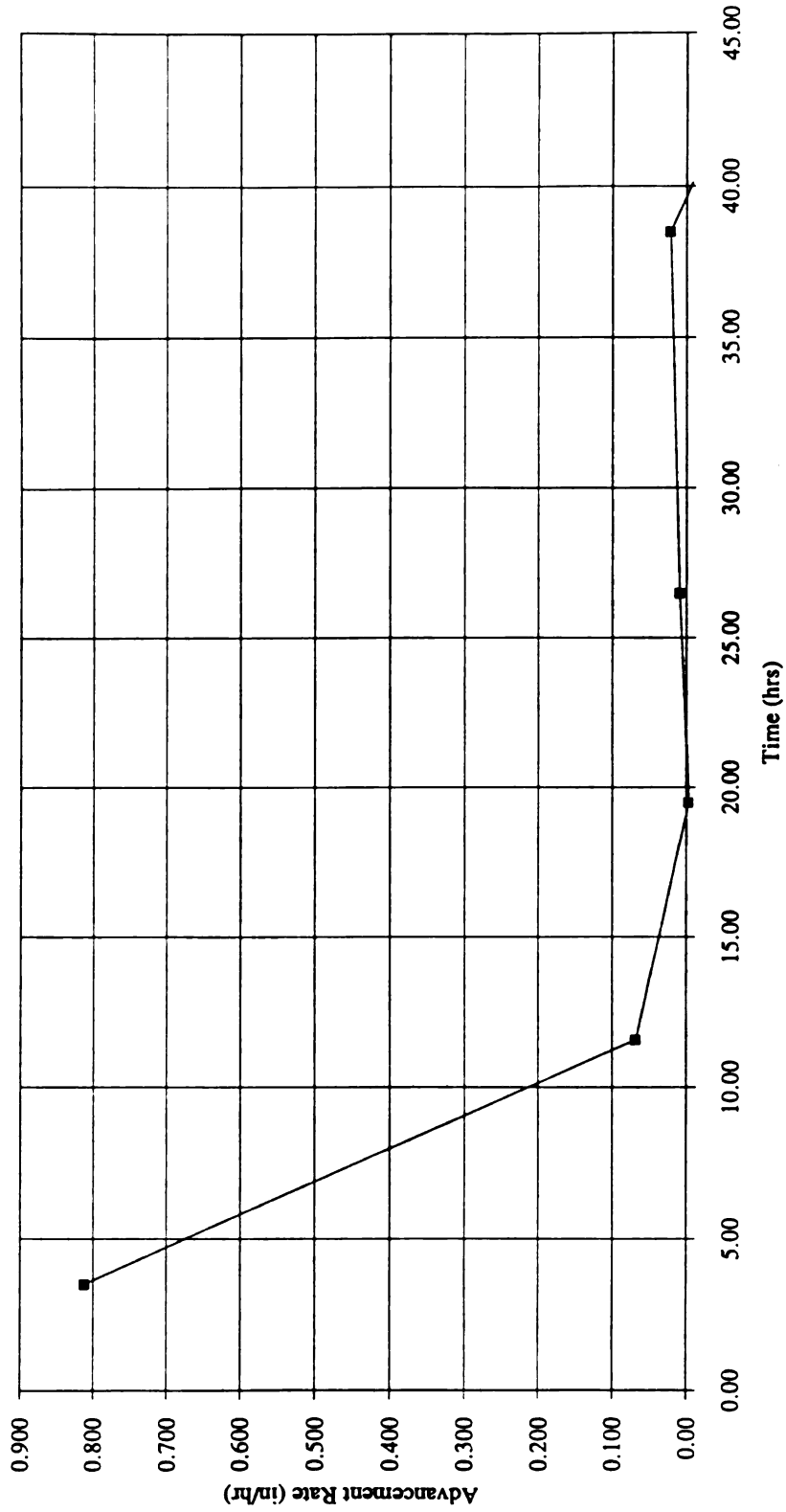


Figure 13: Advancement vs Time for Flow = 53 ml/min

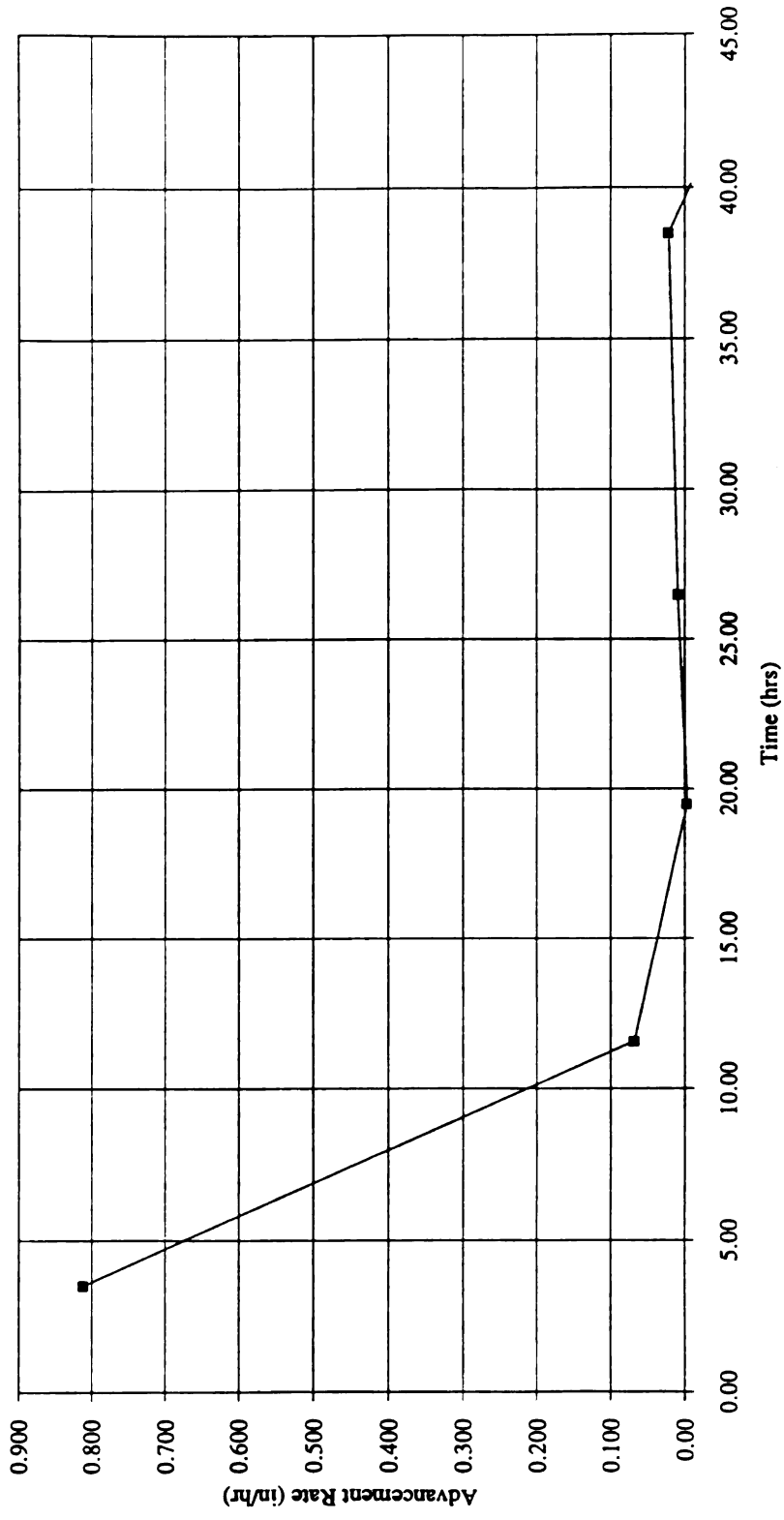


Figure 13: Advancement vs Time for Flow = 53 ml/min

or not this rate is the only one that will prove to be highly efficient, or even if it will improve the success of the controlled freezing technique over the results of this research. The effectiveness of removing trapped residual contaminant was not compared to or graphed against the freeze front advancement rate because it varied for each experiment. Instead, the capillary number was compared with the removal effectiveness. Removal effectiveness is the topic of the next section and will be discussed in greater detail there.

4.3 Contaminant Removal

The second and ultimate goal of this research was to determine if this proposed technique in contaminant removal was indeed effective and if so, how effective and under what conditions. The results of the research indicate that this method is effective, although not 100 percent efficient. There are many factors which give the results of this procedure a moderate range of uncertainty. While the percentage of removal results do not have to be precise to give a general idea of the success of this procedure, the inherent uncertainty is an important aspect in examining the true value of this removal technique. The uncertainty and the parameters affecting it will be examined later in this chapter.

The effectiveness of removal was obtained for five runs, three with a capillary number of 0.00030, one with a capillary number of 0.00037 and one with a capillary number of 0.00045. The results are presented in Table 7. The results vary widely, ranging from 76 percent down to 25 percent of the trapped residual contaminant that was removed after this controlled freezing technique was applied. The first of these five runs was the second overall experimental run performed using dodecane. The initial experimental run using dodecane provided no removal effectiveness results. This was due to minor problems throughout the experiment which did not allow collection of the residual contaminant that was removed by the freezing process to be done in a controlled

manner. While no data could be attained for this first trial, it appeared to effectively remove the residual contaminant by pushing it out in front of the freeze front. Also, very little residual appeared to remain in the frozen media. Thus, by visual observation,

Capillary Number	Residual Initial Total (ml)	Total Width (in)	Width Frozen (in)	Residual Within Width Frozen (ml)	Residual Removed From Width Frozen (ml)	Percent Removed
0.00045	120	30	2.01	8.1	2.0	25
0.00030	120	30	4.12	16.5	8.0	49
0.00030	95	30	2.50	7.9	6.0	76
0.00037	95	30	2.14	6.8	2.5	37
0.00030	125	30	4.56	19.0	5.0	26

Table 7: Removal Effectiveness

the removal of the contaminant seemed to be very effective. However, the second and third trials, with capillary numbers of 0.00045 and 0.00030 respectively, as shown in Table 7, did not perform in the same impressive manner that the first experimental run did. The removal effectiveness was only 25 and 49 percent respectively. After these two experiments, which obviously lacked repetitiveness, the method of cleaning the glass beads was examined and then modified. The cleaning method was altered to include a thorough cleaning in acetone that ensured the entire surface area of each glass bead came into contact with the acetone (for a more detailed description of the cleaning process, see the experimental procedure in Chapter 3). The fourth run was then made using the modified cleaning technique with the capillary number equal to 0.00030. Based on visual appearance, this run performed closely to the initial experimental run, although it was still not quite as visually impressive as the initial trial. This run had a removal

effectiveness of 76 percent. Figures 14 and 15 show this trial before and after freezing. Figure 14 shows the residual set up before the freezing process was started, while Figure 15 shows the freeze front after 2 hours. In Figure 15, the frost line is indicated by an arrow pointing to the leading edge of it. The buildup of residual just past the frost line into the unfrozen media indicates that the freeze front is indeed freeing the trapped residual and pushing it out in front. Some residual is still apparent in the frozen media, however, it is considerably less than the initial amount on the unfrozen side.

The results from Table 7 appear to demonstrate only one somewhat predictable occurrence. This is the improved removal effectiveness of the freezing process after the glass beads were cleaned in acetone for the first time. This improved cleaning technique seemed to greatly improve the removal effectiveness. However, the next two runs did not show the same results. From this observation, the cleanliness of the glass beads becomes an extremely important variable. It would be impossible to determine how clean the beads actually were before each experiment without a great deal of time and extra equipment. It is also difficult to determine how much the experiments were affected by the adsorption of dodecane by the glass beads. The presence of dodecane coating the beads initially would alter the interfacial tensions that normally occur in the porous media. This fact alone could have made this controlled freezing process much less effective. The total uncertainty of the experiment should be examined to determine how much the removal effectiveness may have been affected.

The results from Table 7 are graphed in Figure 16. This figure illustrates that none of the capillary numbers used had a conclusive effect on the removal effectiveness under these experimental conditions and constraints. It is important to remember that these

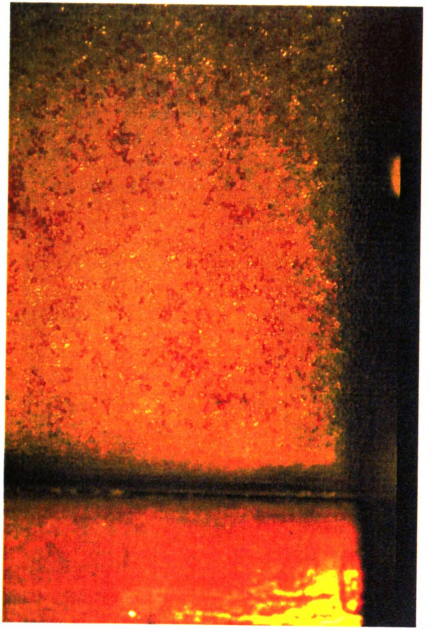


Figure 14 Picture of Residual Setup Before Freezing

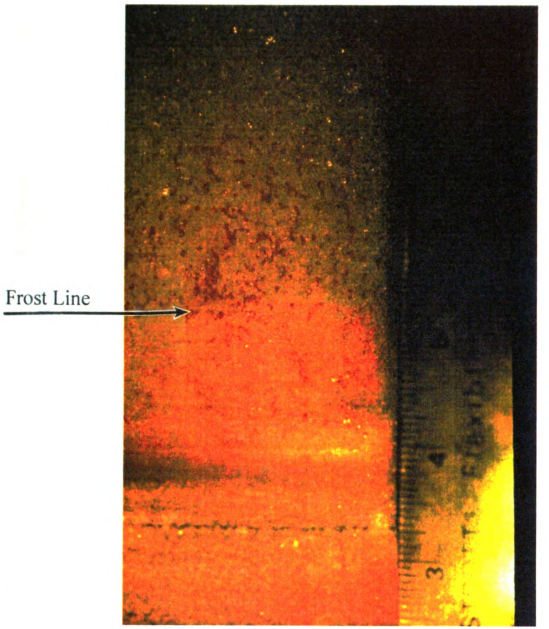


Figure 15: Picture of Residual Setup After Freezing

results include two experimental runs in which there is uncertainty in the cleanliness of the beads. This figure does not show anything else unusual that could not be seen in Table 7. It does reveal the fact that this method has some effectiveness on the removal of residual contaminant from a porous media and presents the results in an illustrative manner.

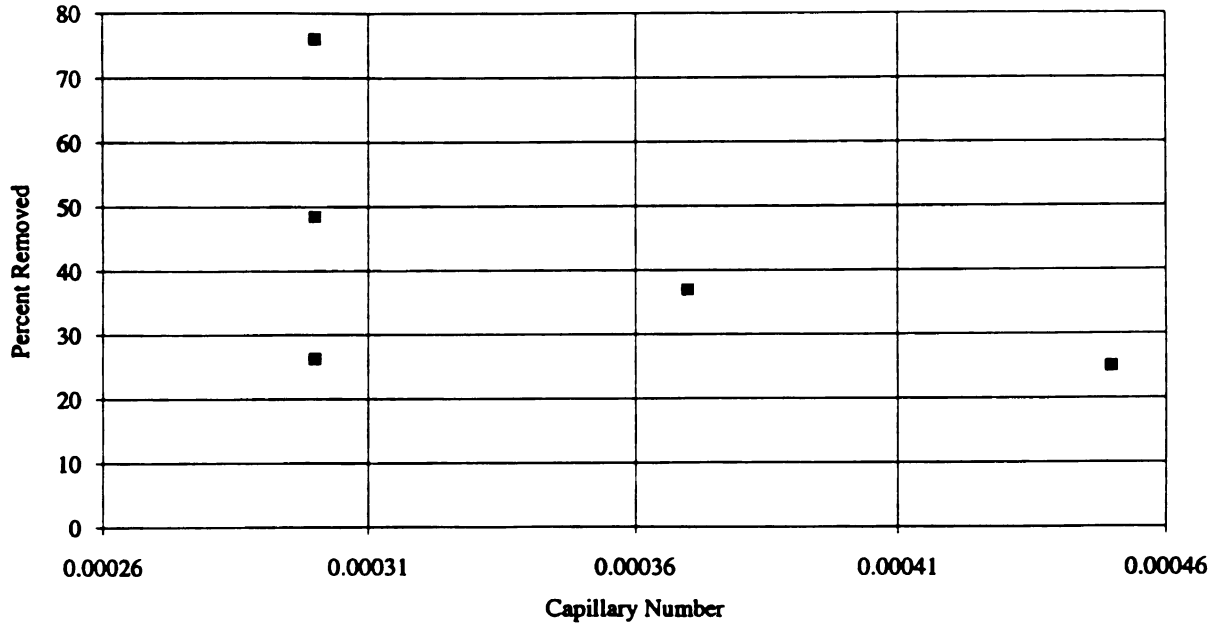


Figure 16: Percent Removed versus Capillary Number

4.4 Uncertainty

As mentioned at the beginning of this chapter, there is a moderate uncertainty attached to these results. Because uncertainty is based on the uncertainty of the individual items that are used to determine the end value, the uncertainty of each item used in the equations or process of obtaining the removal effectiveness results needs to be examined. The most basic uncertainty in the experimental process that effects the

removal effectiveness is transferring the dodecane from container to container and accurately measuring its volume. The beakers and graduated cylinders used to measure the dodecane were graduated and could be read to the nearest 0.5 ml. However, when retrieving the dodecane that had been removed by the freezing process, it was collected with large amounts of water. The water and dodecane were then separated and the dodecane measured in a graduated cylinder. This process involved collecting the water and dodecane in a 5 gallon plastic container, pouring this into a glass separator and then pouring whatever dodecane was removed into a graduated cylinder. Warm water was used to rinse each container to remove any remaining dodecane, however, because of the small amount of dodecane recovered and the large container, any extra that remained on the sides of the plastic or glass could greatly effect the final measurement.

The next place there is uncertainty is in the final calculation for percent removal. This calculation is the amount of dodecane recovered divided by the amount of residual contaminant within the area of media frozen during the experiment. In order to determine the amount of residual within the frozen area, the assumption must be made that the residual contaminant is homogeneously distributed throughout the cell. This assumption must be made because a known amount of residual was set up in the cell over the entire area. There is no way to determine exactly how much is in each area of the cell. From visual observation, this assumption of homogeneity appears to be true, however, it is not realistic to assume that the residual contaminant is perfectly homogeneous. However, it is probably se and would thus, not affect the percent removal results substantially.

The controlled freezing process does remove residual contaminant from a porous media. However, the extent of its efficiency is not totally understood. From the uncertainty variables, it appears that the results are within a small uncertainty range. Only a vague value can be placed on the uncertainty because the uncertainty of the variables are difficult to place values on. However, as an estimate, an uncertainty of 10 percent seems reasonable. This uncertainty does not affect the results of this research significantly because the values obtained are only indications of the effectiveness of this freezing process, and they are by no means final answers to a complex problem.

CHAPTER 5

FIELD APPLICATIONS

The goals of this research were to determine how effective this controlled freezing method is at removing trapped residual contaminant and to obtain gradient information. The gradient information is what will allow the successful experimental procedure to applied effectively in the field. The utilization of vertical freeze pipes to create a horizontal freeze wall and the use of water to flush the freed contaminant makes the gradient data even more similar to what would be used in the field.

5.1 Field Setup and Arrangement

There are a couple possible setups for a field site as shown in Figures 17 and 18. In Figure 17, the horizontal freeze pipes are placed throughout the bottom of the decontamination area and around the sides, forming a box. Freeze pipes are then placed symmetrically throughout the box along with injection wells in a pattern as shown in Figure 19a. The pipes around and under the box would then be frozen and have water added into the enclosed box until it is saturated. At this point the interior freeze pipes sould be turned on along with the injection wells. Figure 19b shows how the area would be frozen over time. The contaminant would then be collected at the surface as it is removed.

Figure 18 shows another possible setup which is similar to Figure 17, except that the sides that enclose the contaminated area are angled toward each other forming a point at the bottom. The freeze pipes and injector wells are placed throughout the contaminated area again as in Figure 19b.

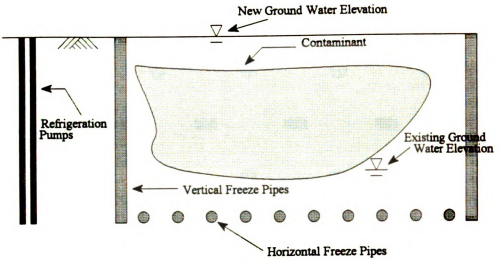
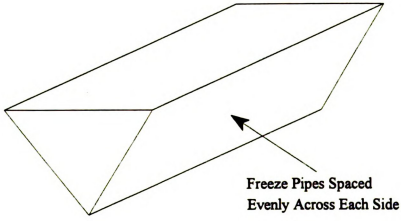


Figure 17: Possible Field Setup For Decontamination
After Andersland 1991



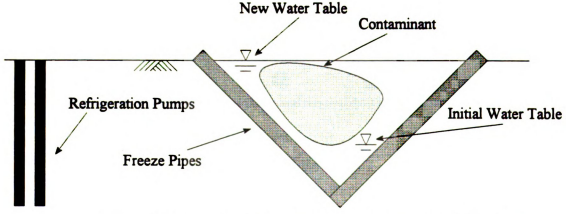
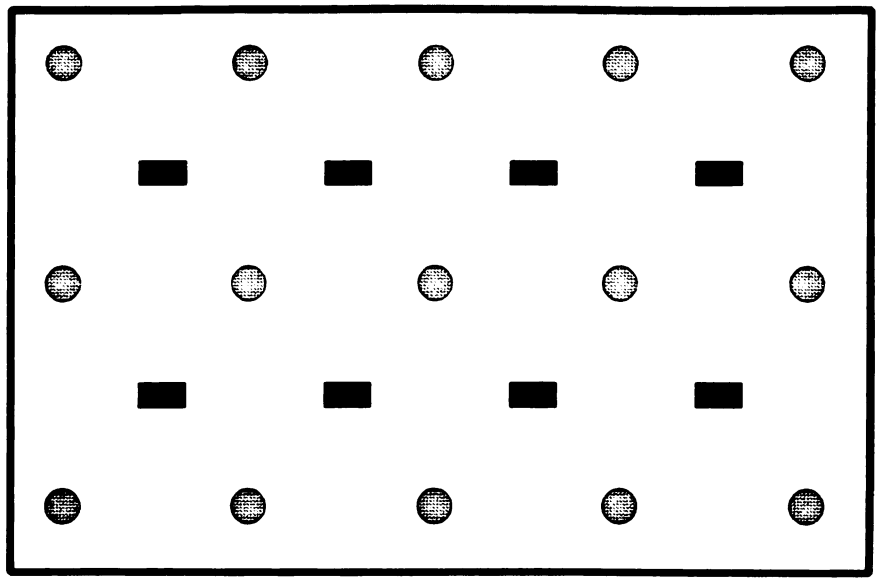


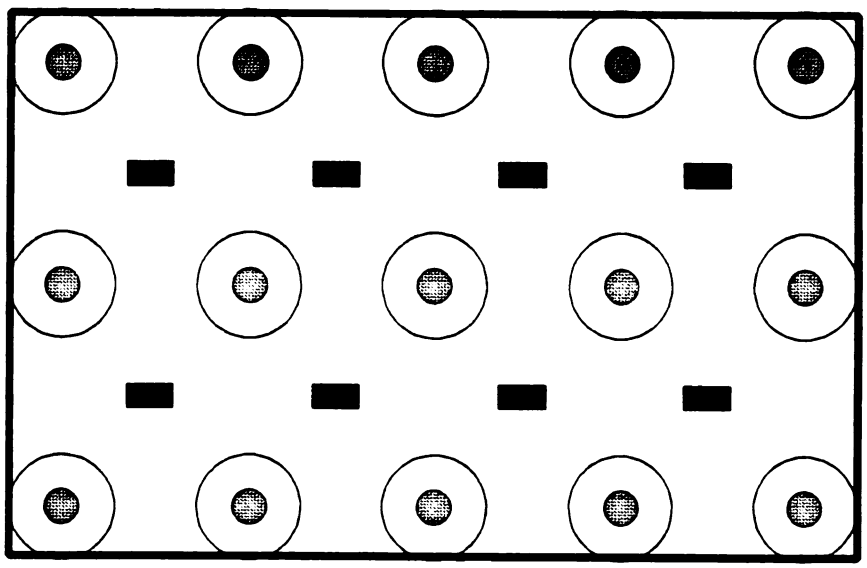
Figure 18: Alternate Field Setup for Decontamination, Shape and Profile Diagrams



Freeze Pipes

Injection Wells

Figure 19a: Plan View of Freeze Pipe Locations



Freeze Pipes

Injection Wells

Figure 19b: Plan View of Freeze Fronts After Some Time, t

CHAPTER 6

FURTHER RESEARCH

The experimentation performed here answered some questions, however, raised a great deal more. There were many things that came up during this research which would be very desirable to examine. However, they were not within the time frame or budget of the current research. Thus, there is a great deal more that can be examined to more fully understand what the true benefits of this controlled freezing procedure are.

6.1 Modifications to The Current Experimentation

There are some factors within this experimentation that created uncertainties which sould be corrected in further research. First, the freezing system should be designed so that the cell will freeze completely. As mentioned earlier in Chapter 4, the cell in this experimentation would not freeze completely, thereby, forcing assumptions to be made about the homogeneity of the trapped residual. Thus, a cell designed to freeze completely would take out this uncertainty. Secondly, the coolant used to create the freeze front varied in temperature by up to 4° C which affected the amount of porous media that would remain frozen. A temperature difference of +/- 1° C should be maintained to achieve more precise results. Finally, the flushing water used to flush the freed residual to the surface of the porous media was not specifically directed at the area of interest, i.e. directly ahead of the freeze front on the unfrozen side. While this models a field application more closely, it is desirable in this initial experimentation to have more control over where the flushing water is applied in order to ensure that the residual

that has been freed by the freeze front is flushed away from the front to allow the freezing to remain continuous.

6.2 Additional Variables for Future Research

While this experimentation covered a great deal, there is much more that can be done to improve the method and the knowledge of the method. The first thing that should be done is to try higher capillary numbers than those used in this experimentation. This should be done because of the uncertainty in the basis for selecting a capillary number, in order to use a velocity in which mobilization of the residual is just beginning. The values used in this research were only approximate and were used only as a starting point.

The next variable that should be modified is using a uniform sand, such as an Ottawa Sand, in the research instead of glass beads. This should be done because the sand could be replaced for each experiment and thus take away the uncertainty in the cleanliness of the porous media as was the case in this experimentation with the glass beads.

Finally, the possibility of using a surfactant in the flushing water was brought up during this research, however, was unable to be examined due to time constraints. This idea could be very beneficial and would be relatively easy to attempt.

LIST OF REFERENCES

1. Andersland, O.B. and Wiggert, D.C. (1993,1994), Personal Communication.

2. Corey, A.T. (1986), Mechanics of Immiscible Fluids in Porous Media, Water Resources Publications, Littleton, Colorado.

3. Hunt, J.R., Sitar, N., Udell, K.S., "Non Aqueous Phase Liquid Transport and Cleanup 1. Analysis of Mechanisms", Water Resources Research, Vol. 24, August 1988, pp. 1247-1258.

4. Iskandar, I.K. (1986), "Effects of Freezing on the Level of Contaminants in Uncontrolled Waste Sites", Cold Regions Research and Engineering Laboratory, U.S. Army Corps of Engineers, Special Report 86-19.

5. Iskandar, I.K., Jenkins, T.F. (1985), "Potential Use of Artificial Ground Freezing for Contaminant Immobilization", Cold Regions Research and Engineering Laboratory, U.S. Army Corps of Engineers, Hanover, N.H., Sept.

6. Morrow, N.R., Chatzis, I., Taber, J.J. 1988. Entrapment and Mobilization of Residual Oil in Bead Packs, SPE Reservoir Engineering, Society of Petroleum Engineering, Vol 3:2:927-934. pp 927-934.

7. Potter, M.C. and Wiggert, D.C. (1991), Mechanics of Fluids, Prentice Hall, Inc.

8. Pounder, E.R. (1965), The Physics of Ice, Pergamon Press, London.

9. Soehnlen, Greg, Cleansing Contaminated, Granular Soils by Controlled Freezing, Masters Report, Michigan State University, 1991

10. Tumeo, Mark A., and Davidson, Bret. 1993. Hydrocarbon exclusion from ground water during freezing. J. of Environmental Engineering, American Society of Civil Engineers, Vol 119:4:715-724.

11. Wilson, J.L., Conrad, S.H., Hanson, W.R., Peplinski, W. Hagen, E., 1990, "Laboratory Investigation of Residual Liquid Organics From Spills, Leaks, and the Disposal of Hazardous Wastes in Groundwater", EPA/600/6-90/004.

APPENDIX A

Location (in)	Temperature (C)								
	t=0 hrs	t=12 hrs	t=15.5 hrs	t=22.5 hrs	t=27.5 hrs	t=38.25 hr	t=46.75 hr	t=62.5 hrs	t=67.75 hr
2.00	-22.1	-0.7	-18.1	-18.7	-3.1	-2.4	-1.7	-3.6	-2.6
3.50	-12.1	2.0	-6.5	-12.7	-3.5	-2.8	-2.0	-4.1	-3.0
4.94	0.6	6.5	3.5	-7.2	-3.4	-2.6	-1.7	-3.9	-2.8
6.38	7.7	8.1	7.3	-4.4	-4.4	-3.5	-2.6	-4.7	-3.8
7.31	11.2	9.0	8.9	-1.6	-5.0	-4.3	-3.4	-5.4	-4.7
8.56	13.2	8.4	8.8	-2.0	-6.4	-5.8	-4.9	-6.9	-6.2
9.50	13.7	6.8	7.3	-4.6	-8.2	-7.7	-6.9	-8.8	-8.1
11.12	13.1	0.7	1.3	-9.9	-12.3	-12.1	-11.4	-13.2	-12.4
12.50	10.7	-9.7	-9.1	-16.0	-17.3	-17.5	-16.9	-18.3	-17.4
15.00	6.9	-22.9	-22.1	-22.1	-22.5	-22.9	-22.4	-23.4	-22.5
16.62	9.4	-15.5	-15.3	-15.8	-16.1	-17.2	-16.6	-17.8	-16.3
17.81	11.0	-9.0	-9.2	-10.1	-10.5	-12.2	-11.6	-12.9	-10.9
18.88	12.2	-4.2	-4.7	-5.9	-6.4	-8.1	-7.7	-9.0	-7.1
20.62	13.8	1.8	1.0	-0.4	-1.0	-2.9	-2.7	-4.1	-2.5
22.56	14.8	5.7	4.9	3.5	2.9	1.0	1.0	-0.3	0.6
24.50	16.1	8.6	7.9	6.9	6.4	4.4	4.7	3.1	4.4
26.25	16.6	9.9	9.5	8.8	8.4	6.2	6.6	4.7	6.5

Table A1: Zero Flow With Dodecane

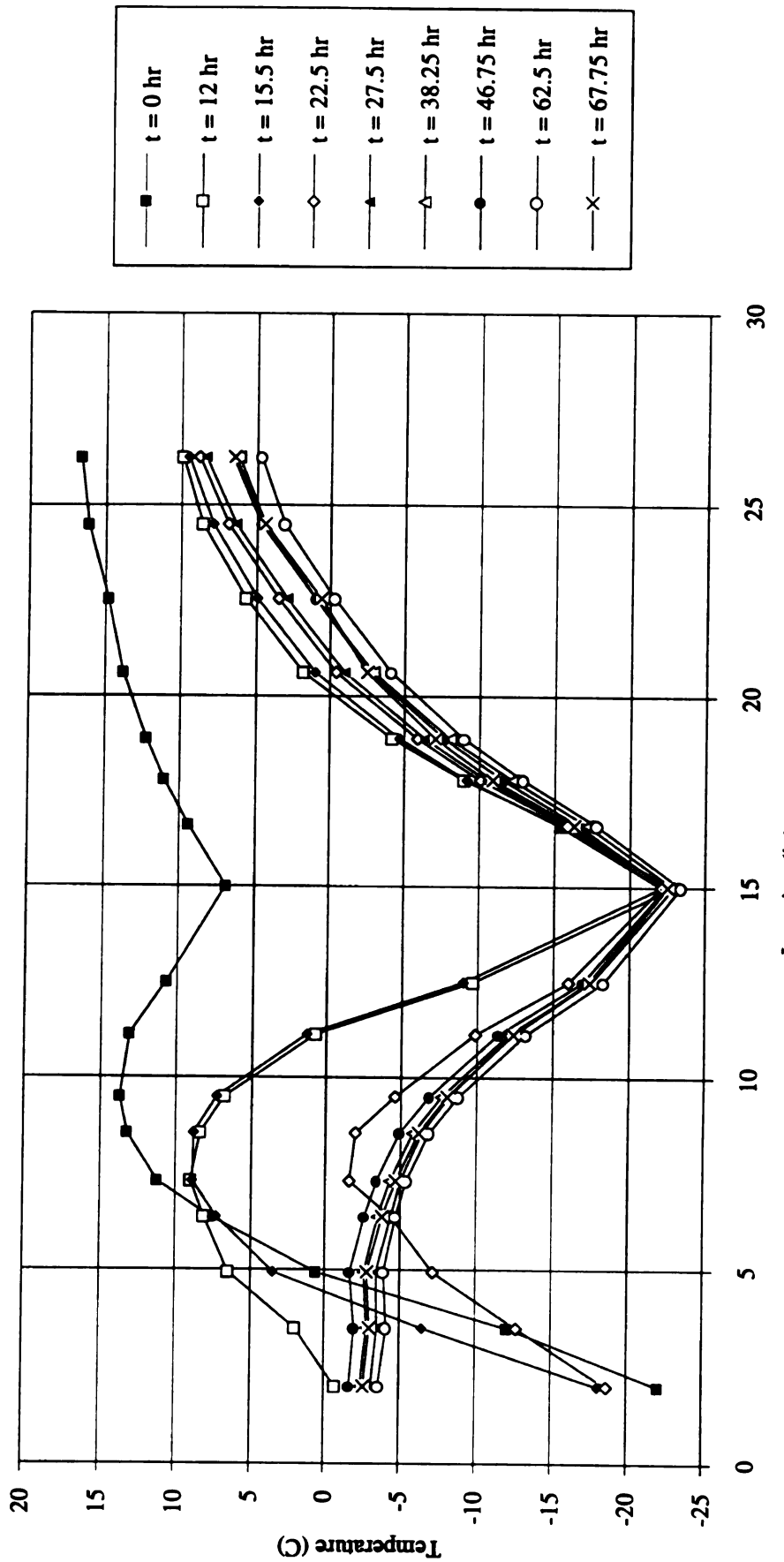


Figure A1: Temperature vs Location for Flow = 0 ml/min with Dodecane

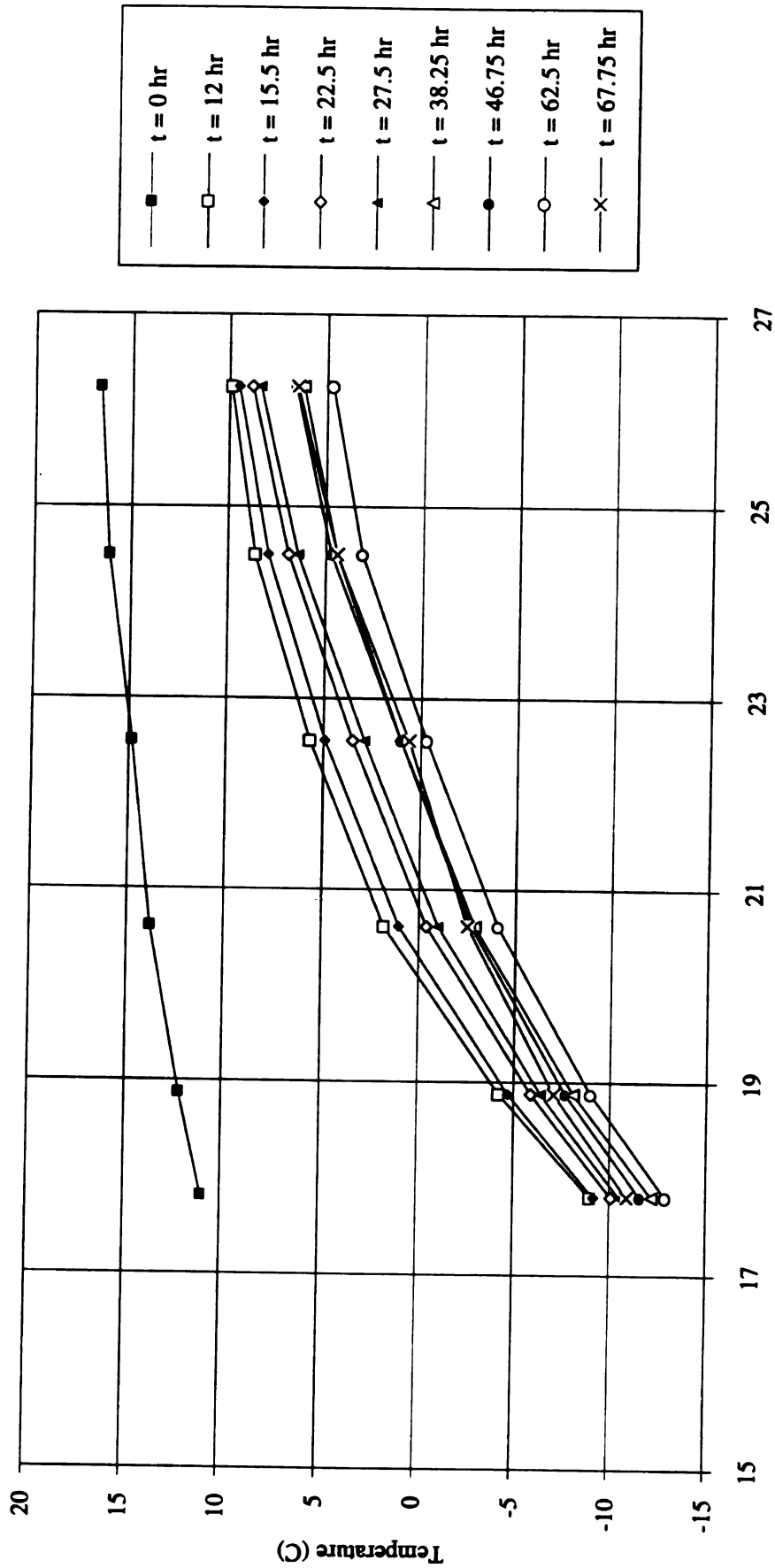


Figure A1.1: Temperature vs Location for Flow = 0 ml/min with Dodecane

Location (in)	Temperature (C)								
	t=0 hr	t=3.5 hr	t=19.5 hr	t=20.25 hr	t=24.5 hr	t=30.83 hr	t=35.33 hr	t=39.5 hr	t=43.5 hr
27.75	21.6	21.8	15.9	16.3	18.7	16.4	15.1	14.7	14.6
25.75	20.2	20.6	14.9	15.1	16.5	14.9	13.3	12.7	12.5
24.00	18.7	19.1	13.8	13.9	14.2	12.8	11.1	10.4	10.0
22.69	17.8	17.8	12.6	12.8	11.4	9.7	8.1	7.3	6.9
20.94	16.2	16.5	11.8	11.9	10.1	8.1	6.4	5.6	5.0
19.31	14.1	14.5	9.8	10.0	6.0	3.4	1.7	0.8	0.1
18.06	11.9	12.3	7.5	7.6	-0.3	-2.9	-4.2	-4.9	-5.6
16.25	8.3	8.2	3.4	0.0	-14.8	-16.2	-17.9	-18.3	-18.6
14.69	6.3	5.7	1.0	-18.6	-22.7	-24.5	-25.0	-25.1	-25.1
13.19	5.9	5.5	0.7	-0.4	-19.3	-21.6	-22.2	-22.5	-22.5
12.31	5.5	5.3	0.5	0.3	-15.3	-18.1	-18.7	-19.2	-19.3
10.69	4.2	4.0	0.0	0.3	-10.8	-14.2	-14.6	-15.1	-15.3
9.63	3.1	2.9	-1.0	-0.8	-9.0	-12.4	-12.6	-13.0	-13.2
8.25	0.7	0.5	-3.9	-3.3	-8.4	-10.5	-10.3	-10.6	-10.7
7.25	-1.5	-1.6	-6.2	-5.6	-9.0	-9.2	-8.7	-8.8	-8.9
5.38	-7.5	-7.7	-12.3	-11.3	-12.5	-8.0	-7.3	-7.3	-7.4
4.31	-13.0	-13.2	-17.2	-16.1	-16.3	-7.5	-6.9	-6.9	-7.0
2.31	-22.4	-22.5	-25.2	-24.4	-22.8	-6.3	-6.3	-6.3	-6.5

Table A2: Zero Flow Without Dodecane

Location (in)	Temperature (C)							
	t=50.33 hr	t=54.08 hr	t=58.17 hr	t=62.17 hr	t=68.08 hr	t=74.83 hr	t=79.67 hr	t=90.0 hr
27.75	13.1	13.9	12.4	11.3	12.6	14.5	14.4	12.4
25.75	11.1	11.9	11.0	9.9	10.2	12.0	12.2	10.1
24.00	8.8	9.4	8.9	7.9	7.7	9.2	9.4	7.5
22.69	5.9	6.3	6.1	5.3	4.8	6.1	6.4	4.7
20.94	4.0	3.9	3.7	2.9	2.2	2.9	3.1	1.5
19.31	-0.8	-0.7	-1.0	-1.6	-2.1	-1.6	-1.6	-3.2
18.06	-6.2	-6.2	-6.7	-7.4	-7.5	-7.0	-7.2	-9.0
16.25	-17.7	-17.4	-18.3	-18.9	-18.2	-17.3	-17.4	-18.9
14.69	-23.4	-23.1	-24.0	-24.5	-23.3	-22.1	-22.2	-23.4
13.19	-21.2	-20.5	-21.2	-21.7	-20.8	-19.4	-19.4	-20.6
12.31	-18.2	-17.3	-17.8	-18.3	-17.6	-16.2	-15.9	-17.0
10.69	-14.4	-13.4	-13.5	-13.9	-13.6	-11.9	-11.5	-12.5
9.63	-12.4	-11.4	-11.3	-11.7	-11.5	-9.8	-9.3	-10.3
8.25	-10.0	-8.9	-8.6	-9.1	-8.9	-7.2	-6.6	-7.7
7.25	-8.2	-7.0	-6.8	-7.2	-7.1	-5.3	-4.7	-5.8
5.38	-6.5	-5.3	-5.3	-5.8	-5.5	-3.7	-3.3	-4.5
4.31	-6.0	-4.8	-5.1	-5.7	-5.1	-3.3	-3.0	-4.3
2.31	-5.1	-4.1	-4.9	-5.5	-4.3	-2.7	-2.6	-3.9

Table A2: Zero Flow Without Dodecane

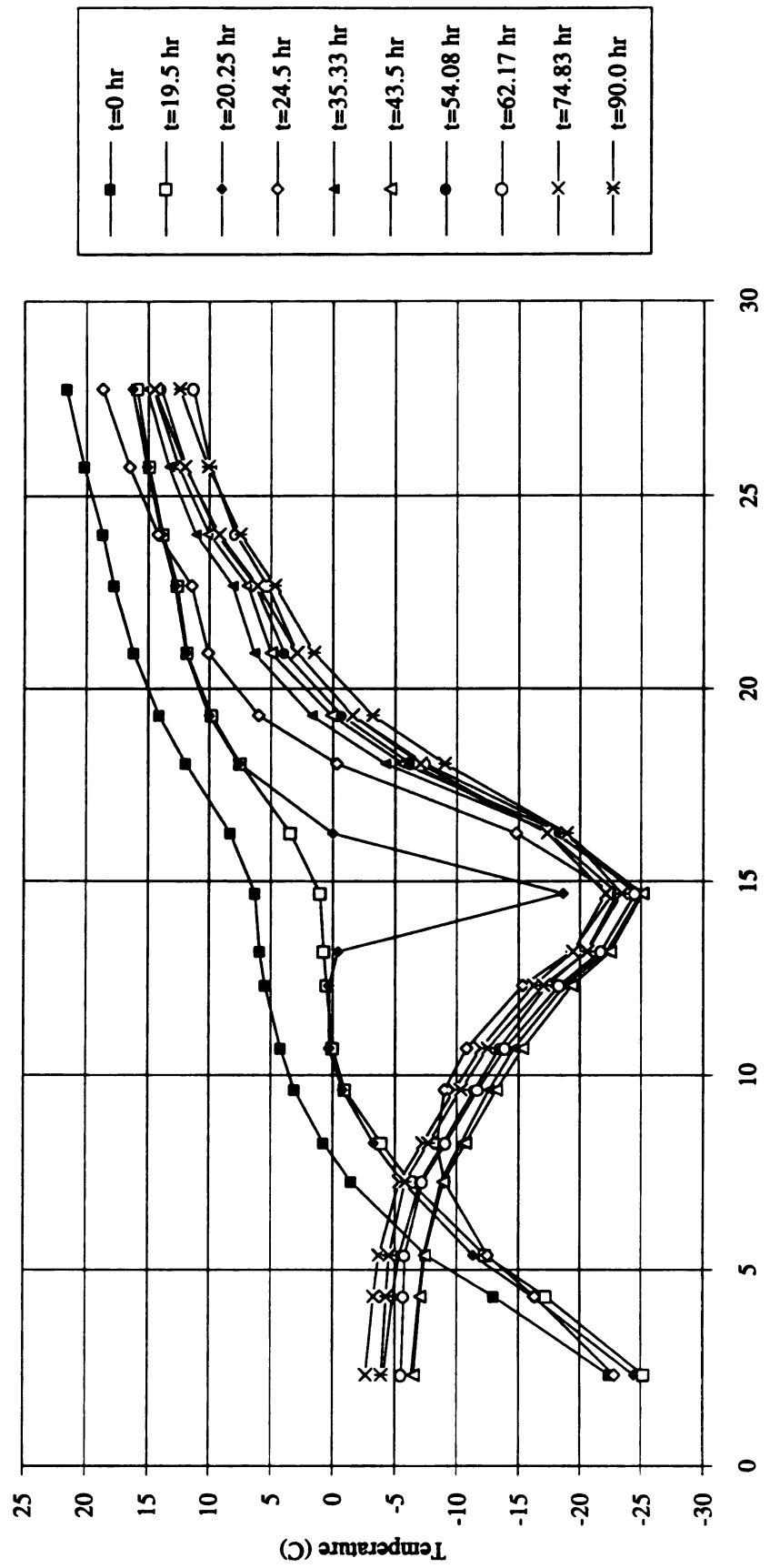


Figure A2: Temperature vs Location for Flow = 0 ml/min Without Dodecane

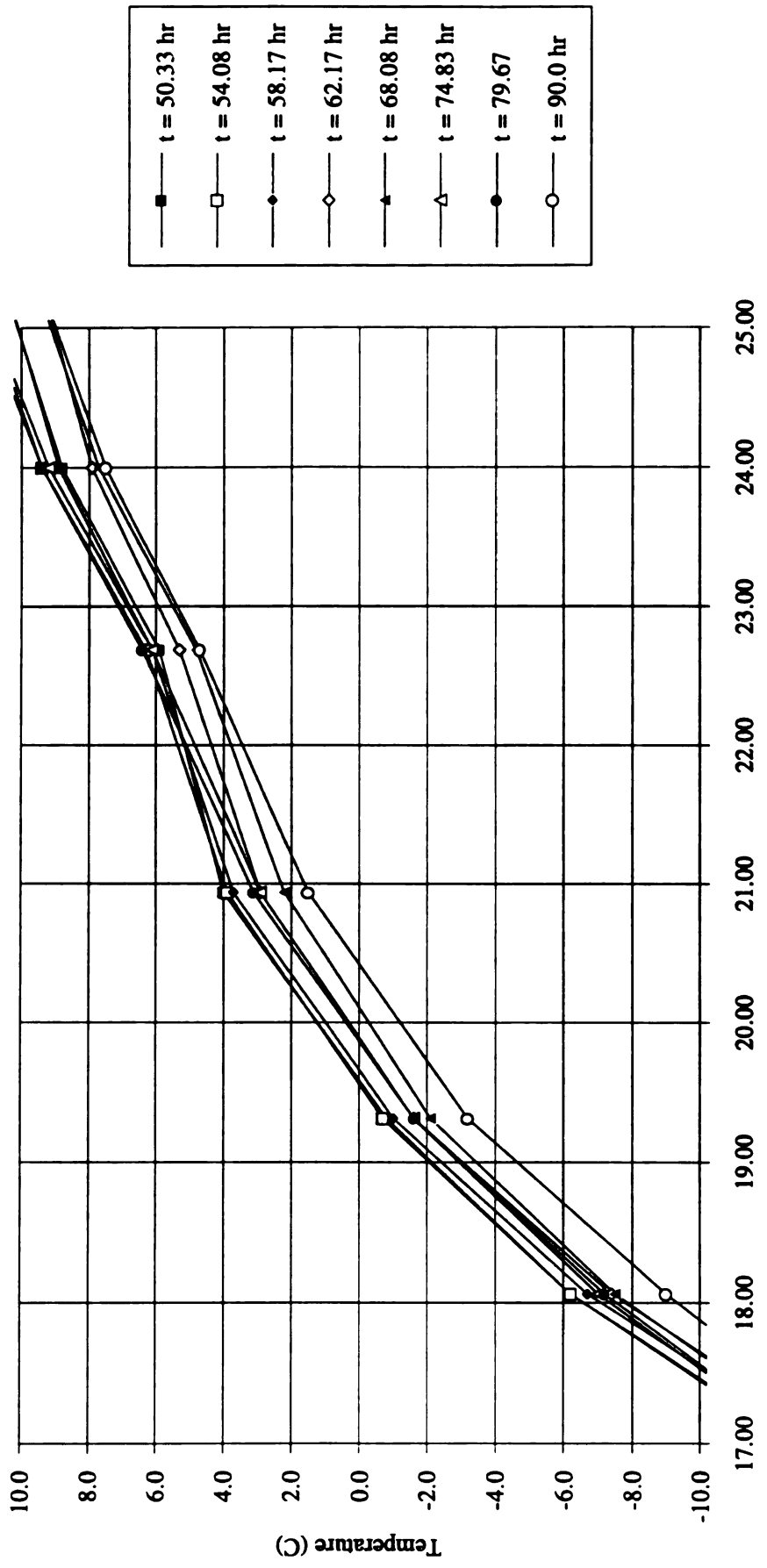


Figure A2.1: Temperature vs Location for Flow = 0 ml/min Without Dodecane

Location (inches)			Temperature (C)				
	t=0 hr	t=2.83 hr	t=11.75 hr	t=24.17 hr	t=30.33 hr	t=38.42 hr	t=50.17 hr
27.75	15.3	16.5	18.5	14.6	18.1	18.6	17.5
25.75	15.5	16.5	18.5	14.7	18.1	18.6	17.5
24	15.3	16.2	18.2	14.4	17.9	18.3	17.2
22.69	14.7	15.4	18.3	13.7	17.1	17.6	16.4
20.94	13.4	13.9	15.9	12.2	15.6	15.9	14.8
19.31	11.1	11.6	13.5	10	13.3	13.6	12.5
18.06	8.8	9.3	11.1	7.7	10.8	11.2	10.2
16.25	4.8	5.6	7	3.8	6.7	7.2	6.4
14.69	4	4.5	5.8	2.7	5.3	5.7	5.2
13.19	4.8	4.3	5.5	2.6	4.6	5.1	4.5
12.31	5.3	4.1	5.1	2.6	3.8	4.3	3.8
10.69	3.9	2.7	3.2	1.5	1.7	2.3	2
9.62	2.2	1.3	1.5	0.2	-0.2	0.6	0.4
8.25	-1.4	-1.7	-1.6	-2.9	-2.9	-2.2	-2.4
7.25	-4.5	-4.6	-4.1	-5.8	-5.3	-4.6	-5
5.38	-11	-10.8	-10	-12.1	-11.1	-10.4	-10.9
4.31	-16.2	-15.7	-14.9	-16.9	-15.7	-15.1	-15.6
2.31	-24.2	-23.4	-22.6	-24.6	-22.7	-22.4	-22.8

Table A3: Flow = 19ml/min Without Dodecane

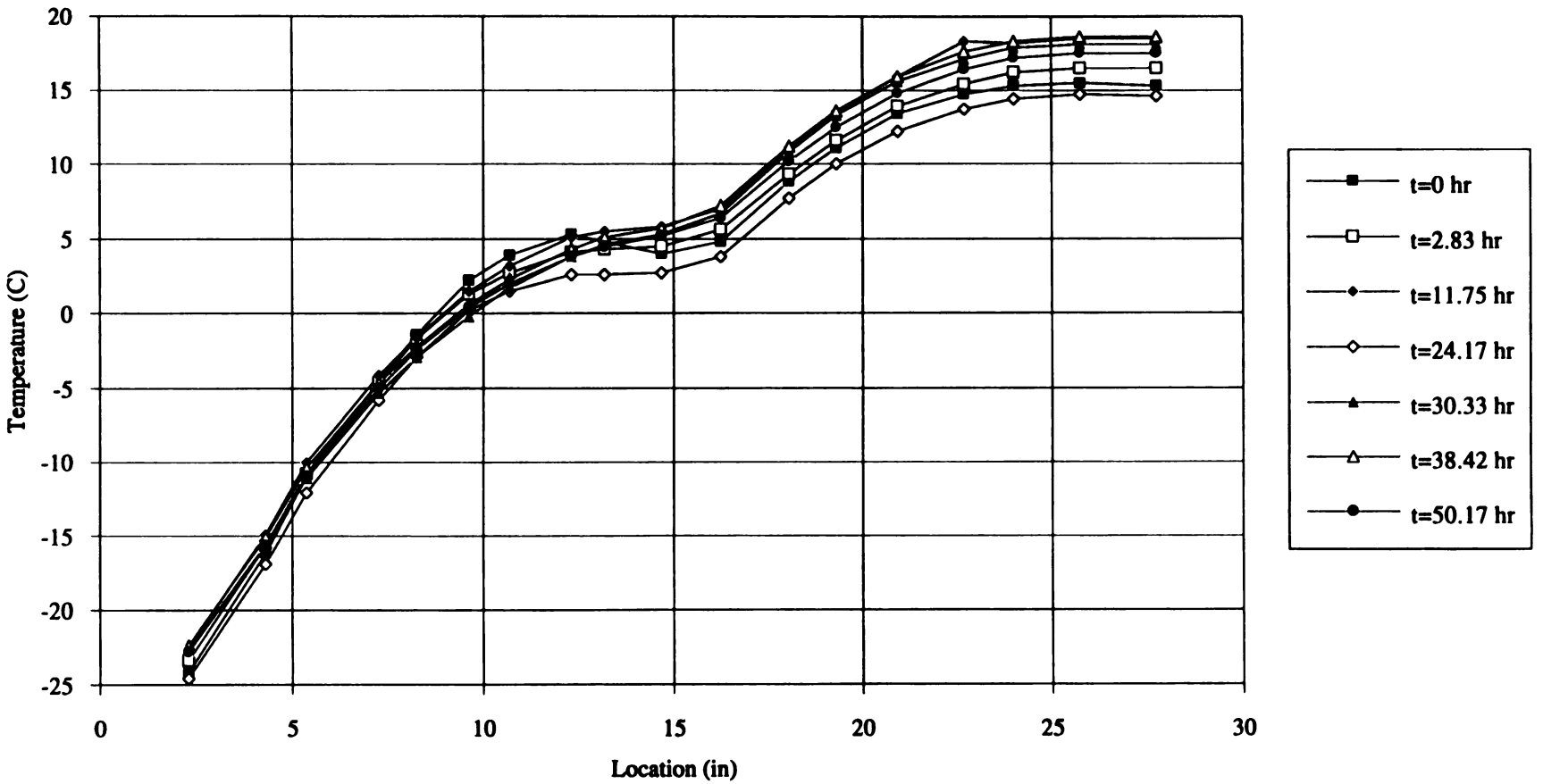


Figure A3: Temperature vs Location for Flow = 19 ml/min Without Dodecane

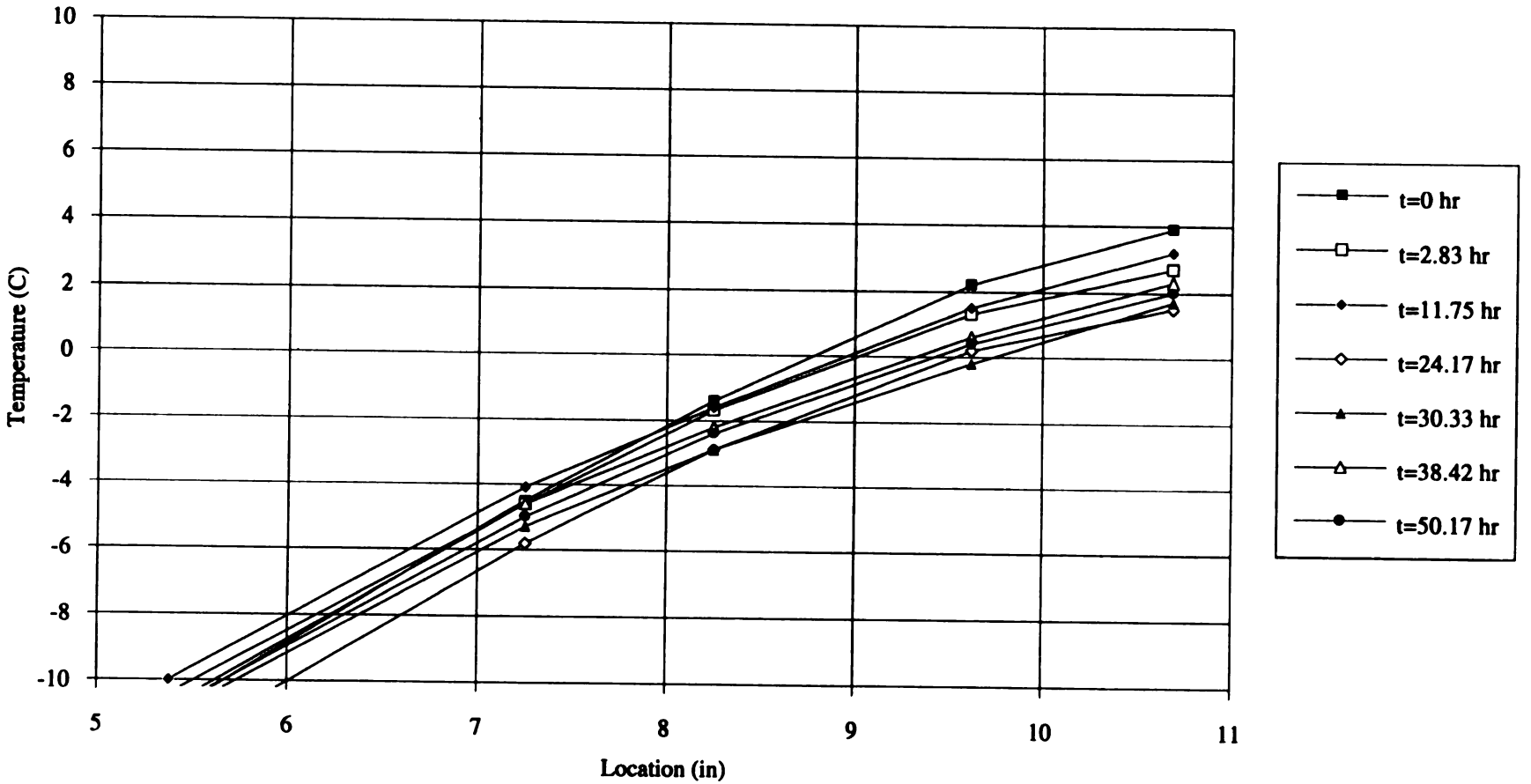


Figure A3.1: Temperature vs Location for Flow = 19 ml/min Without Dodecane

Location (in)	Temperature (C)										
	t=0 hr	t=6.51 hr	t=11.33 hr	t=16.5 hr	t=25.13 hr	t=32.5 hr	t=40.33 hr	t=50 hr	t=54.51 hr	t=63.33 hr	t=72.51 hr
27.75	14.6	16.0	16.6	13.8	12.2	13.8	13.1	14.6	16.9	17.9	15.3
25.75	14.9	16.3	16.8	14.1	12.5	14.1	13.4	14.9	17.1	18.1	15.5
24.00	14.8	16.1	16.5	13.9	12.4	13.9	13.3	14.8	16.9	17.8	15.3
22.69	14.6	15.4	16.2	13.5	11.9	13.4	12.8	14.2	16.3	17.3	14.7
20.94	13.7	14.0	14.7	12.2	10.6	12.1	11.5	13.0	15.0	15.9	13.4
19.31	12.0	11.6	12.4	10.1	8.5	9.8	9.3	10.7	12.7	13.6	11.1
18.06	9.7	9.2	10.1	7.8	6.2	7.4	7.0	8.3	10.3	11.1	8.8
16.25	5.2	5.4	6.1	3.9	2.3	3.4	3.0	4.0	6.2	6.9	4.8
14.69	4.8	4.8	5.6	3.2	1.5	2.6	2.1	3.0	5.1	6.0	4.0
13.19	7.6	6.0	7.2	5.1	2.7	3.3	2.9	3.3	5.1	6.6	4.8
12.31	9.2	6.7	8.1	6.1	3.4	3.5	3.1	3.0	4.6	6.6	5.3
10.69	8.9	5.8	6.8	5.3	2.3	1.8	1.4	0.9	1.9	4.3	3.9
9.63	7.7	4.3	5.0	3.6	0.9	-0.1	-0.4	-0.9	-0.3	2.3	2.2
8.25	3.9	0.8	0.8	0.0	-2.5	-3.2	-3.5	-3.8	-2.9	-1.4	-1.4
7.25	-0.3	-2.6	-2.6	-3.4	-5.5	-6.0	-6.2	-6.4	-5.4	-4.1	-4.5
5.38	-8.4	-9.5	-9.3	-10.4	-11.8	-11.8	-12.2	-12.1	-11.0	-10.0	-11.0
4.31	-14.9	-15.0	-14.8	-16.1	-16.8	-16.5	-16.8	-16.7	-15.5	-14.9	-16.2
2.31	-25.1	-23.6	-23.7	-25.1	-24.5	-23.9	-24.4	-23.6	-22.5	-22.7	-24.2

Table A4: Flow = 35 ml/min Without Dodecane

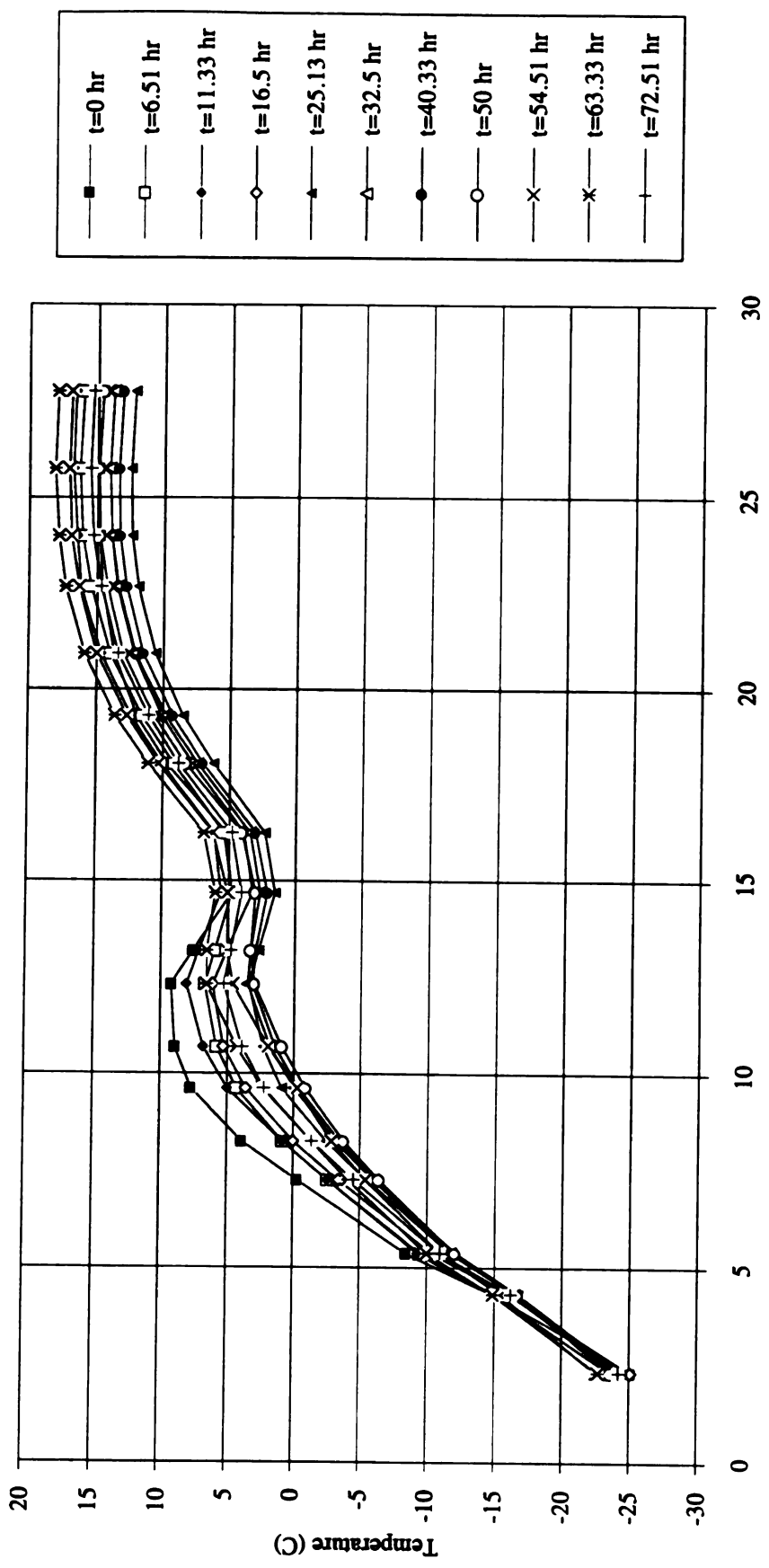


Figure A4: Temperature vs Location for Flow = 35 ml/min Without Dodecane

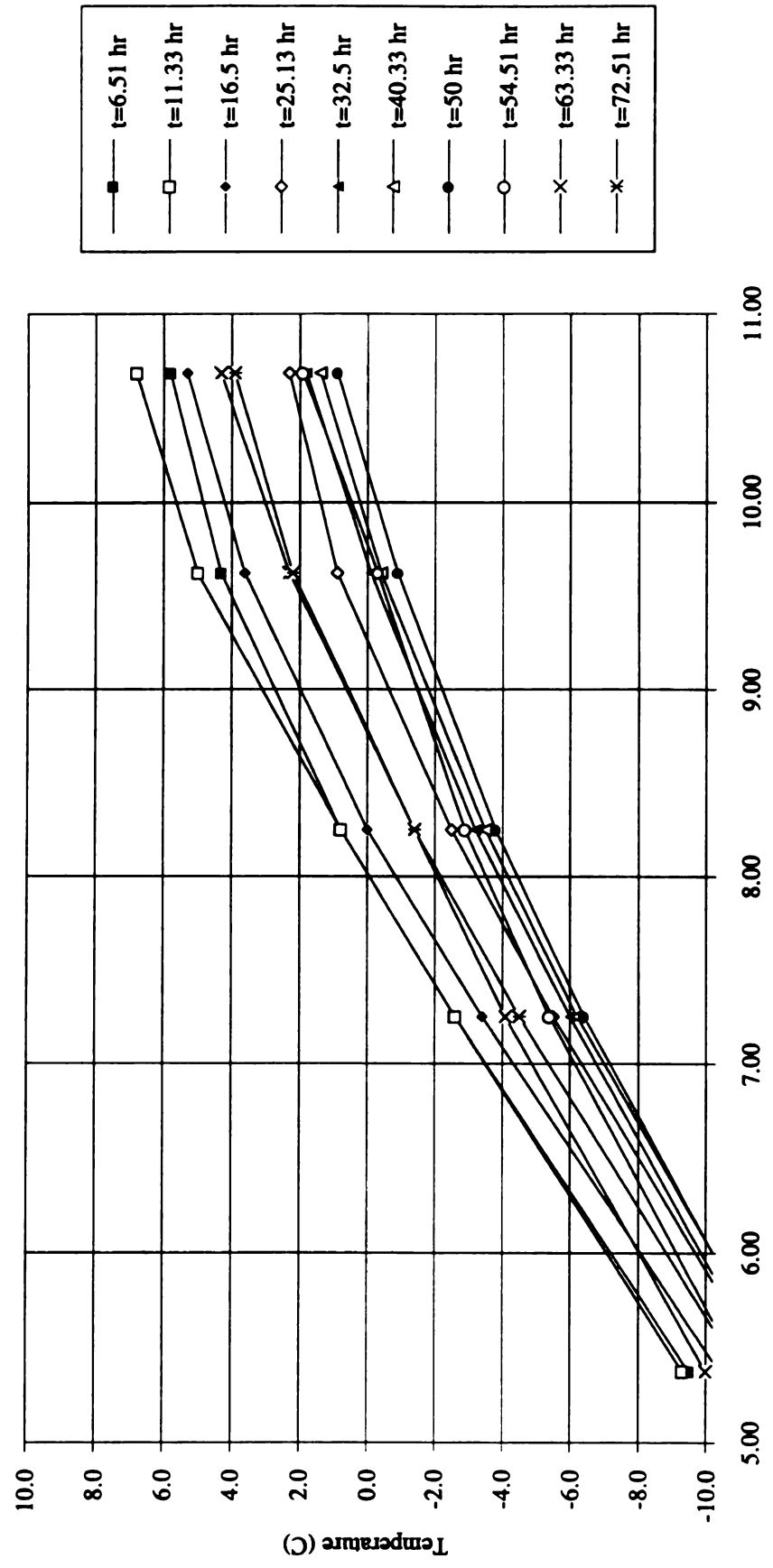


Figure A4.1: Temperature vs Location for Flow = 35 ml/min Without Dodecane

Location (in)	Temperature (C)								
	t=0 hr	t=5.5 hr	t=11.25 hr	t=18.5 hr	t=26.08 hr	t=32 hr	t=36.5 hr	t=40.25 hr	t=49.67 hr
27.75	14.3	13.6	15.1	14.6	15	16.9	17.3	16.1	14.6
25.75	14.4	13.9	15.3	14.8	15.2	17.1	17.3	16.3	14.9
24	14.3	13.7	15.2	14.6	15.1	17	17.2	16.2	14.8
22.69	14.4	13.8	15.2	14.7	15.1	16.8	17.1	16.1	14.6
20.94	14.2	13.6	14.9	14.3	14.6	16.1	16.3	15.2	13.7
19.31	14.1	13.4	14.5	13.6	13.5	14.7	14.8	13.6	12
18.06	13.3	12.3	13.3	12.2	11.7	12.5	12.7	11.3	9.7
16.25	8.6	7.2	8	6.7	6.5	8	8.4	6.9	5.2
14.69	5.3	3.9	5.3	4.7	5	7.2	7.8	6.4	4.8
13.19	6.1	4.5	6	5.9	6.8	9.2	10	9	7.6
12.31	7.3	5.3	6.8	7	8.2	10.4	11.5	10.5	9.2
10.69	7.9	5.4	6.3	6.6	7.8	9.4	10.9	10.4	8.9
9.62	7.6	4.6	4.9	5	6.1	7.4	9.2	9.1	7.7
8.25	5.7	2.2	1.4	1.1	1.7	2.9	4.9	5.4	3.9
7.25	3	-0.5	-1.9	-2.3	-2	-1.1	0.2	1.1	-0.3
5.38	-5.1	-8	-8.4	-9	-8.9	-7.9	-7	-7.1	-8.4
4.31	-12.2	-14.1	-14	-14.6	-14.6	-13.5	-12.8	-13.5	-14.9
2.31	-25.1	-24.8	-23.8	-24.2	-24	-22.8	-22.5	-24	-25.1

Table A5: Flow = 49 ml/min Without Dodecane

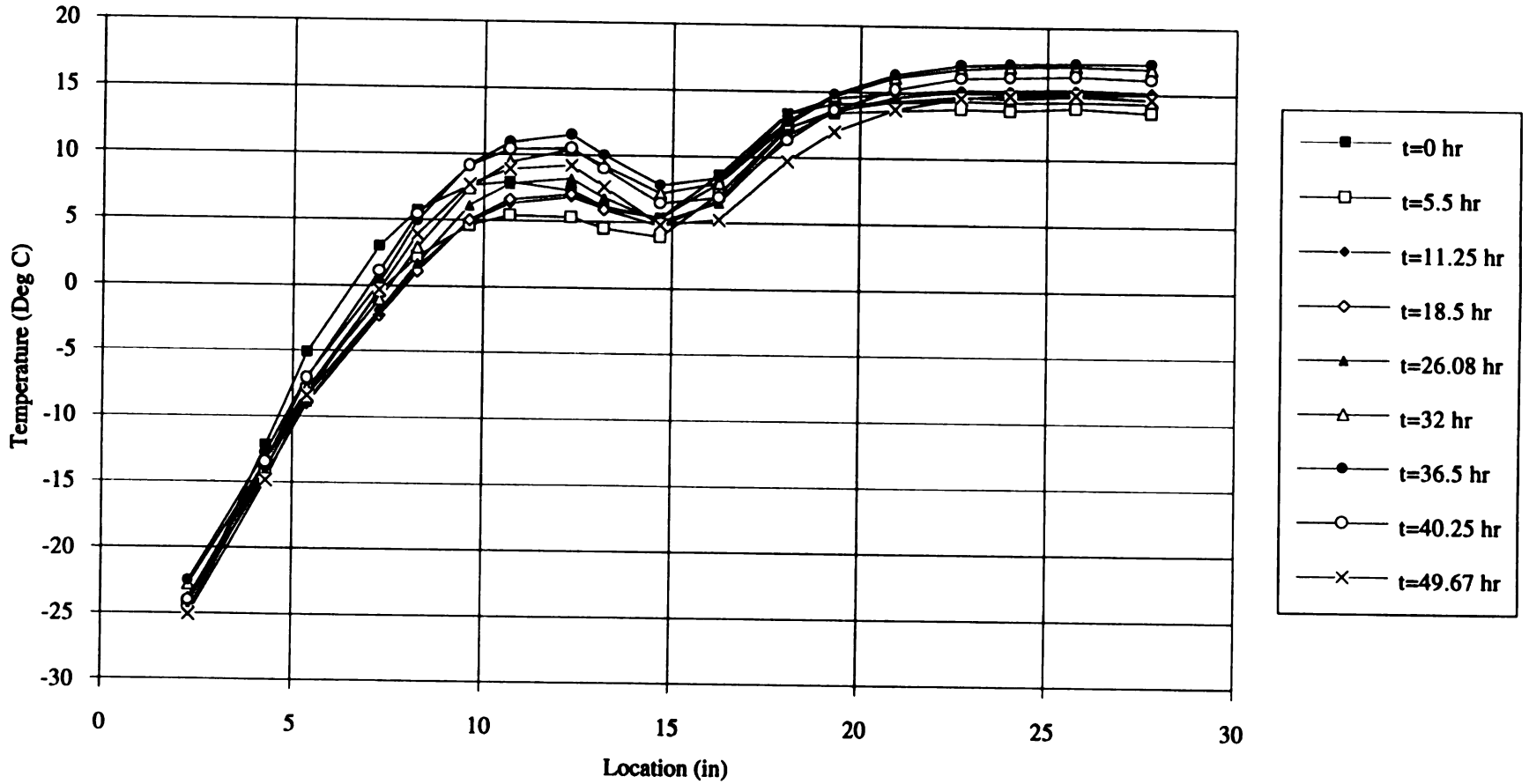


Figure A5: Temperature vs Location for 49 ml/min Without Dodecane

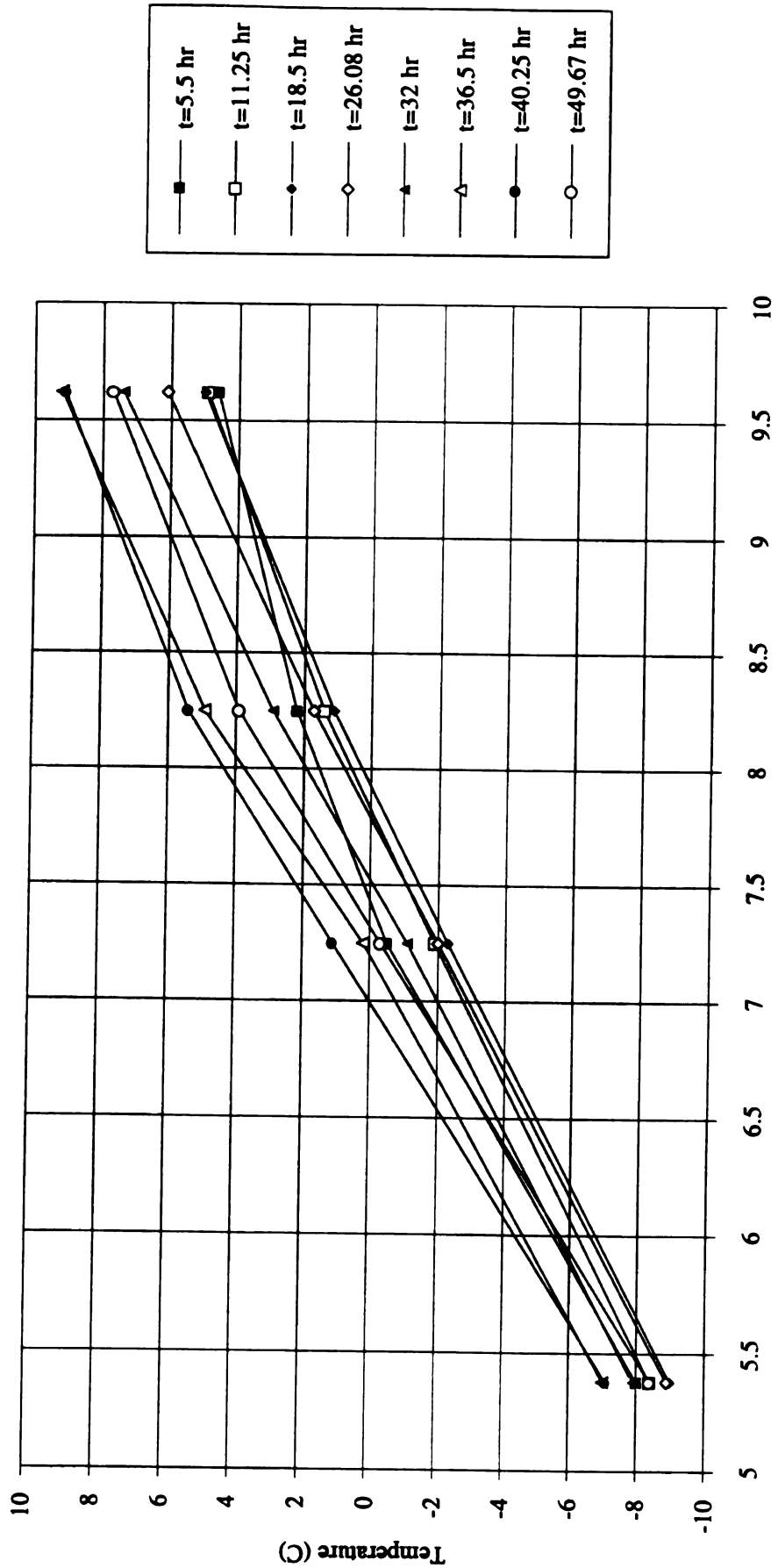


Figure A5.1: Temperature vs Location for 49 ml/min Without Dodecane

Location			Temperature (C)				
(in)	t=0 hr	t=3.5 hr	t=11.58 hr	t=19.5 hr	t=26.5 hr	t=38.5 hr	t=41 hr
27.75	18.4	17.1	15.3	17.6	17.2	17.0	17.4
25.75	17.9	17.0	15.3	17.4	17.0	16.9	17.2
24.00	17.8	16.9	15.0	16.8	16.5	16.2	16.5
22.69	17.8	16.7	14.5	16.1	15.8	15.3	15.6
20.94	17.3	15.4	12.4	13.2	12.8	11.9	12.2
19.31	16.6	12.2	7.8	8.1	7.5	6.0	6.4
18.06	14.9	5.1	-0.1	0.1	-0.3	-1.9	-1.5
16.25	10.6	-12.3	-15.6	-15.0	-15.2	-16.3	-16.0
14.69	10.0	-21.3	-23.3	-22.1	-22.0	-22.7	-22.2
13.19	12.9	-14.8	-19.3	-18.4	-18.4	-19.0	-18.5
12.31	14.4	-6.9	-14.5	-14.0	-13.9	-14.4	-13.9
10.69	14.5	1.5	-8.6	-8.7	-8.6	-8.9	-8.3
9.62	13.9	3.6	-5.7	-6.3	-6.2	-6.5	-5.8
8.25	11.7	4.5	-1.9	-3.5	-3.7	-3.9	-3.3
7.25	8.4	3.7	-0.1	-1.5	-2.1	-2.2	-1.7
5.38	-0.4	0.3	-0.1	-0.3	-1.2	-1.1	-0.6
4.31	-7.7	-1.6	-1.2	-1.0	-1.3	-1.0	-0.5

Table A6: Flow = 49 ml/min With Dodecane

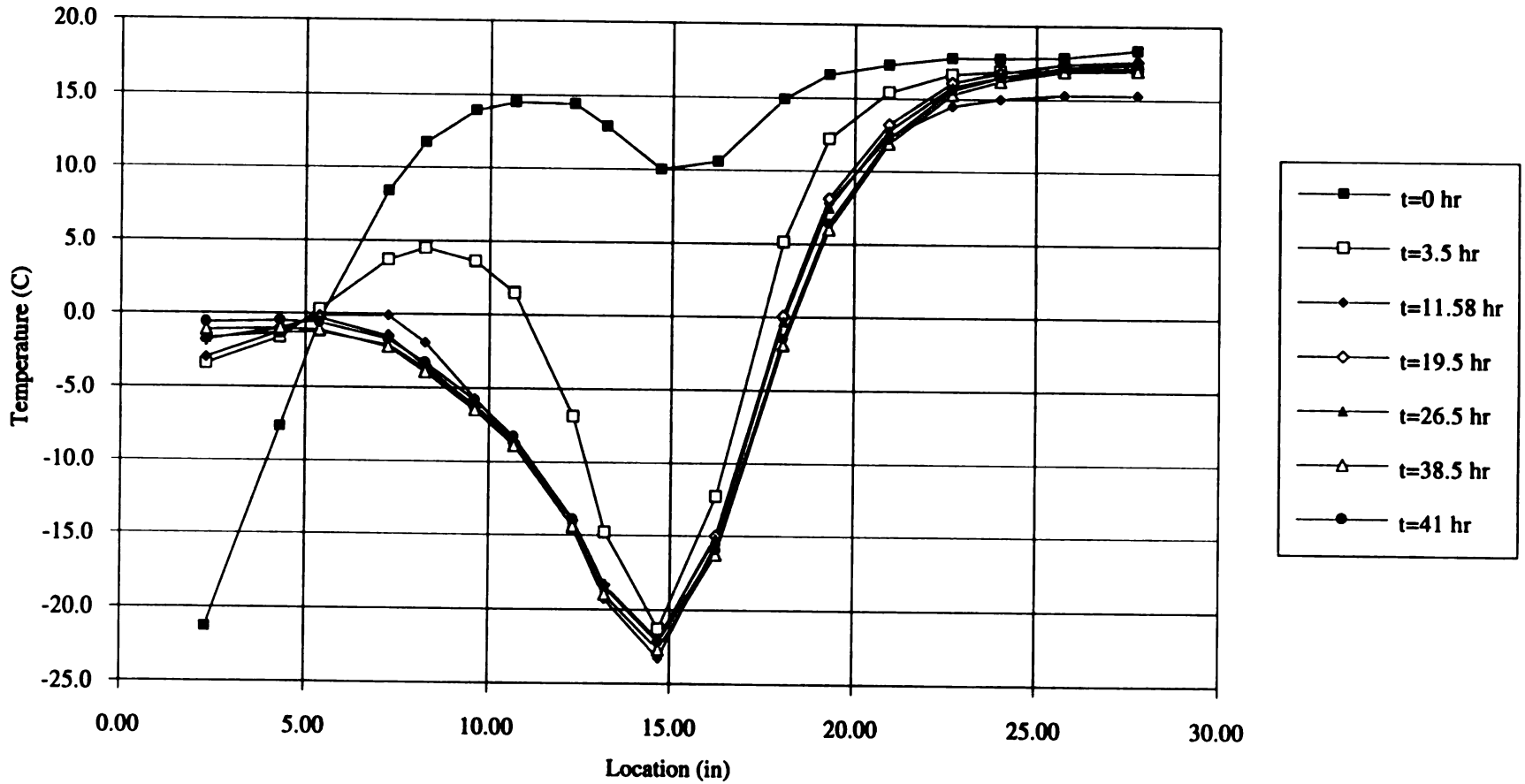


Figure A6: Temperature vs Location for Flow = 49 ml/min With Dodecane

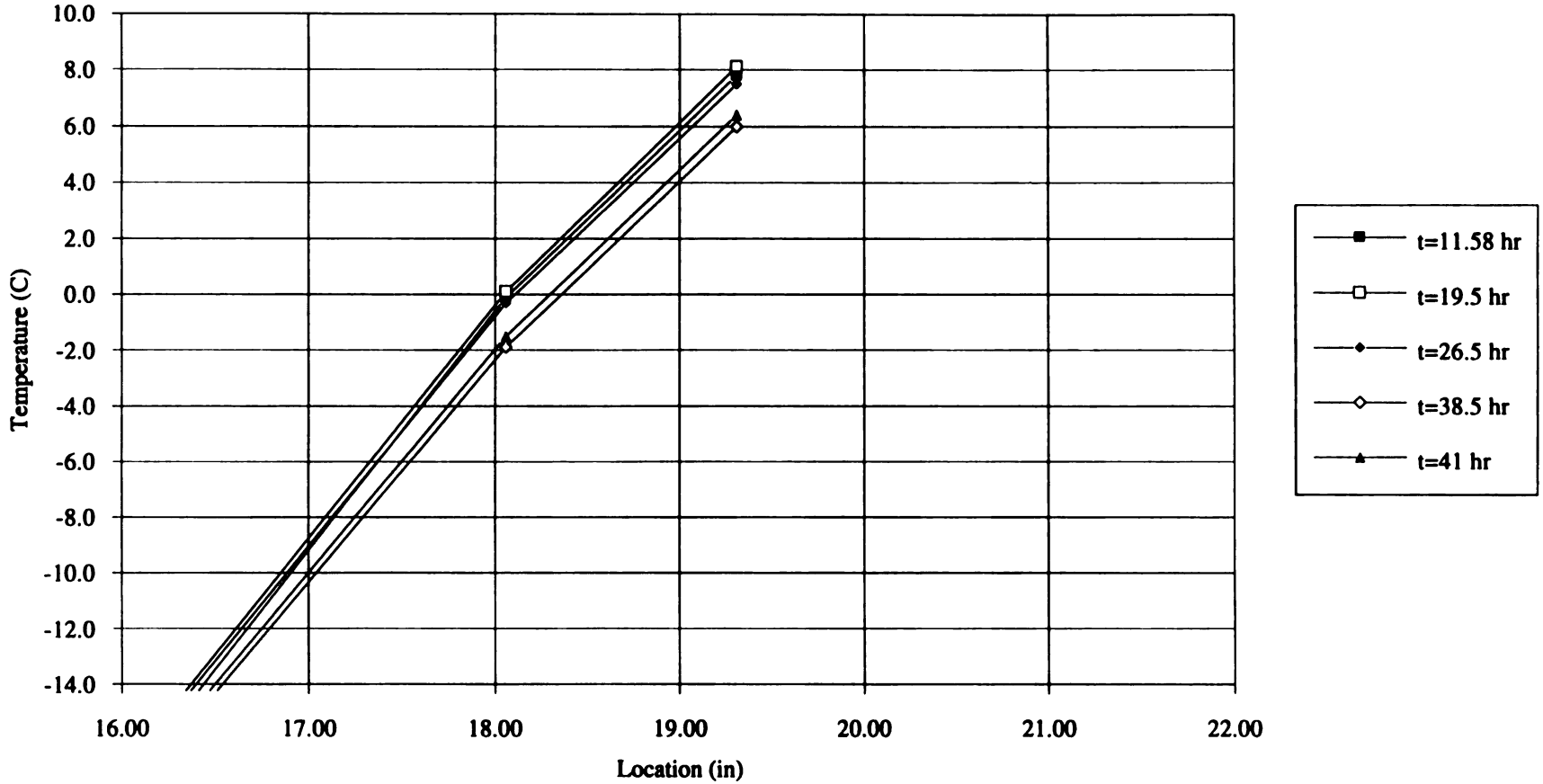


Figure A6.1: Temperature vs Location for Flow = 49 ml/min With Dodecane

Location				Temperature (C)				
(in)	t=0 hr	t=1.42 hr	t=3 hr	t=6.67 hr	t=12.17 hr	t=17.5 hr	t=20.83 hr	t=26.5 hr
27.75	22.7	19.6	17.9	15.9	15.0	16.5	17.4	17.8
25.75	22.6	19.3	17.8	15.9	14.9	16.2	16.9	17.5
24.00	22.4	19.2	17.7	16.0	14.7	16.2	16.6	17.2
22.69	22.5	19.5	17.9	16.0	14.9	16.1	16.6	17.4
20.94	22.3	18.8	17.4	15.4	14.3	15.8	16.2	16.8
19.31	22.5	19.1	17.1	14.6	13.7	15.3	15.7	16.1
18.06	22.2	18.0	15.8	13.0	12.4	13.9	14.1	14.3
16.25	22.4	15.7	12.1	8.9	8.1	9.5	9.9	10.1
14.69	22.3	14.9	11.1	8.0	7.2	8.7	9.2	9.6
13.19	22.2	16.7	13.6	10.7	10.1	11.6	11.9	12.4
12.31	22.3	17.8	15.2	12.5	11.6	13.1	13.4	13.8
10.69	22.4	18.0	15.7	13.1	12.0	13.3	13.6	14.0
9.62	22.4	18.0	15.6	12.9	11.8	12.9	13.1	13.4
8.25	22.4	17.6	14.6	11.6	10.4	10.9	11.0	11.2
7.25	22.4	16.9	12.7	9.0	7.8	7.6	7.7	7.8
5.38	22.2	11.1	5.7	1.6	-0.1	-1.2	-1.0	-1.0
4.31	22.0	1.8	-2.7	-6.4	-8.0	-8.7	-8.4	-8.5
2.31	22.4	-20.3	-20.7	-21.7	-22.6	-21.8	-21.4	-21.5

Table A7: Flow = 53 ml/min With Dodecane, Run #1

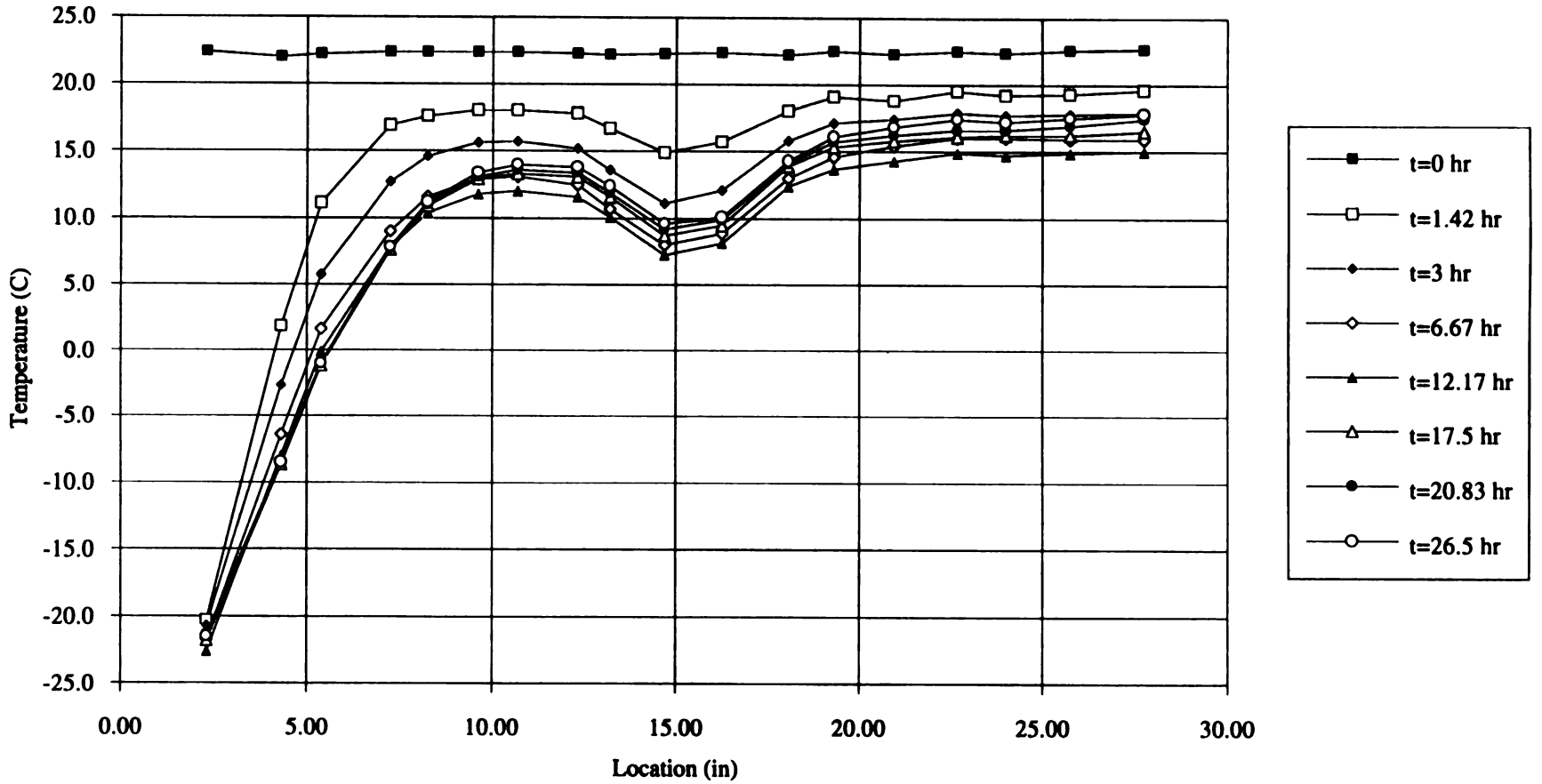


Figure A7: Temperature vs Location for Flow = 53 ml/min With Dodecane, Run #1

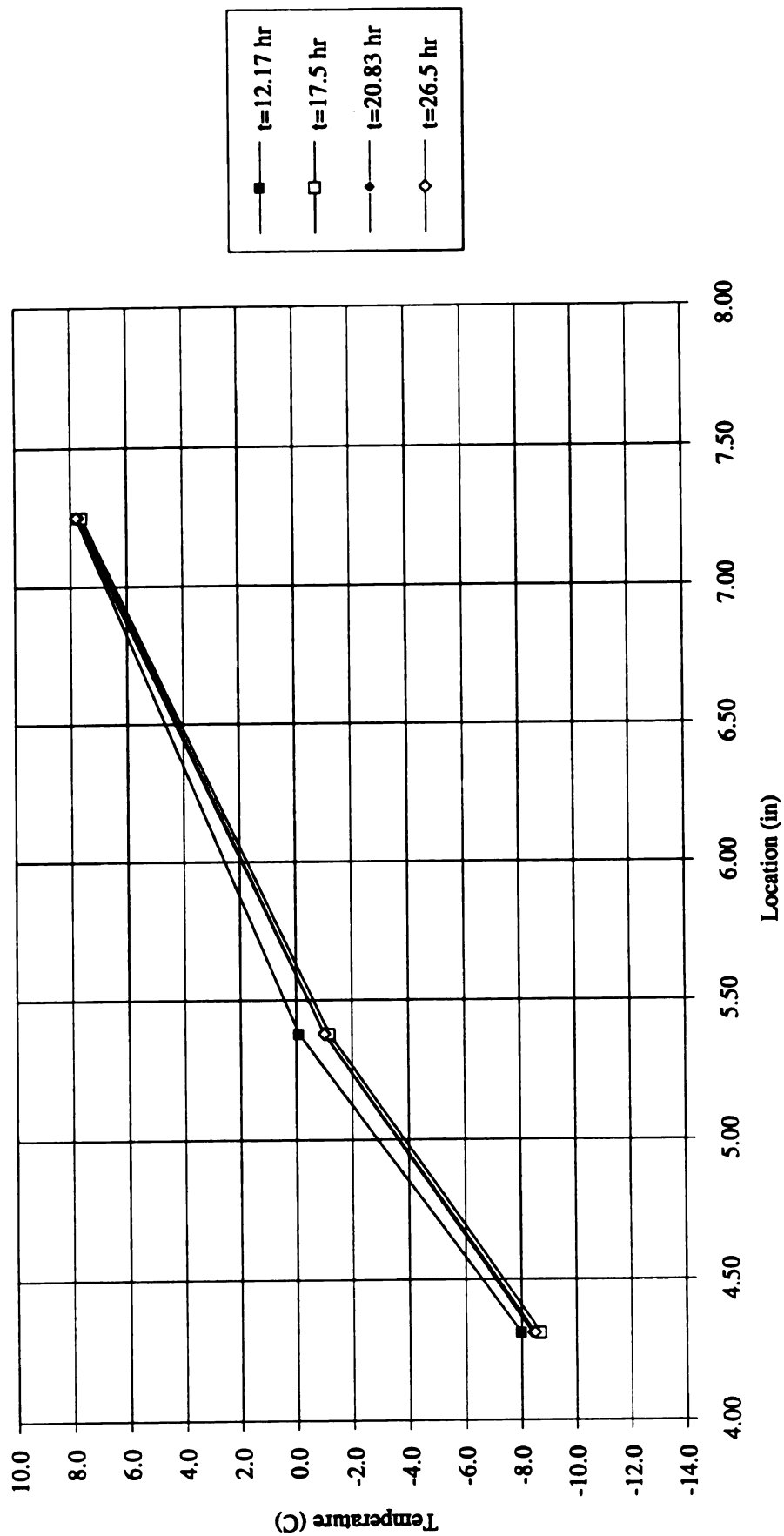


Figure A7.1: Temperature vs Location for Flow = 53 ml/min With Dodecane, Run #1

Location			Temperature (C)			
(in)						
	t=0 hrs	t=1 hrs	t=2 hrs	t=9.25 hrs	t=11 hrs	t=16.5 hrs
2	14.6	-21.2	-21.7	-23.6	-23.5	-22.2
3.88	14.3	-7.8	-12.8	-18.4	-18.9	-18
4.62	14.7	5.5	-0.7	-10.8	-11.9	-11.6
5.88	14.8	10.8	6	-3.8	-5.5	-5.7
7	14.7	12.6	9.2	1.8	-0.3	-1
8.38	14.8	13.5	11.1	6.1	4.1	4.5
9.5	14.7	13.6	11.6	8	6.5	8
10.62	14.6	13.6	11.7	9	7.9	10.4
15	14.4	10.4	7	2.6	2	5
16.56	14.7	12.1	10	7.9	6.5	8.6
17.62	14.9	13.1	11.8	10.5	9.4	12
19	15.4	13.5	12.7	11.6	10.8	14.2
20.44	15.3	13.7	12.8	11.5	10.9	14.6
21.38	15.5	14	13	11.6	11	14.9
23	15.4	13.9	12.9	11.5	10.9	14.8

Table A8: Flow = 53 ml/min With Dodecane, Run #2

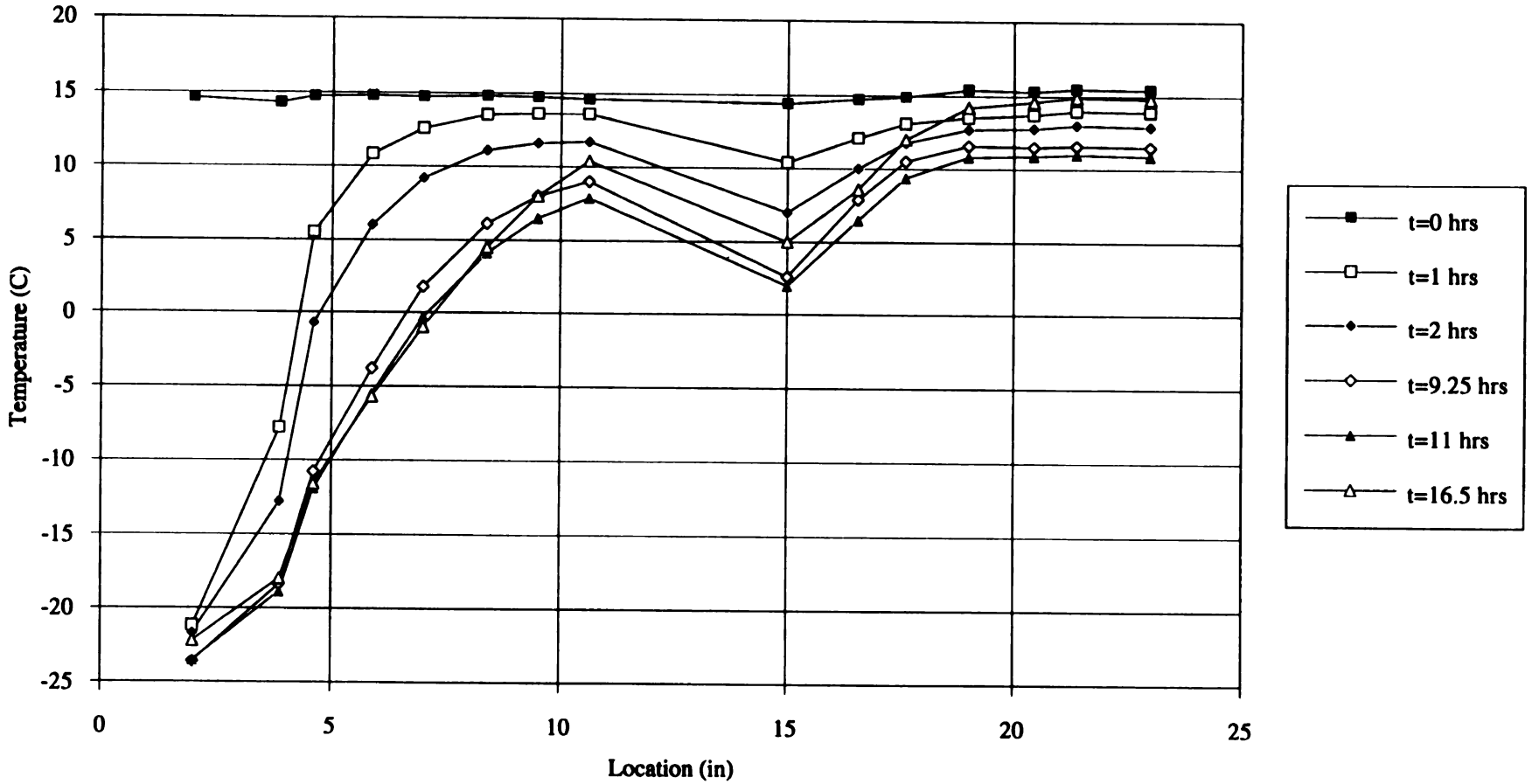


Figure A8: Temperature vs Location for Flow = 53 ml/min With Dodecane, Run #2

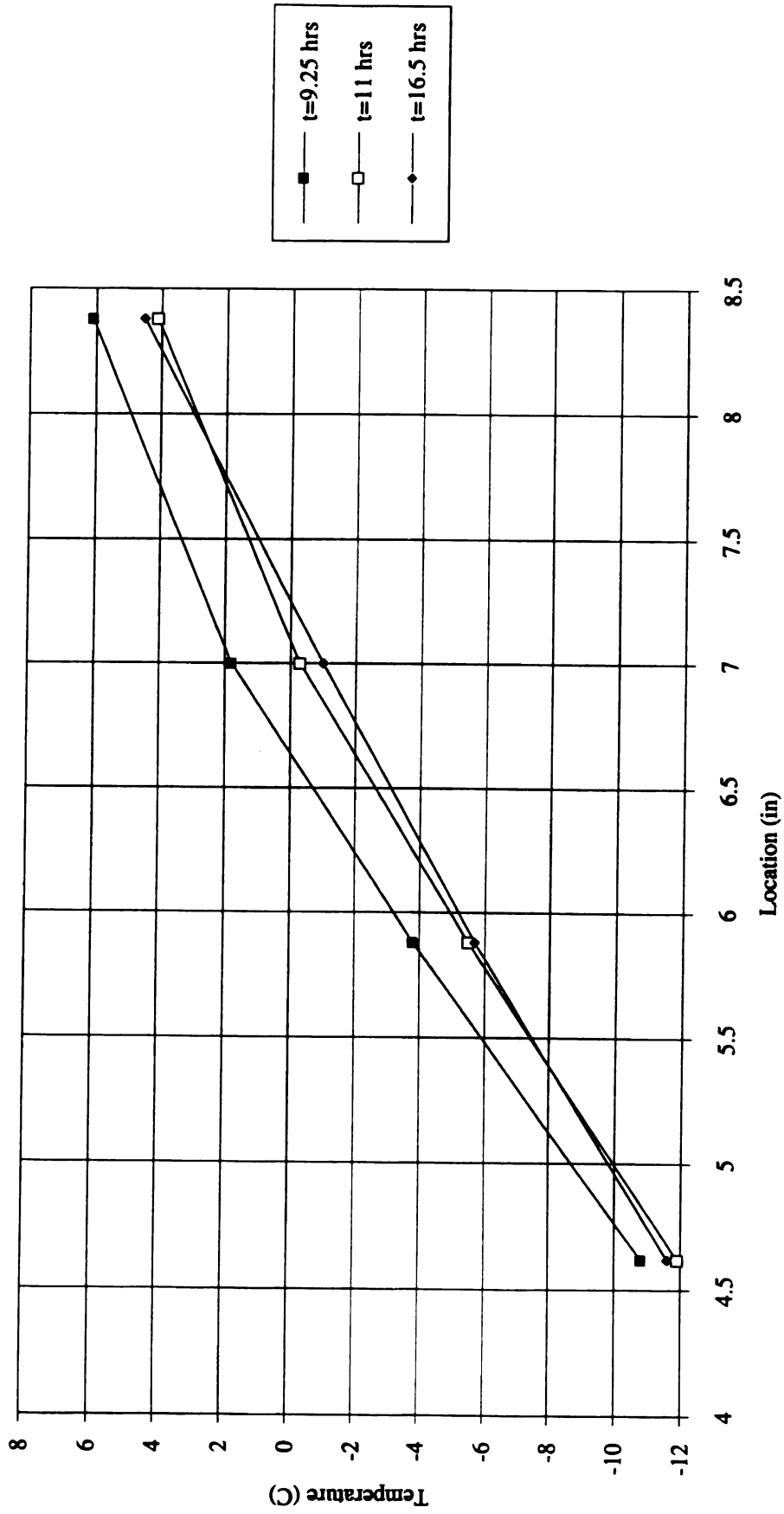


Figure A8.1: Temperature vs Location for Flow = 53 ml/min With Dodecane, Run #2

Location			Temperature (C)		
(in)					
	t=0 hrs	t=2 hrs	t=9 hrs	t=12.5 hrs	t=17.75 hrs
2.75	19.3	-18	-19.9	-19.5	-19.2
4.12	19.2	-3.1	-10.5	-10	-9.2
5.44	18.8	4	-3.6	-3.2	-1.9
6.38	19	7	0.8	1.4	3
7.5	18.8	8.5	4.3	5.3	7.3
8.75	18.5	9.3	7.3	8.6	10.6
10.12	18.4	9.7	9	10.3	12.2
11.69	18	9.4	8.9	10.3	12
16.12	18.5	8.4	7.8	9.2	10.6
17.19	17.7	9.3	10.1	11.6	13.3
19.94	16.2	9.8	12.2	13.7	15.4
21.62	16.3	10.1	12.5	14.1	15.8
23.31	16.3	9.9	12.3	13.9	15.6

Table A9: Flow = 53 ml/min With Dodecane, Run #3

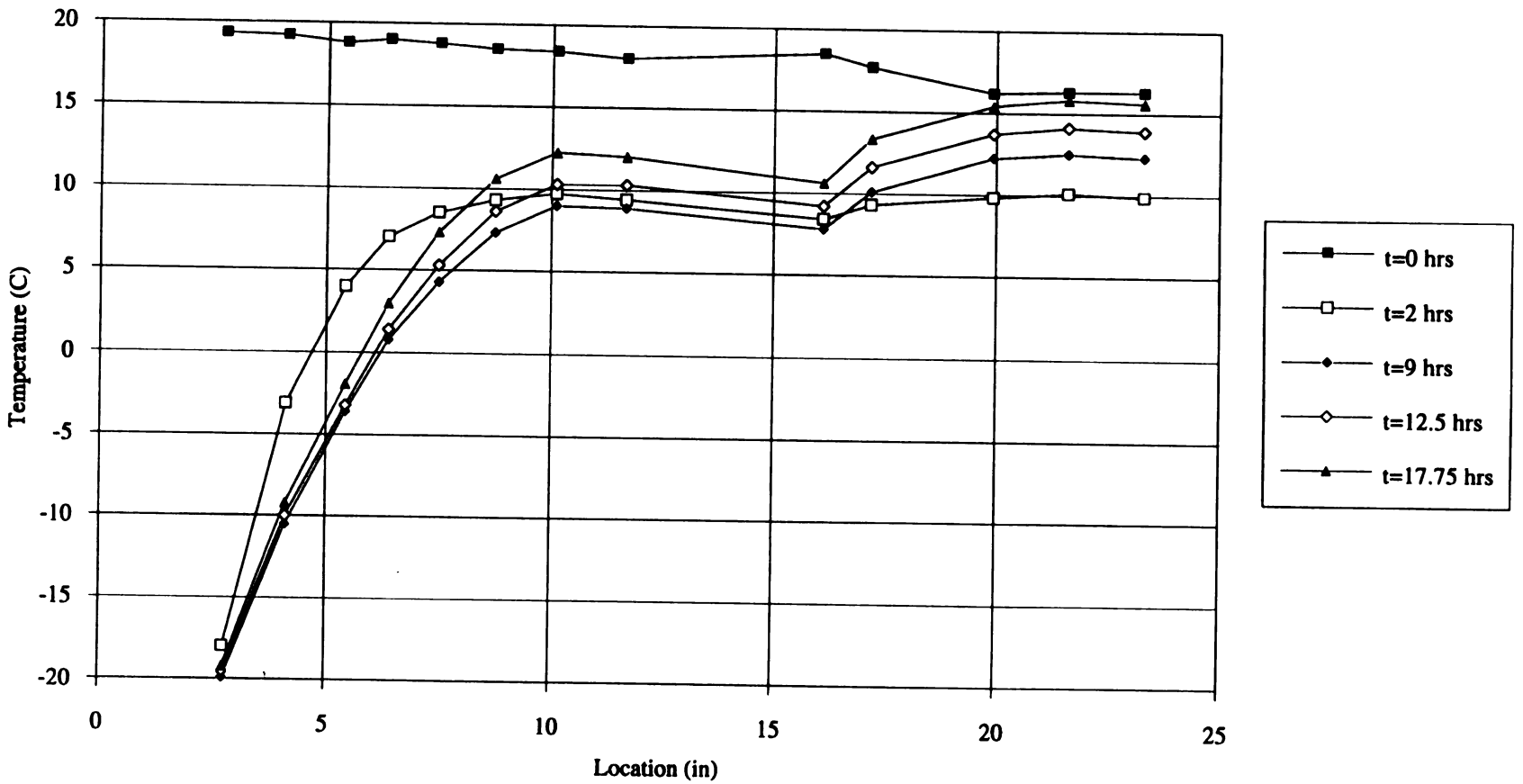


Figure A9: Temperature vs Location for Flow = 53 ml/min With Dodecane, Run #3

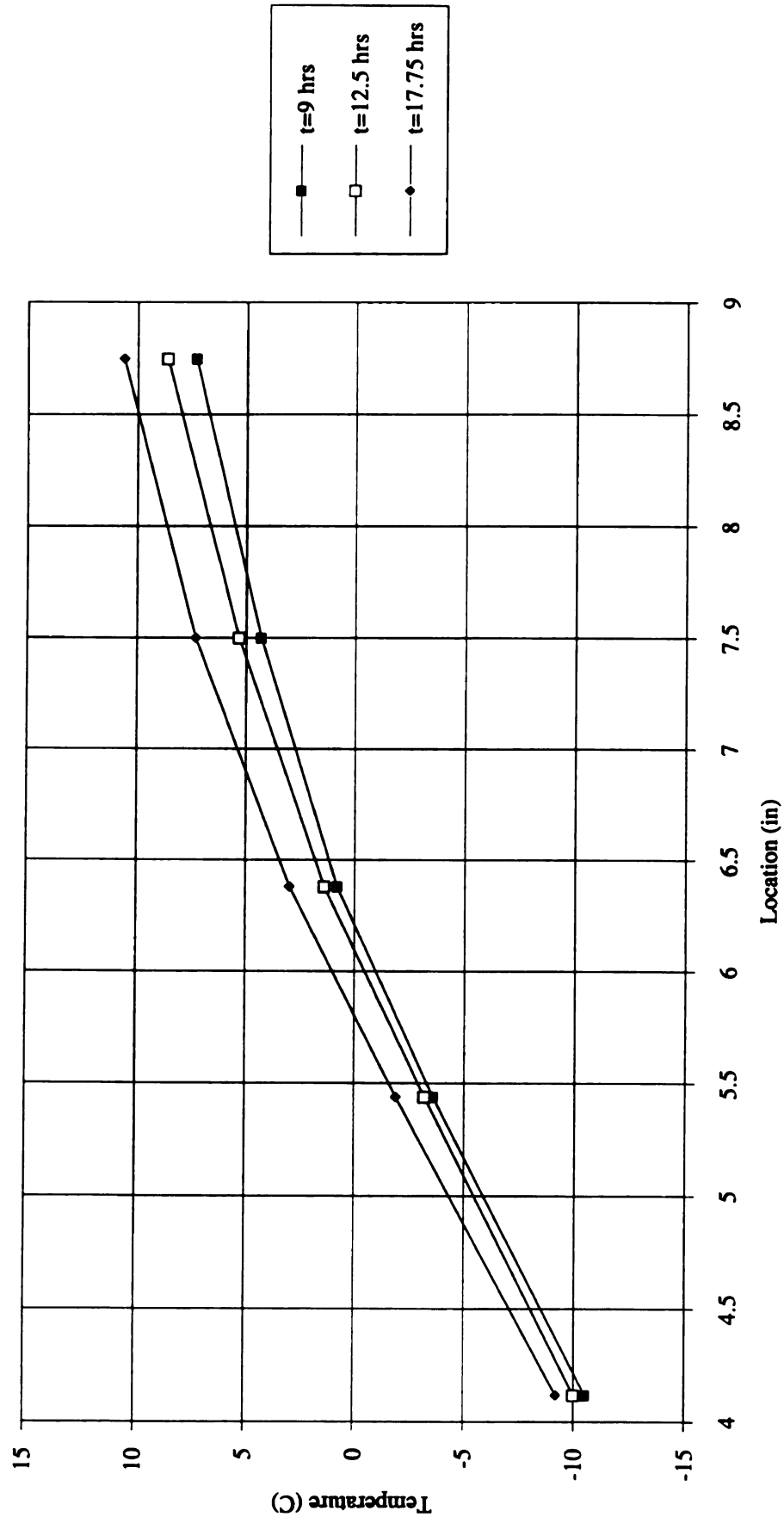


Figure A9.1: Temperature vs Location for Flow = 53 ml/min with Dodecane, Run #3

Location		Temperature (C)				
(in)						
	t=0 hrs	t=5 hrs	t=11 hrs	t=18.5 hrs	t=23.25 hrs	t=29.5 hrs
2	20	-17.9	-19.9	-20.8	-20.7	-20
4	20.7	-9.7	-12.6	-14	-14.3	-14.1
4.88	20.9	-3.4	-6.9	-8.6	-9.4	-9.4
6.19	21.1	2.9	-0.5	-2.5	-3.8	-4.2
7.12	21.3	5.3	2.4	0.5	-1.2	-1.5
8.25	21.3	7.3	4.9	3.3	1.6	1.5
9.5	21.3	8.6	6.7	5.5	3.9	4.2
15.12	20.2	6.2	5.5	4	3.4	5.7
17.88	20.8	9.2	7.4	6.1	5.3	7
18.38	20.9	10.8	9.7	8.8	8.5	10.9
19.81	21.1	11.6	10.9	9.8	9.4	12.1
20.69	21.3	12.1	11.6	10.3	9.6	12.5

Table A10: Flow = 53 ml/min With Dodecane, Run #4

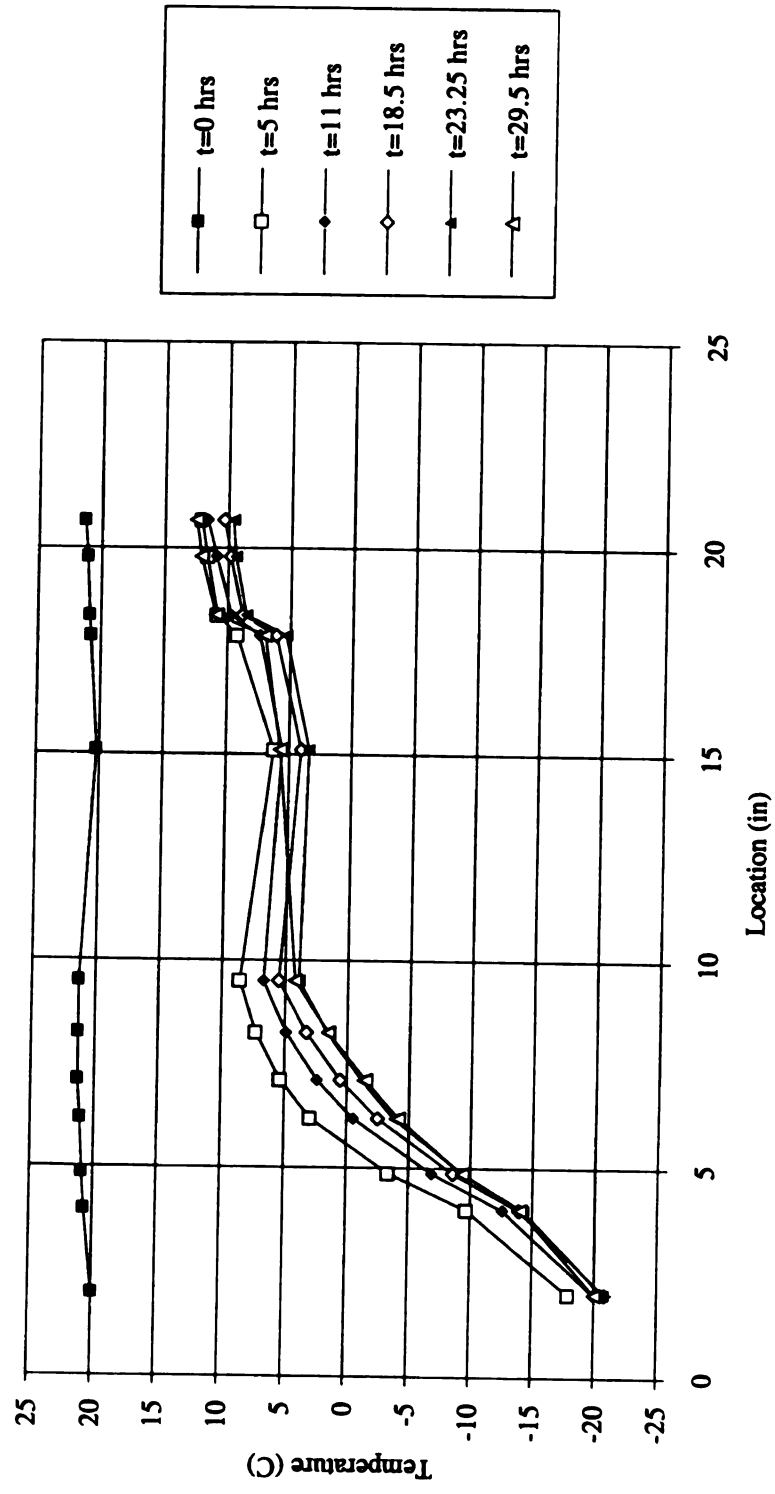


Figure A10: Temperature vs Location for Flow = 53 ml/min With Dodecane, Run #4

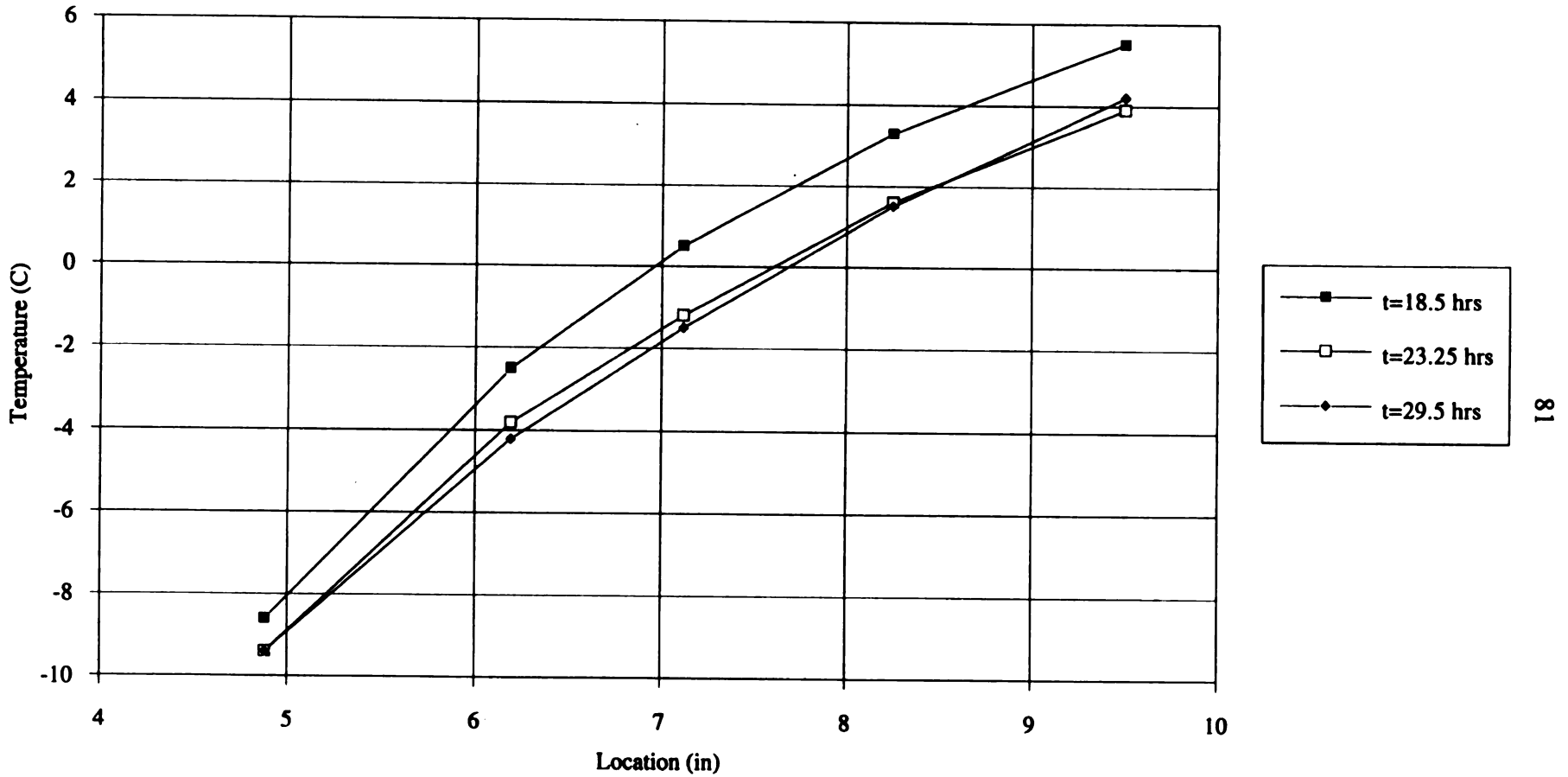


Figure A10.1: Temperature vs Location for Flow = 53 ml/min With Dodecane, Run #4

Location (inches)	Temperature (C)												
	t=0 hr	t=2.83 hr	t=5.75 hr	t=9.67 hr	t=15.0 hr	t=20.58 hr	t=26.25 hr	t=33.58 hr	t=41.17 hr	t=47.0 hr	t=51.58 hr	t=57.25 hr	t=64.67 hr
27.75	23.4	22.1	18.7	18.2	14.3	13.6	15.1	14.6	15.0	16.9	17.3	16.1	14.6
25.75	23.4	22.3	18.5	18.3	14.4	13.9	15.3	14.8	15.2	17.1	17.3	16.3	14.9
24.00	23.2	22.2	18.4	18.2	14.3	13.7	15.2	14.6	15.1	17.0	17.2	16.2	14.8
22.69	23.3	22.2	18.6	18.3	14.4	13.8	15.2	14.7	15.1	16.8	17.1	16.1	14.6
20.94	23.1	22.0	18.2	18.0	14.2	13.6	14.9	14.3	14.6	16.1	16.3	15.2	13.7
19.31	23.2	21.9	17.9	17.7	14.1	13.4	14.5	13.6	13.5	14.7	14.8	13.6	12.0
18.06	23.0	21.1	16.8	16.7	13.3	12.3	13.3	12.2	11.7	12.5	12.7	11.3	9.7
16.25	23.1	16.1	12.1	11.5	8.6	7.2	8.0	6.7	6.5	8.0	8.4	6.9	5.2
14.69	22.9	13.7	10.1	8.8	5.3	3.9	5.3	4.7	5.0	7.2	7.8	6.4	4.8
13.19	22.9	15.9	11.5	9.7	6.1	4.5	6.0	5.9	6.8	9.2	10.0	9.0	7.6
12.31	23.0	18.0	13.0	10.9	7.3	5.3	6.8	7.0	8.2	10.4	11.5	10.5	9.2
10.69	23.1	19.4	14.3	11.7	7.9	5.4	6.3	6.6	7.8	9.4	10.9	10.4	8.9
9.62	23.1	19.6	14.4	11.6	7.6	4.6	4.9	5.0	6.1	7.4	9.2	9.1	7.7

Table A11: Flow = 53 ml/min Without Dodecane, Run #1

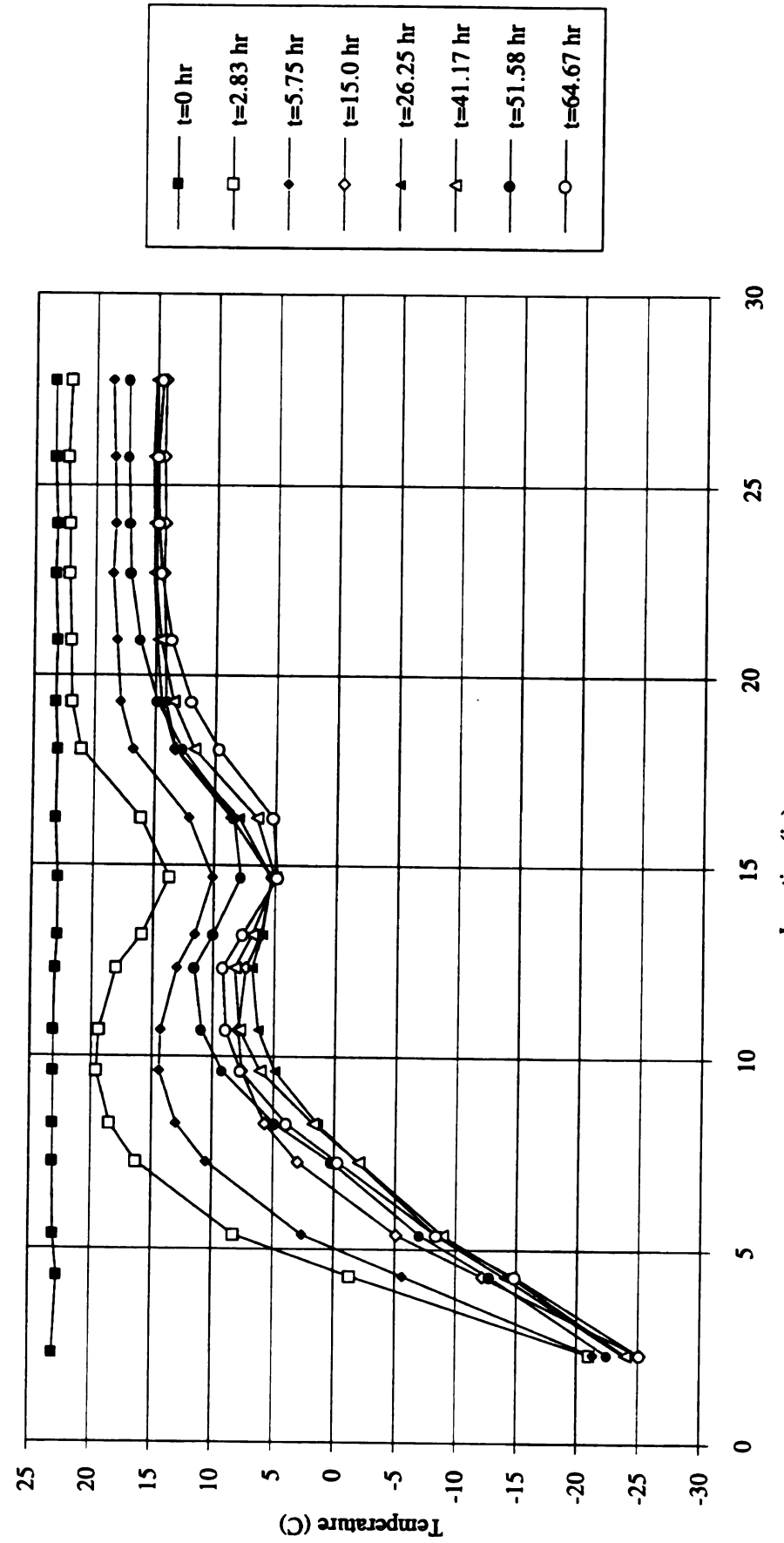


Figure A11: Temperature vs Location for flow = 53 ml/min Without Dodecane, Run #1

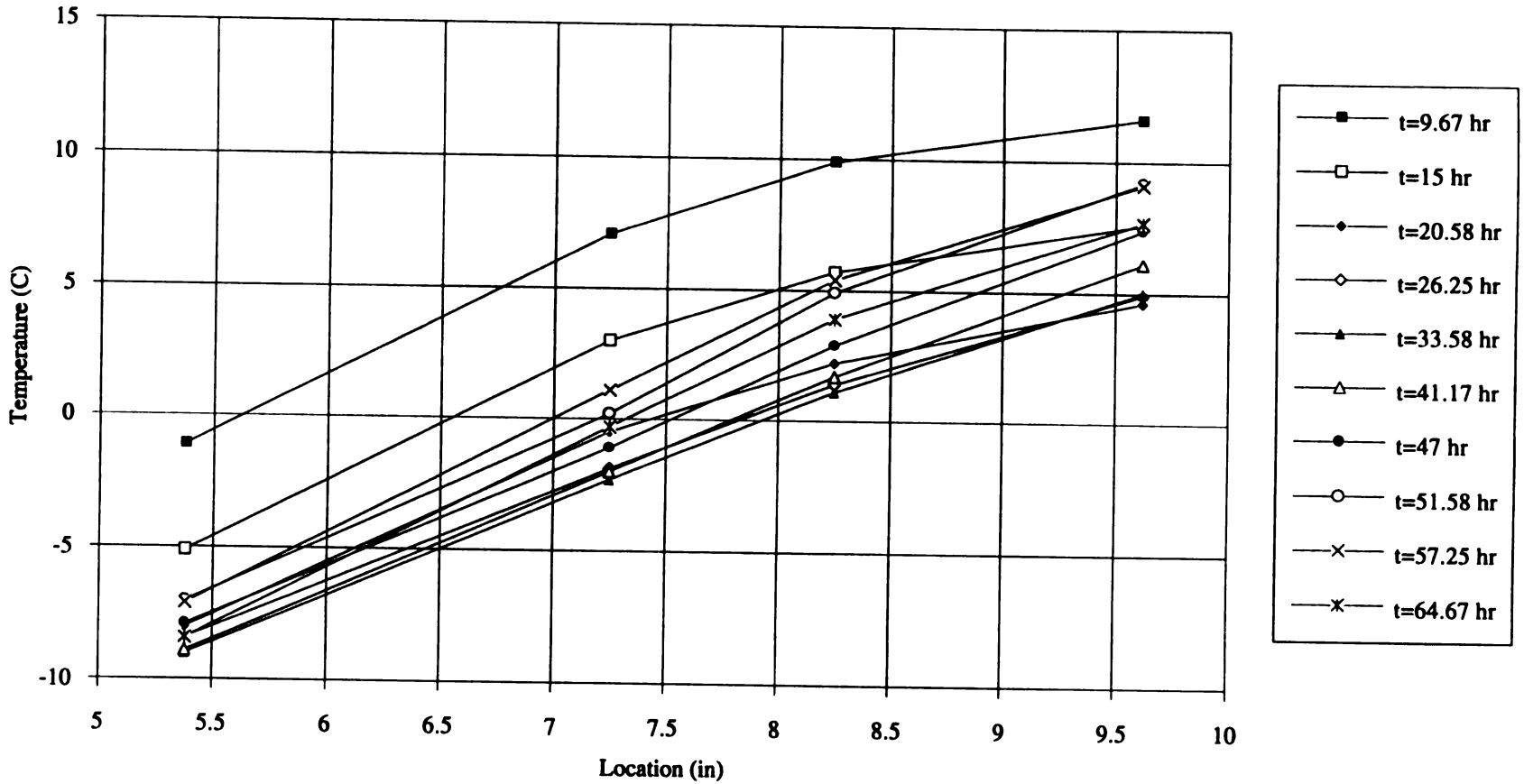


Figure A11.1: Temperature vs Location for Flow = 53 ml/min Without dodecane, Run # 1

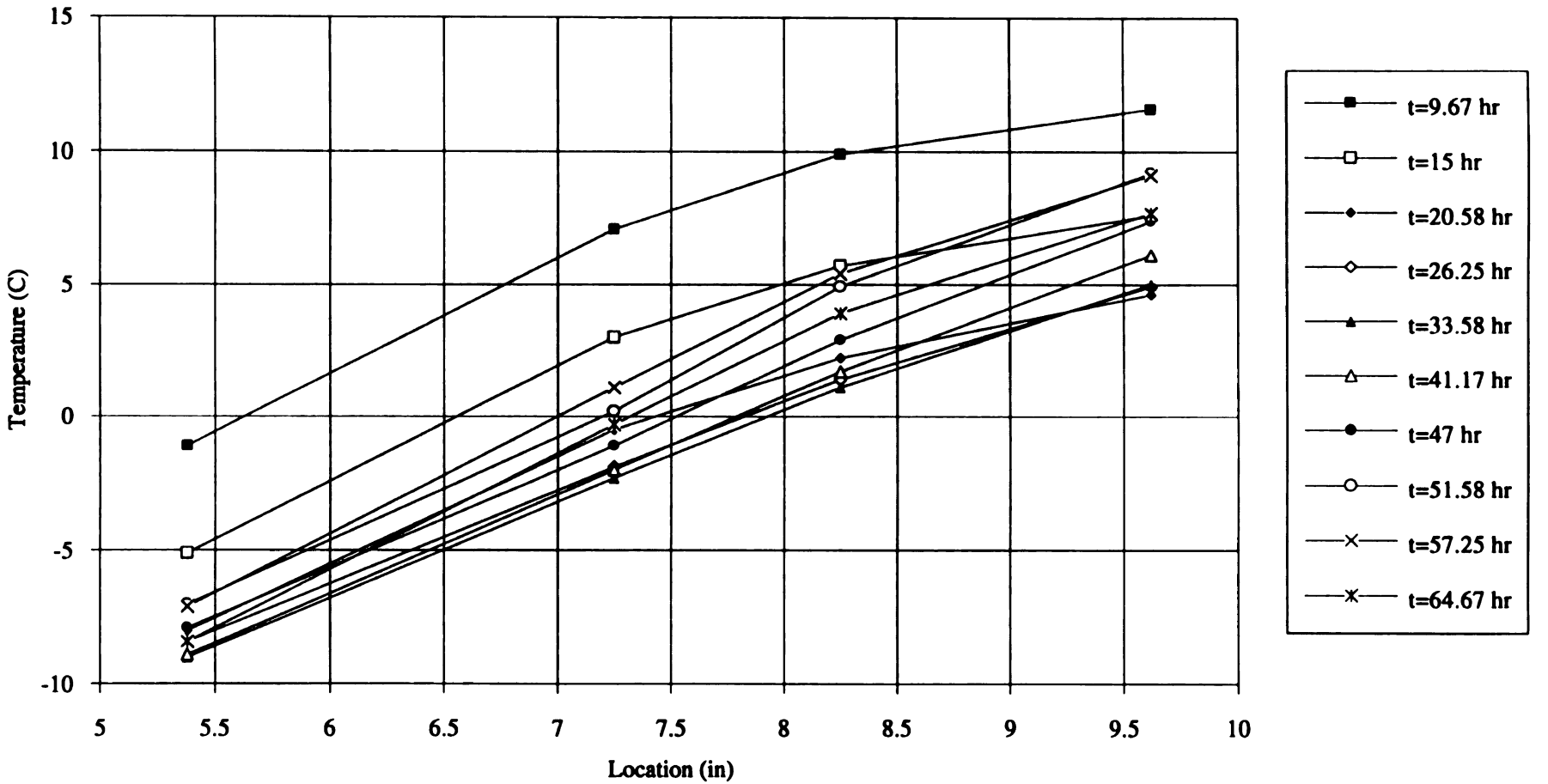


Figure A11.1: Temperature vs Location for Flow = 53 ml/min Without dodecane, Run # 1

Location		Temperature (C)			
(in)					
	t=0 hr	t=6.5 hr	t=11.67 hr	t=16.17 hr	t=22.67 hr
2	23.7	-22	-21	-20.7	-21.1
3.88	23.6	-16.4	-16.2	-15.9	-16.1
4.62	24.1	-7.5	-8.4	-8.2	-8.1
5.88	24.2	0.7	-1.5	-1.3	-1.1
7	24.2	7.6	5.2	5.4	5.8
8.38	24.2	11.8	10.2	10.8	11.1
9.5	24.2	13.2	12.3	13.2	13.5
10.62	24.2	14	13.4	14.5	14.7
15	23.6	6.3	7.3	8.3	8.3
16.56	23.9	10.3	10.6	11.4	11.6
17.62	23.9	13.6	13.5	14.5	14.7
19	24.2	15.8	15.6	16.8	17
20.44	24.1	16	15.9	17.3	17.5
21.38	24.3	16.2	16.1	17.5	17.8
23	24.1	16	16	17.5	17.7

Table A12: Flow = 53 ml/min Without Dodecane, Run #2

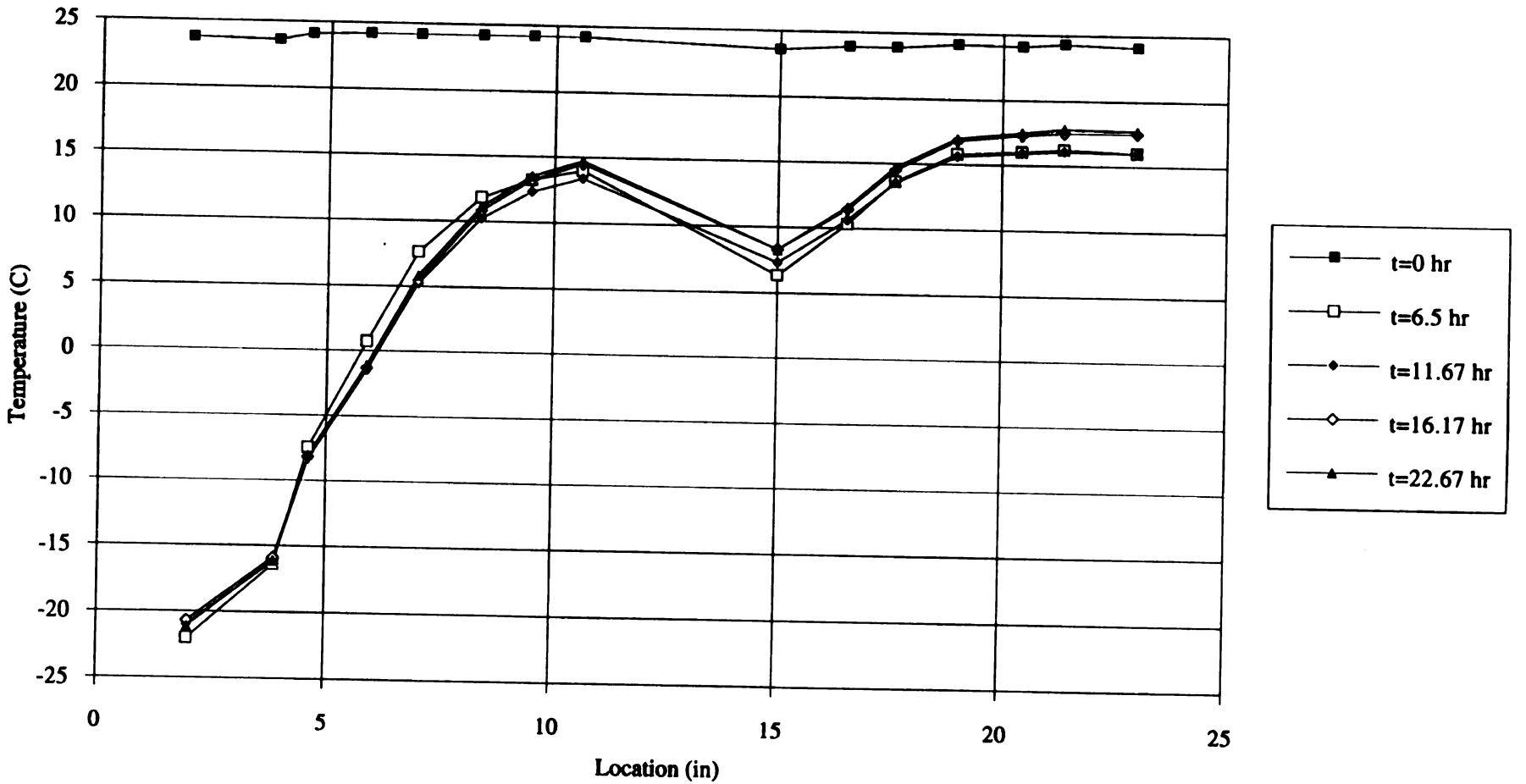


Figure A12: Temperature vs Location for Flow = 53 ml/min Without Dodecane, Run #2

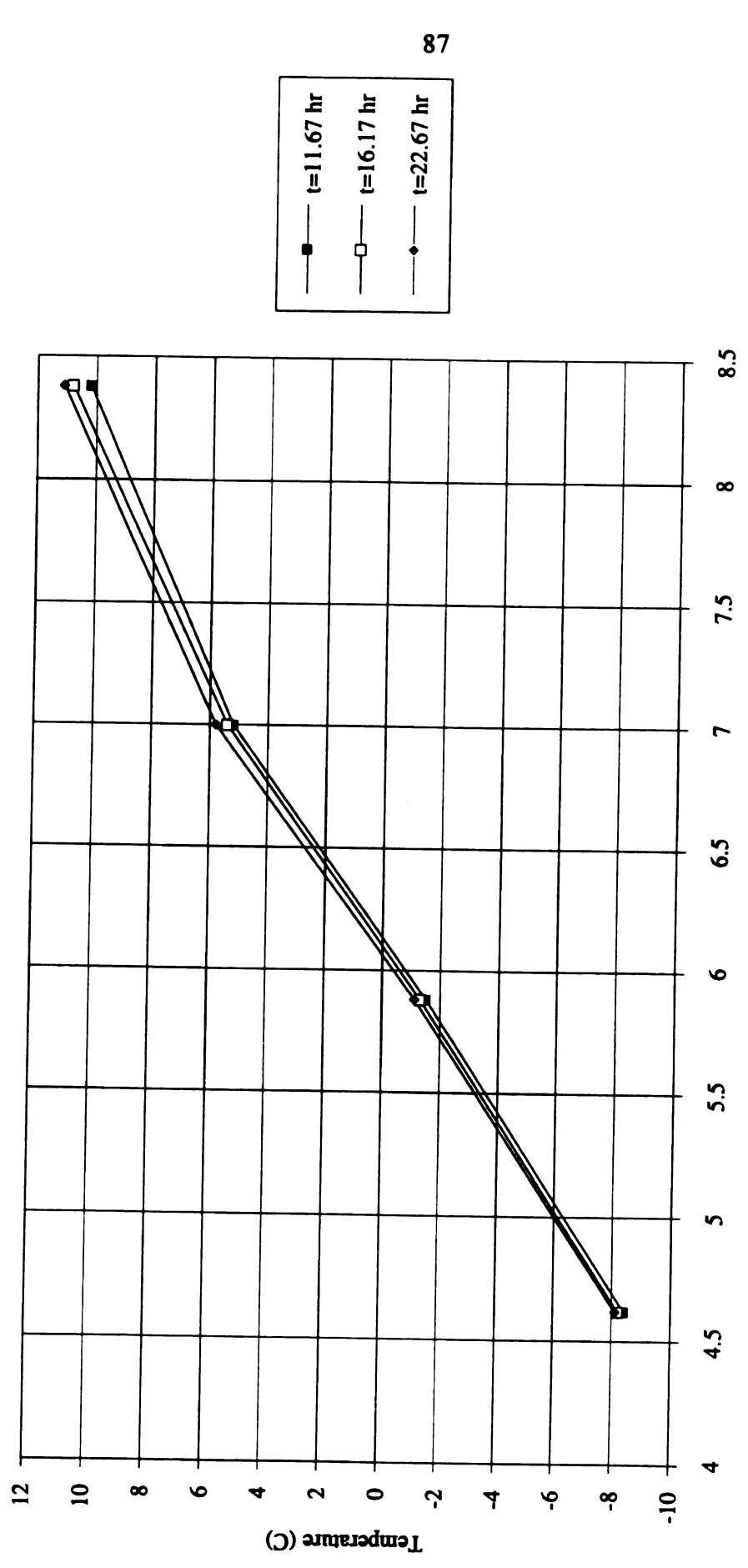


Figure A12.1: Temperature vs Location for Flow = 53 ml/min Without Dodecane, Run #2

Location		Temperature (C)	
(in)			
	t=0 hrs	t=6 hrs	t=14.75 hrs
2	-22.2	-4.5	-6
3.88	-18	-3.9	-6.1
4.62	-11.6	-2.3	-5.5
5.88	-5.7	-1.1	-5.5
7	-1	-0.3	-6.2
8.38	4.5	-0.1	-7.3
9.5	8	-0.7	-9.2
10.62	10.4	-5	-11.8
15	5	-22.9	-23
16.56	8.6	-13.5	-16.2
17.62	12	-4.4	-9.3
19	14.2	5.3	-1.1
20.44	14.6	10.8	7.2
21.38	14.9	11.9	10.1
23	14.8	12.2	11.7

Table A13: Flow = 65 ml/min With Dodecane, Run #1

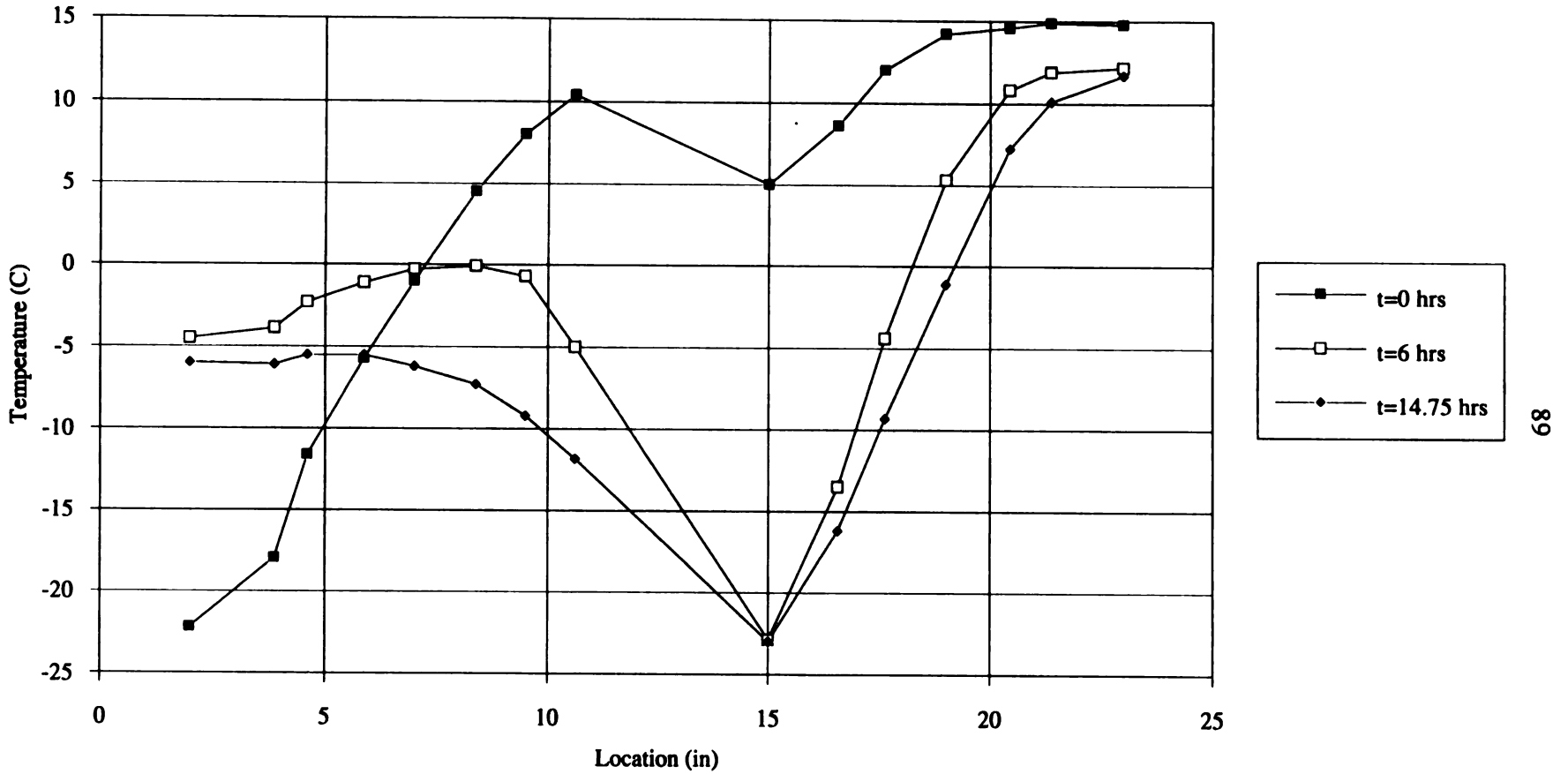


Figure A13: Temperature vs Location for Flow = 65 ml/min With Dodecane, Run #1

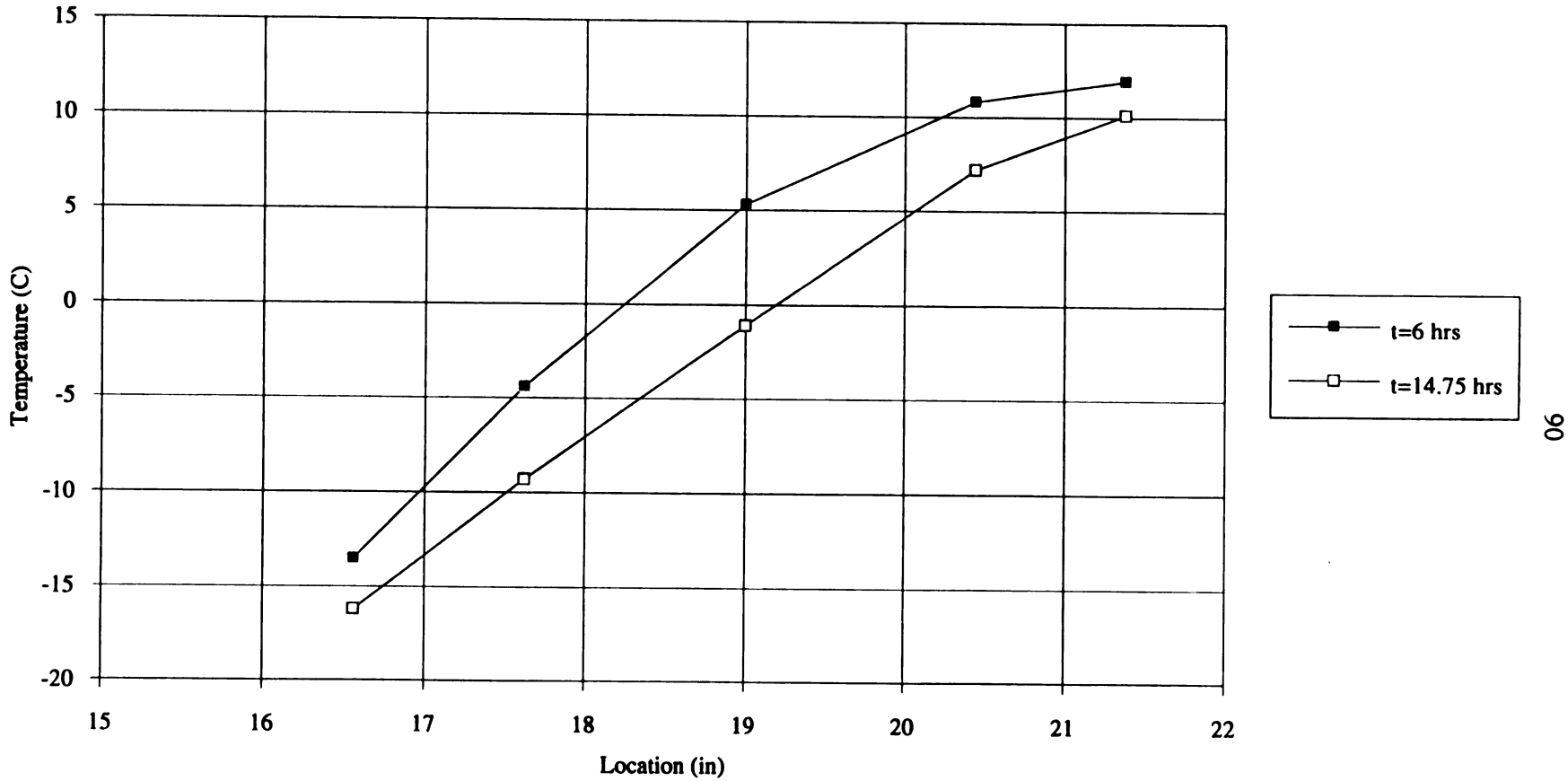


Figure A13.1: Temperature vs Location for Flow = 65 ml/min With Dodecane, Run #1

Location		Temperature (C)		
(in)				
	t=0 hrs	t=4 hrs	t=12.5 hrs	t=17 hrs
2.75	-19.2	-1.8	-3.5	-1.8
4.12	-9.2	-0.7	-1.3	-0.6
5.44	-1.9	0.6	0	-0.1
6.38	3	2.2	0.2	0
7.5	7.3	3.4	0	-0.9
8.75	10.6	3.5	-2.4	-3.4
10.12	12.2	1.7	-6.5	-7
11.69	12	-5	-12.6	-12.4
16.12	10.6	-13.1	-17.3	-16.5
17.19	13.3	-0.3	-8.2	-7.6
19.94	15.4	13.9	8.9	9.8
21.62	15.8	15	12.2	14.1
23.31	15.6	14.7	11.8	13.6

Table A14: Flow = 65 ml/min With Dodecane, Run #2

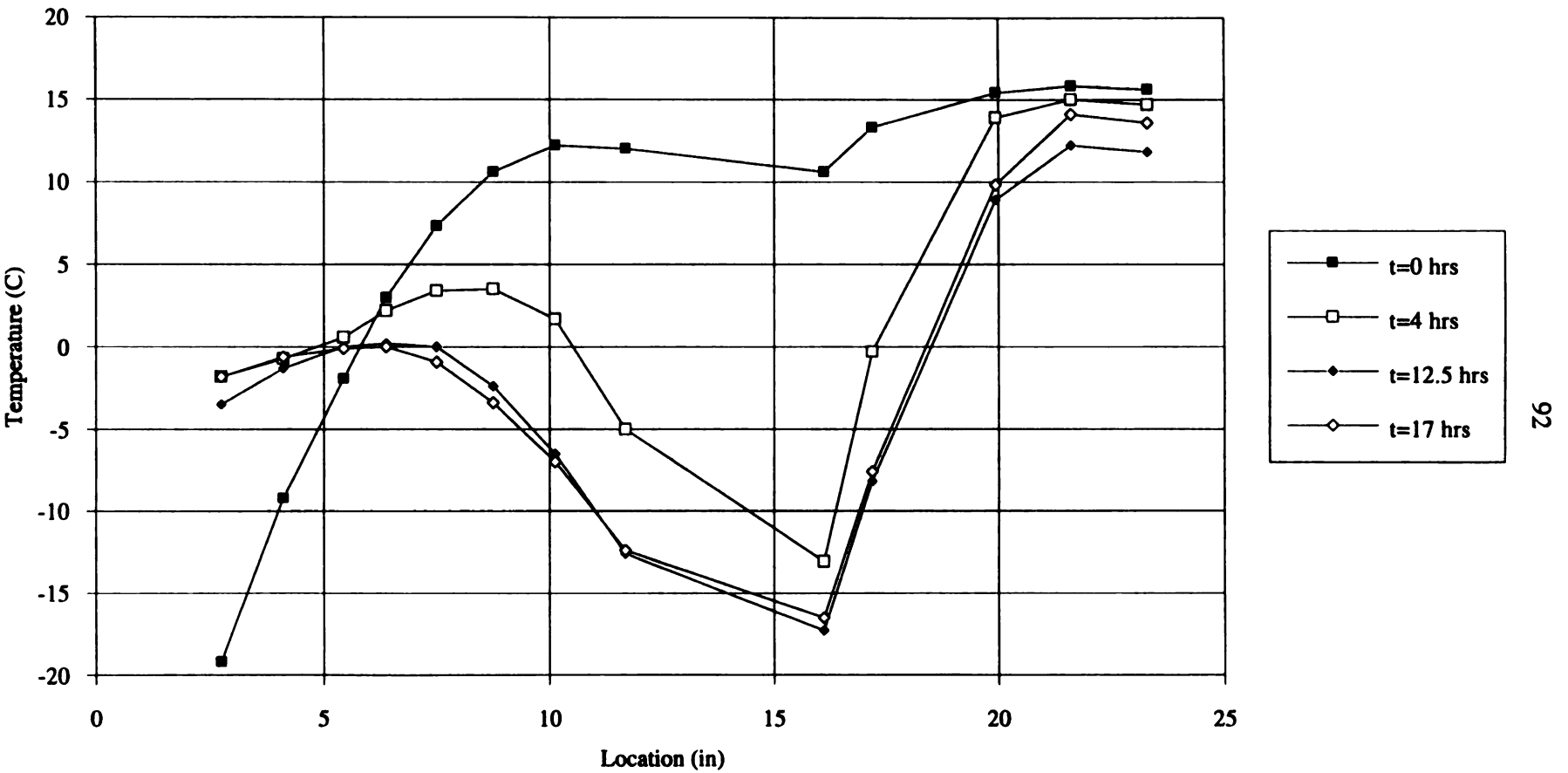


Figure A14: Temperature vs Location for Flow = 65 ml/min With Dodecane, Run #2

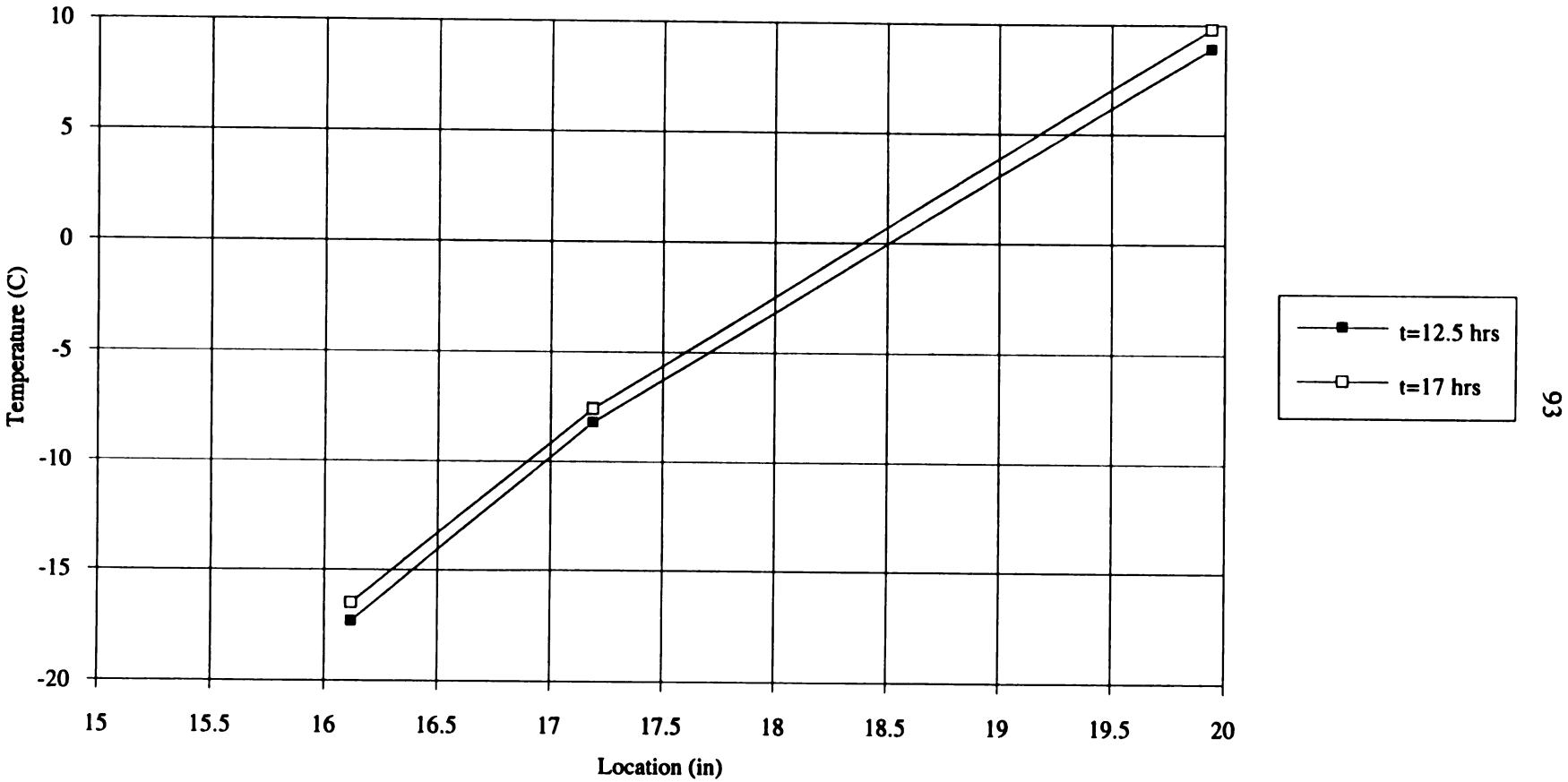


Figure A14.1: Temperature vs Location for Flow = 65 ml/min With Dodecane, Run #2

Location (in)	Temperature (C)			
	t=0 hrs	t=8.67 hrs	t=16.5 hrs	t=21.25 hrs
2	-21.1	-2.8	-1.3	-1.4
3.88	-16.1	-2.5	-1.4	-1.5
4.62	-8.1	-1.1	-0.6	-0.8
5.88	-1.1	-0.1	-0.2	-0.9
7	5.8	0.1	-0.8	-1.8
8.38	11.1	-0.1	-2.8	-3.5
9.5	13.5	-2.5	-5.2	-5.7
10.62	14.7	-6.5	-8.4	-8.8
15	8.3	-22.7	-21.6	-21.9
16.56	11.6	-14.1	-13.3	-13
17.62	14.7	-5.6	-5	-4.3
19	17	5.1	5.6	6.3
20.44	17.5	12.6	13.6	13.8
21.38	17.8	14.1	15.5	15
23	17.7	14.7	16.5	15.8

Table A15: Flow = 65 ml/min Without Dodecane, Run #1

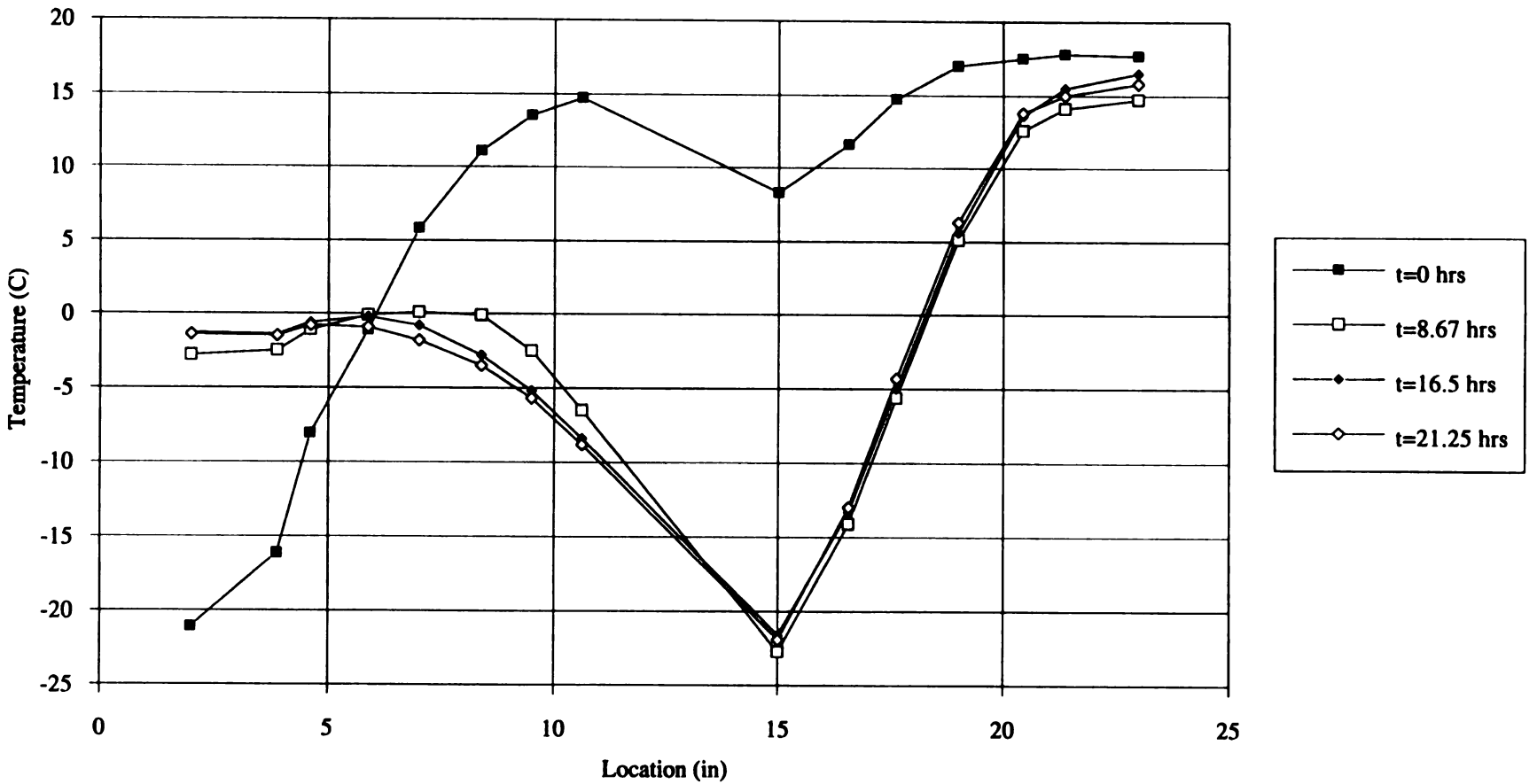


Figure A15: Temperature vs Location for Flow = 65 ml/min Without Dodecane

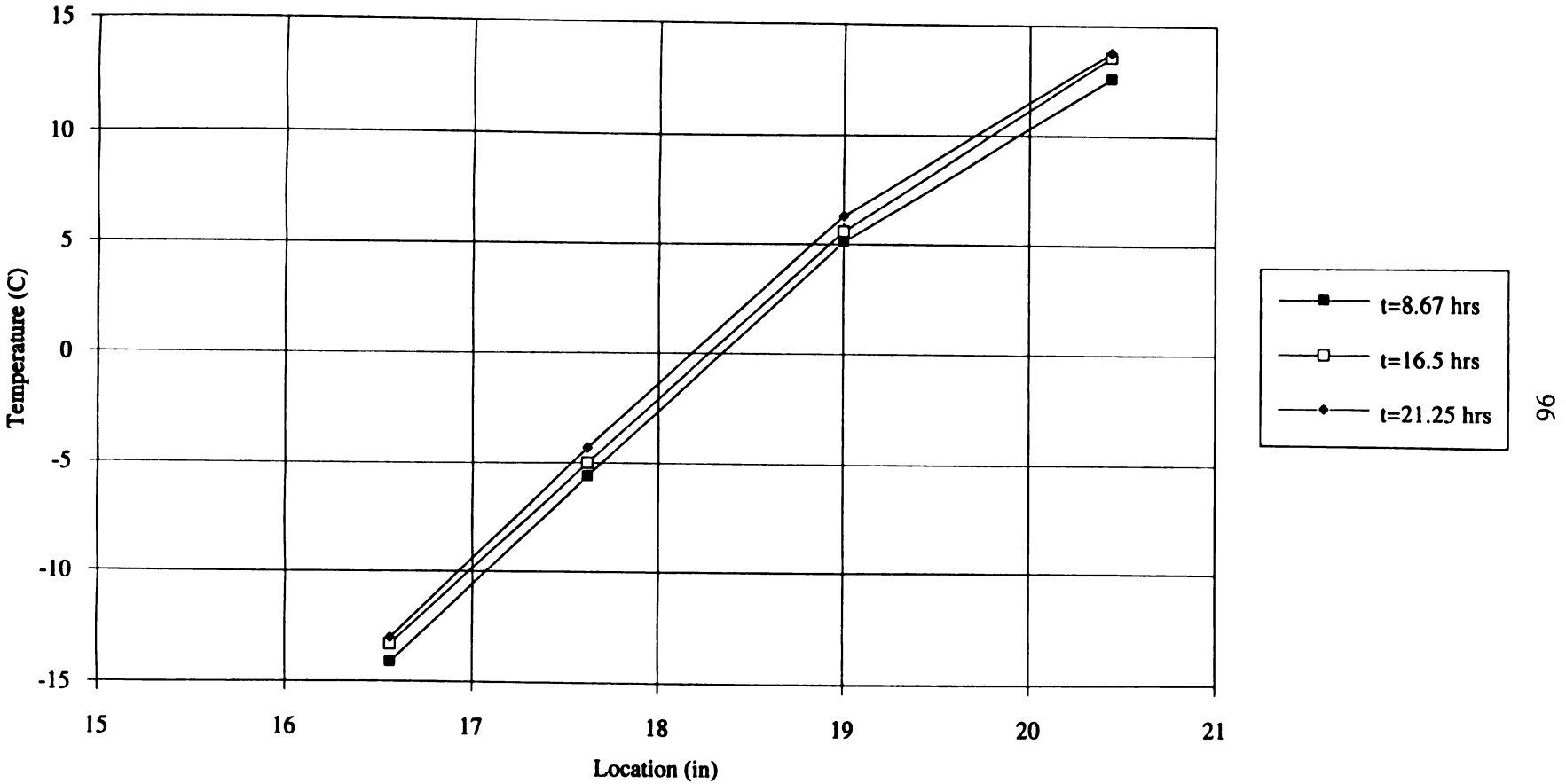


Figure A15.1: Temperature vs Location for Flow = 65 ml/min Without Dodecane

Location			Temperature (C)		
(in)					
	t=0 hrs	t=2.5 hrs	t=8 hrs	t=17 hrs	t=20 hrs
2	15.6	4.3	-0.1	-4.3	-3.2
3.88	14.7	6.6	0.4	-3.5	-3
4.62	14.6	9.9	2.6	-1.4	-1.7
5.88	14.1	11.3	4	-0.2	-0.8
7	13.7	11.4	4.1	-0.4	-2
8.38	13.2	11.3	3.3	-2.9	-3.9
9.5	13.8	9.8	1.1	-5.7	-6.4
10.62	14.5	6.5	-2.8	-9.2	-9.6
15	16.6	-20.8	-21.4	-22.9	-22.1
16.56	17.2	-8.4	-11.7	-14.3	-13.7
17.62	17.7	3.3	-1.9	-5.6	-5.1
19	18.4	11.9	9.4	5.3	5.8
20.44	18.5	14.3	14.5	12.2	12.8
21.38	18.8	14.8	15.3	13.4	14.1
23	18.6	14.7	15.3	13.6	14.4

Table A16: Flow = 79 ml/min With Dodecane

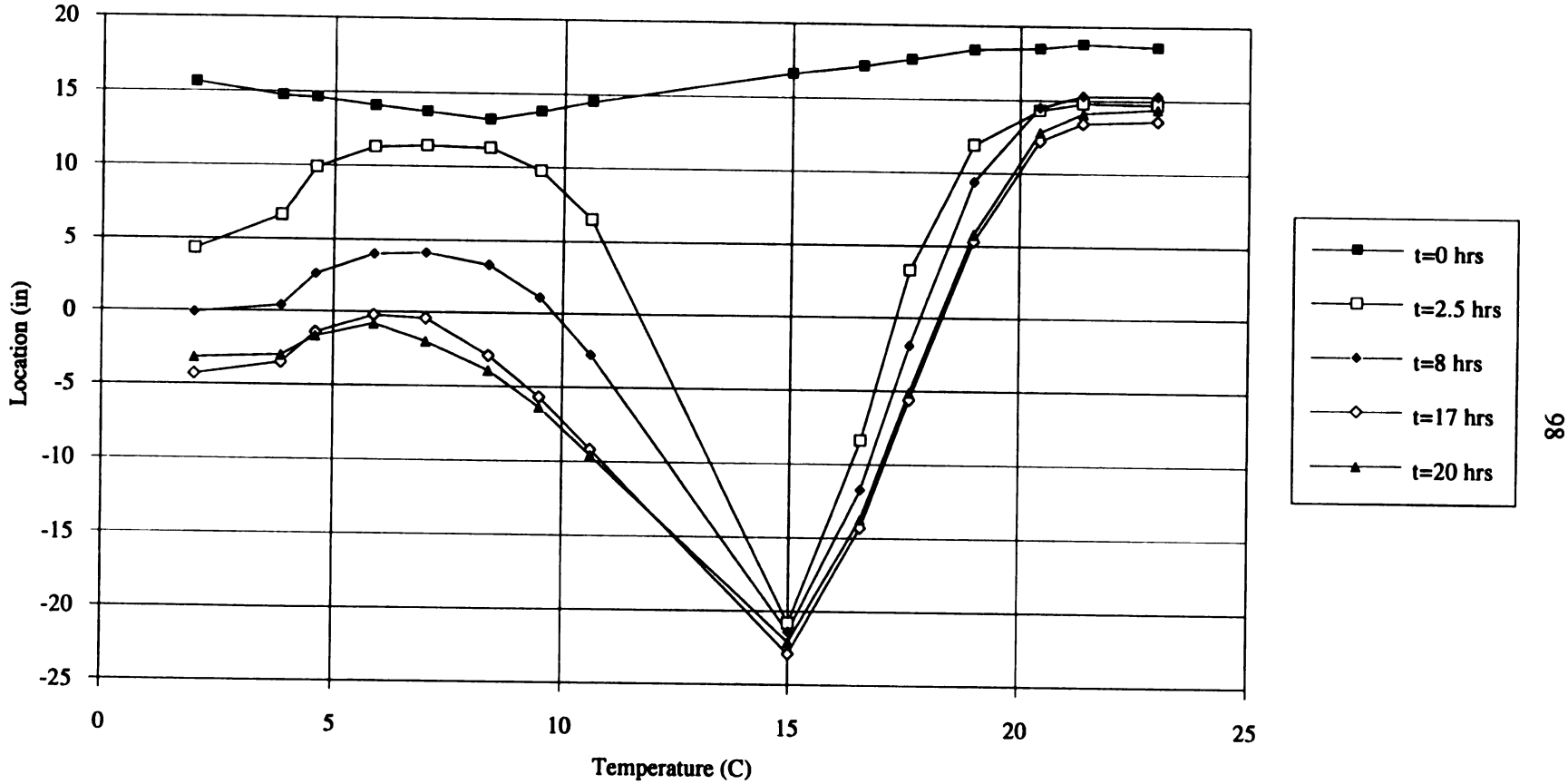


Figure A16: Temperature vs Location for Flow = 79 ml/min With Dodecane

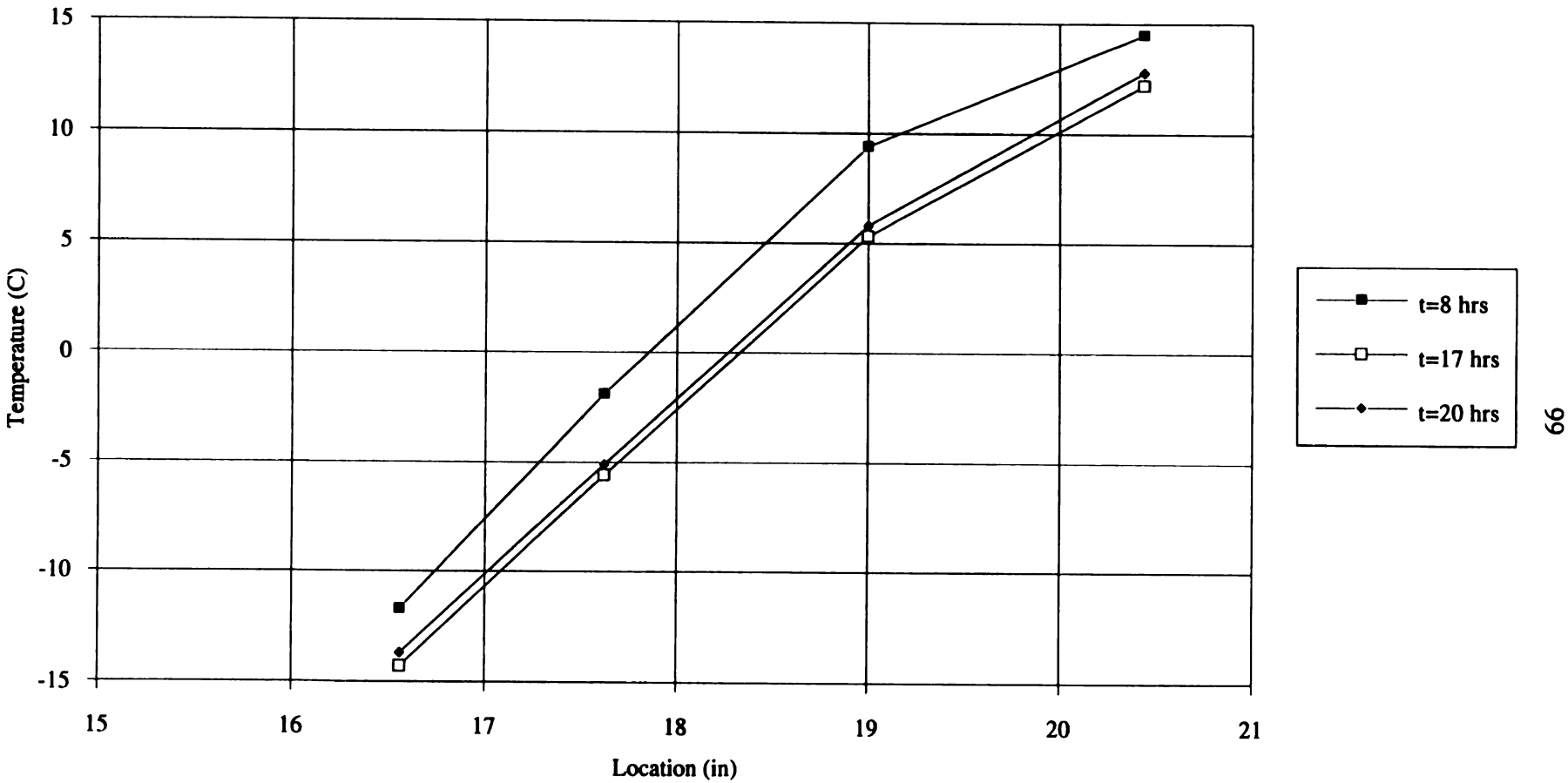


Figure A16.1: Temperature vs Location for Flow = 79 ml/min With Dodecane

Appendix B

Freeze Front Advancement with CN = 0

* With Dodecane Run #1					** Without Dodecane Run #1					* Without Dodecane Run #2				
Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Mvment (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)
0	0	0			0	0	0			0	0	0		
3.03	7.70	12.00	0.253	0.641	0.0800	0.203	3.50	0.0229	0.0581	3.12	7.92	8.67	0.360	0.914
1.28	3.25	3.50	0.366	0.929	2.68	6.81	16.00	0.168	0.425	0.520	1.32	7.83	0.0664	0.169
0.500	1.27	7.00	0.0714	0.181						0.310	0.787	4.50	0.0689	0.175
0.300	0.762	5.00	0.0600	0.152						0.180	0.457	4.17	0.0432	0.110
0.950	2.41	10.75	0.0884	0.224						0.150	0.381	4.00	0.0375	0.0953
										0.290	0.737	6.83	0.0425	0.108
										0.520	1.32	17.75	0.0293	0.0744

Freeze Front Advancement for CN = 0.00028

* With Dodecane					** Without Dodecane				
Net Mvment (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)
0	0	0			0	0	0		
2.84	7.21	3.25	0.874	2.22	0.880	2.24	5.50	0.160	0.406
0.571	1.45	8.33	0.0685	0.174	0.390	0.991	5.75	0.0678	0.172
-0.100	-0.254	7.92	-0.0126	-0.0321	0.100	0.254	7.25	0.0138	0.0350
0.200	0.508	7.00	0.0286	0.0726					
0.160	0.406	12.00	0.0133	0.0339					

* = Began readings at second freeze pipe

** = Began readings after first freeze pipe was already turned on

Table B1: Freeze Front Advancement for Capillary Numbers of 0 and 0.00028 With and Without Dodecane

Freeze Front Advancement for CN = 0.00030 with Dodecane

Run #1					Run #2				
Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)
0	0	0			0	0	0		
1.84	4.67	1.42	1.30	3.29	2.31	5.87	1.00	2.31	5.87
0.510	1.30	1.58	0.323	0.820	0.440	1.12	1.00	0.440	1.12
0.510	1.30	3.67	0.139	0.353	1.89	4.80	7.25	0.261	0.662
0.234	0.594	5.50	0.0425	0.108	0.400	1.02	1.75	0.229	0.581
0.240	0.610	5.33	0.0450	0.114	0.200	0.508	5.50	0.0364	0.0924
-0.0400	-0.102	3.33	-0.0120	-0.0305					

Run #3					Run #4				
Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)
0	0	0			0	0	0		
1.95	4.95	2.00	0.975	2.48	3.59	9.12	5.00	0.718	1.82
1.51	3.84	7.00	0.216	0.548	0.760	1.93	6.00	0.127	0.322
-0.120	-0.305	3.50	-0.0343	-0.0871	0.610	1.55	7.50	0.0813	0.207
					0.640	1.63	4.75	0.135	0.342
					0.0900	0.229	6.25	0.0144	0.0366

Freeze Front Advancement for CN of 0.00030 Without Dodecane

Run #1					Run #2				
Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)
0	0	0			0	0	0		
2.15	5.46	2.83	0.760	1.93	3.77	9.58	6.50	0.580	1.47
0.580	1.47	2.92	0.199	0.505	0.360	0.914	5.17	0.0696	0.177
0.590	1.50	3.92	0.151	0.382	-0.0300	-0.0762	4.50	-0.00667	-0.0169
0.930	2.36	5.33	0.174	0.443					
0.880	2.24	5.58	0.158	0.401					
0.390	0.991	5.67	0.0688	0.175					
0.100	0.254	7.33	0.0136	0.035					

* = Began readings at second freeze pipe

** = Began readings after first freeze pipe was already turned on

Table B2: Freeze Front Advancement for Capillary Number of 0.00030 With and Without Dodecane

Freeze Front Advancement for CN = 0.00037

* With Dodecane Run #1					* With Dodecane Run #2					* Without Dodecane Run #1				
Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)	Net Movement (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)
0	0	0			0	0	0			0	0	0		
2.24	5.69	6.00	0.373	0.948	2.25	57.15	4.00	0.563	14.29	2.34	5.94	8.67	0.270	0.686
0.940	2.39	8.75	0.107	0.273	1.26	32.00	8.50	0.148	3.77	-0.0700	-0.178	7.83	-0.00894	-0.023
					-0.120	-3.05	4.50	-0.0267	-0.677					

Freeze Front Advancement for CN = 0.00045

* With Dodecane				
Net Mvment (in)	Net Movement (cm)	Net Time (hrs)	Rate (in/hr)	Rate (cm/hr)
0	0	0		
1.82	4.62	2.50	0.728	1.85
0.530	1.35	5.50	0.0964	0.245
0.780	1.98	9.00	0.0867	0.220

* = Began readings at second freeze pipe

** = Began readings after first freeze pipe was already turned on

Table B3: Freeze Front Advancement for Capillary Numbers of 0.00037 and 0.00045 With and Without Dodecane

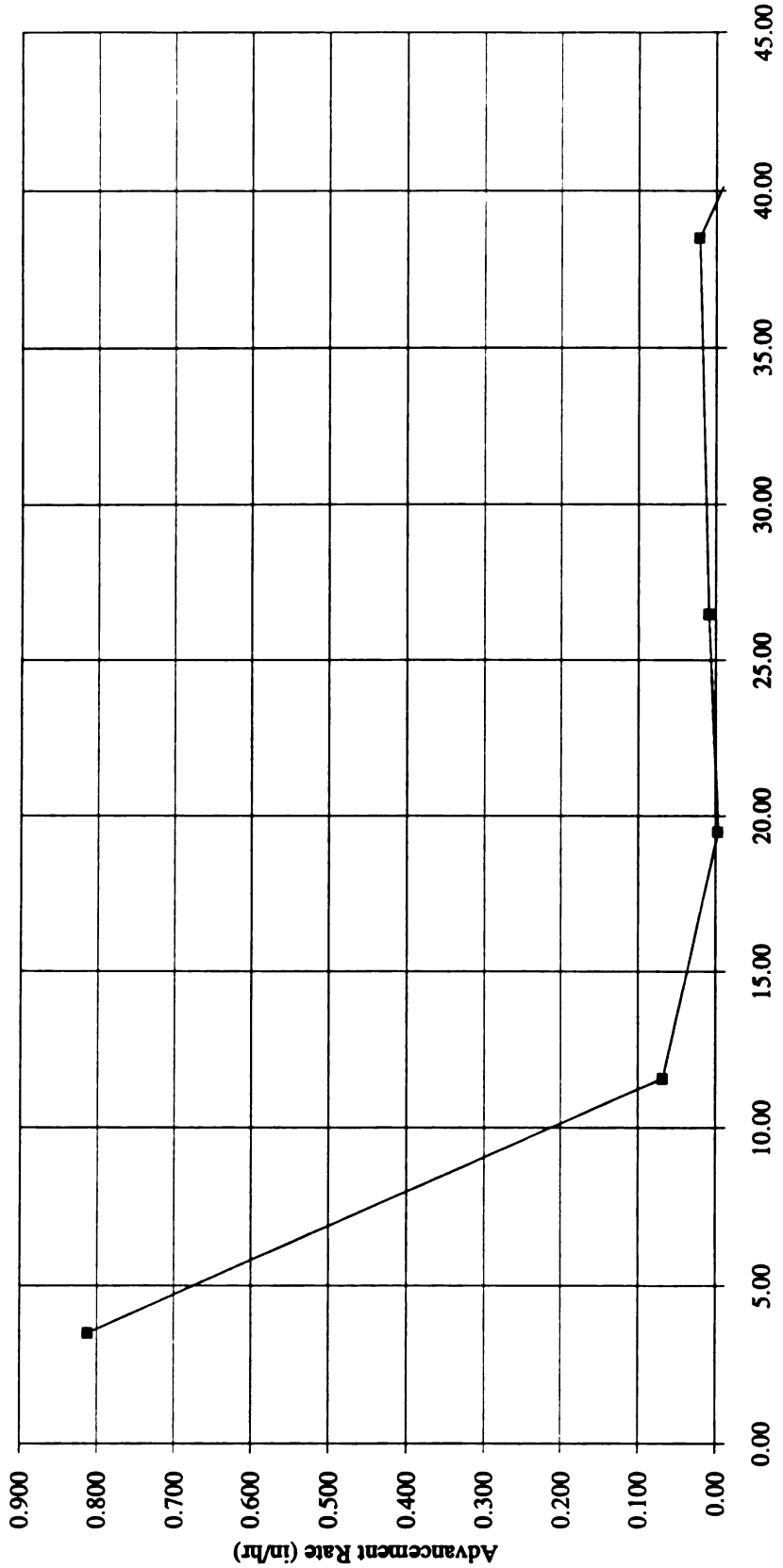


Figure B.1: Advancement Rate vs Time for 49 ml/min with Dodecane

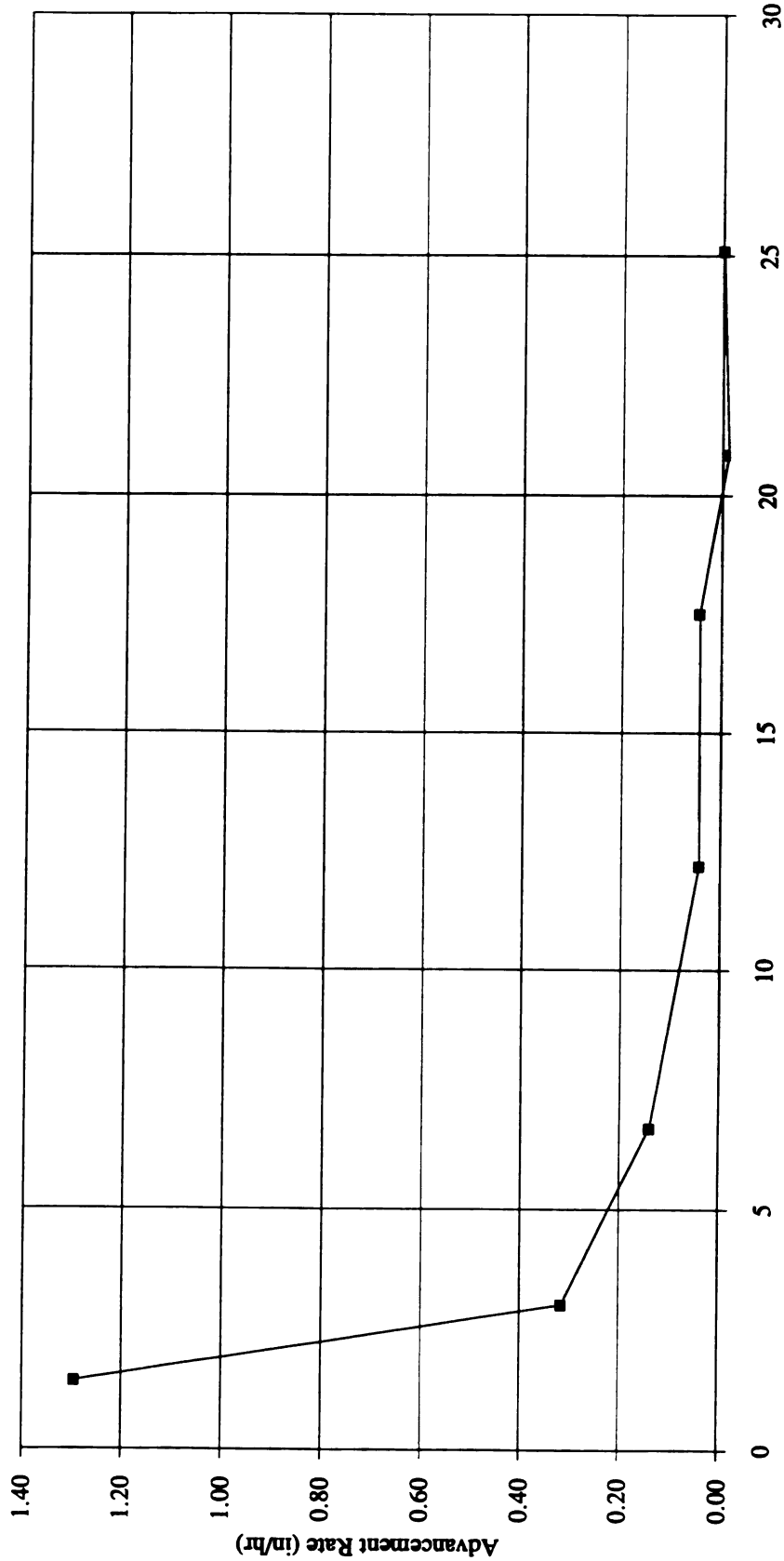


Figure B2.1: Advancement Rate vs Time for 53 ml/min with Dodecane

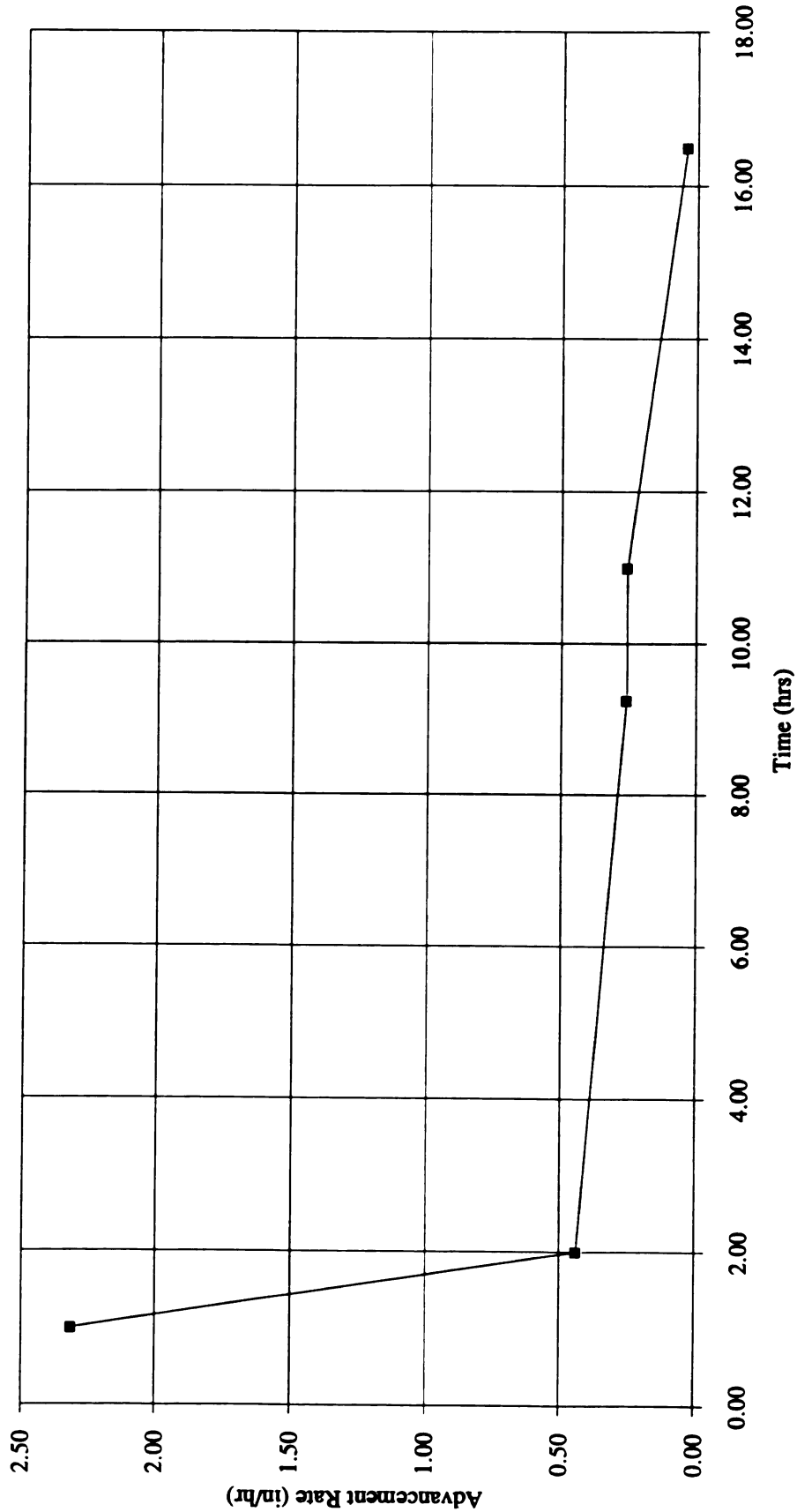


Figure B3.1: Advancement Rate vs Time for 53 ml/min with Dodecane

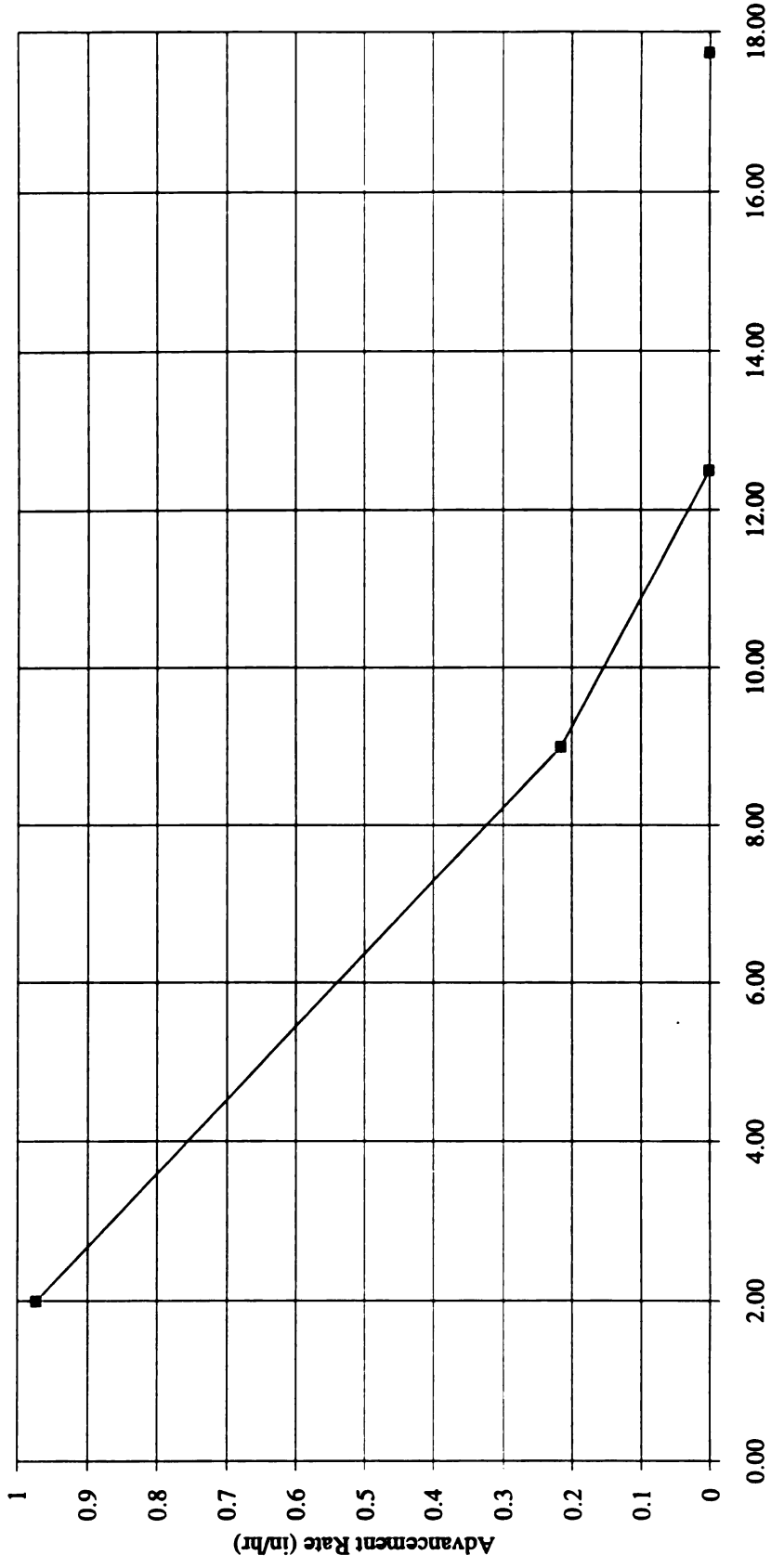


Figure B4.1: Advancement Rate vs Time for 53 ml/min with Dodecane

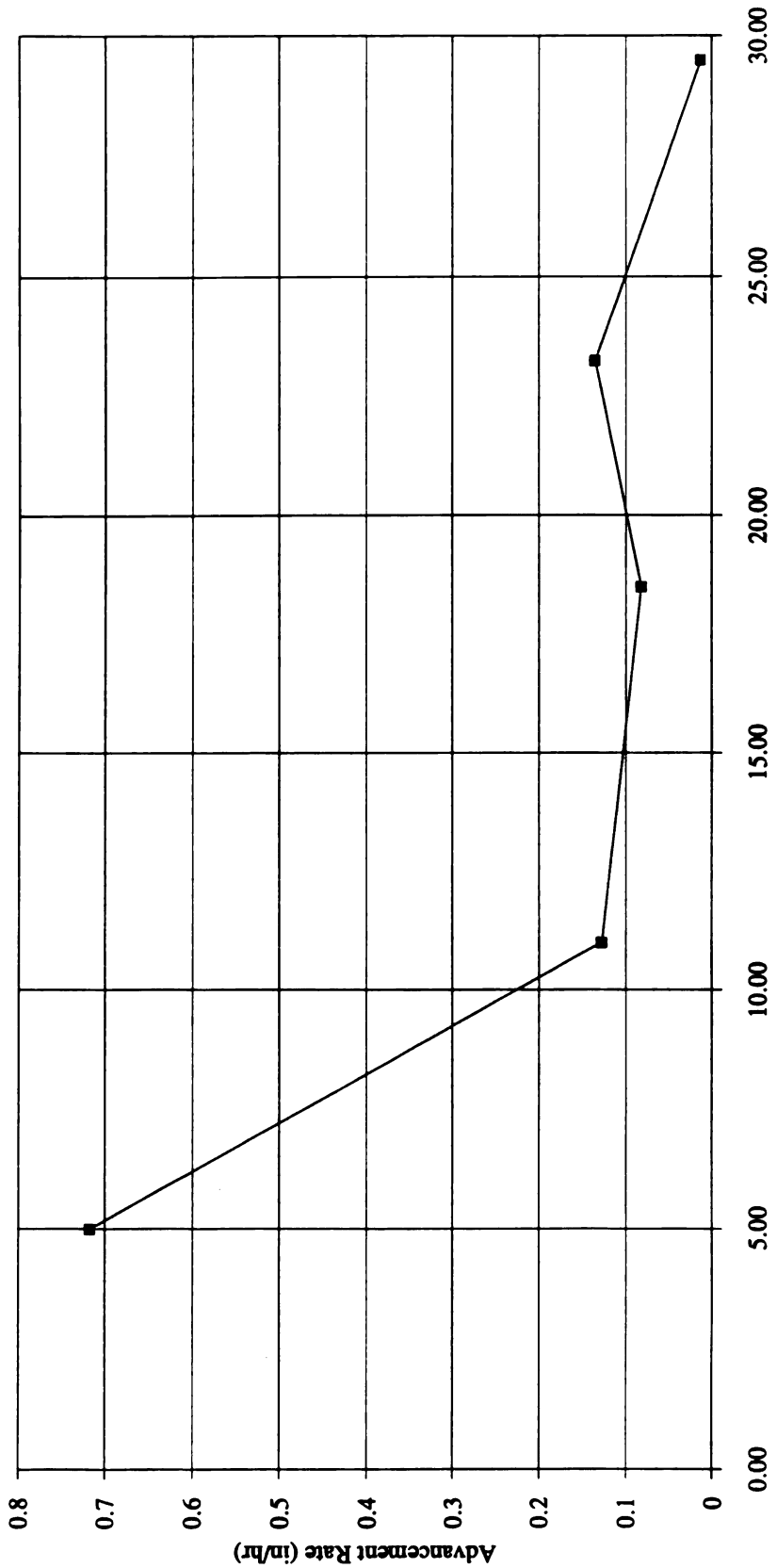


Figure B5.1: Advancement Rate vs Time 53 ml/min with Dodecane

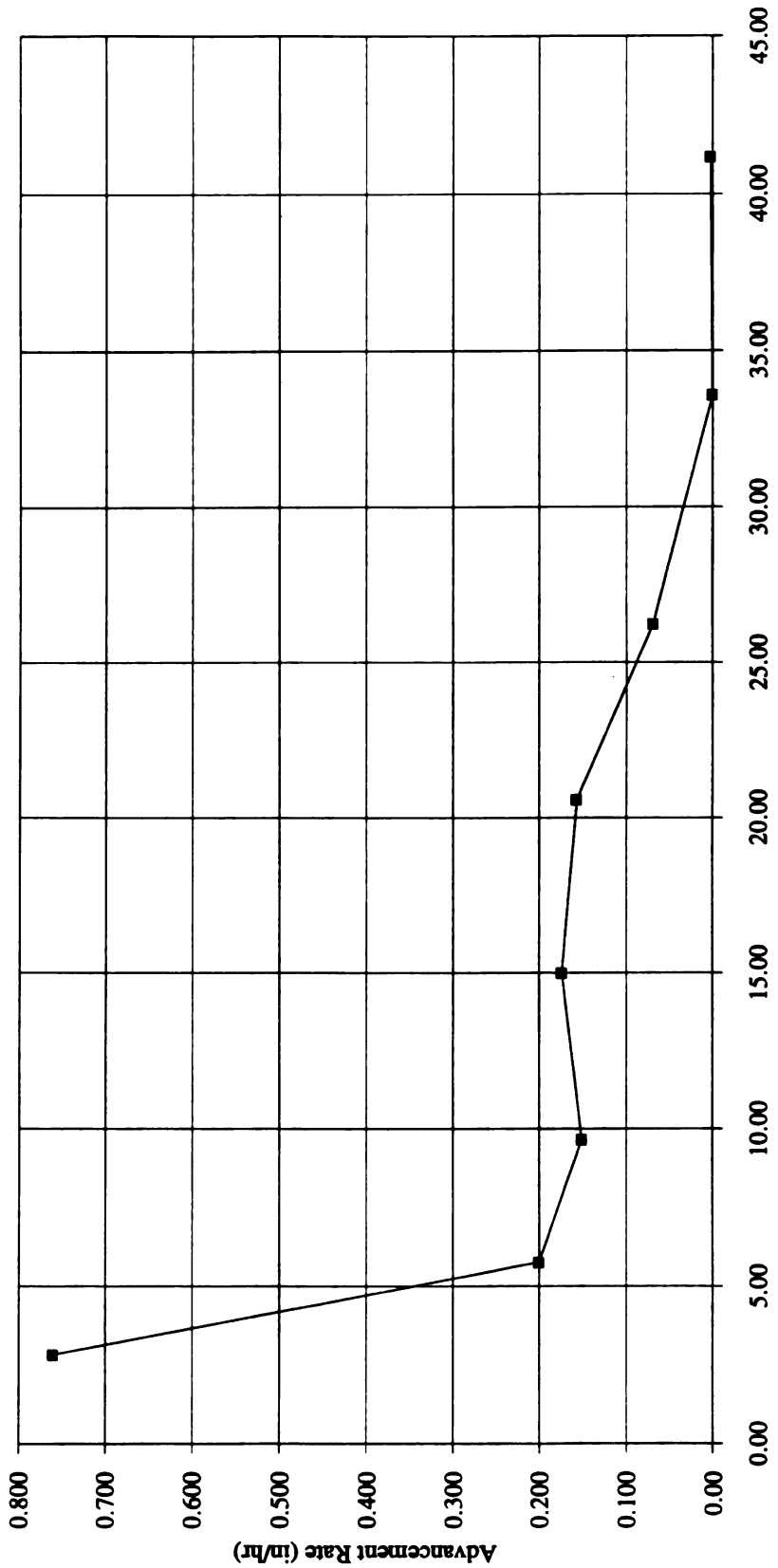


Figure B6.1: Advancement vs Time for 53 ml/min Without Dodecane

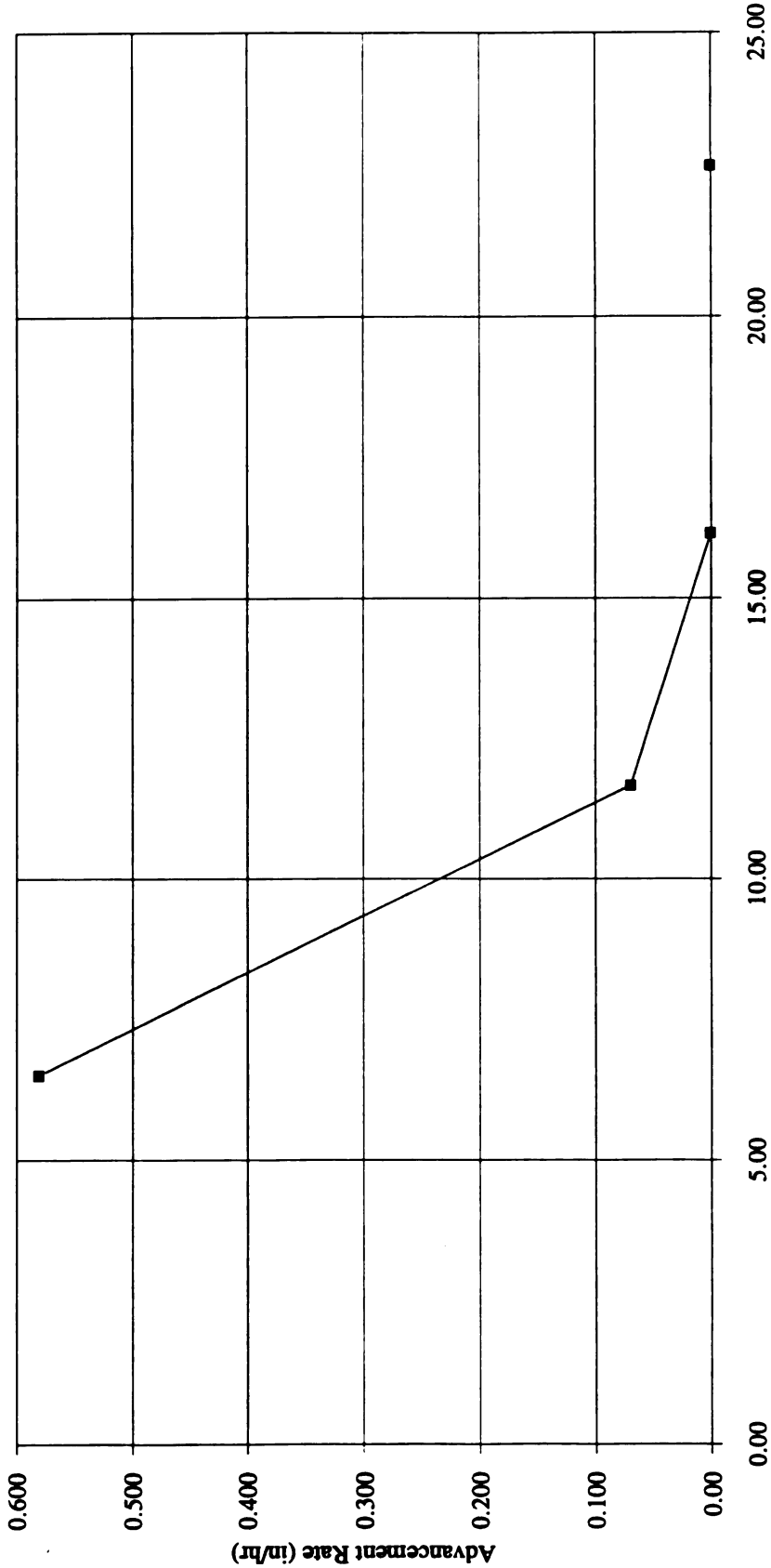


Figure B7.1: Advancement Rate vs Time for 53 ml/min Without Dodecane

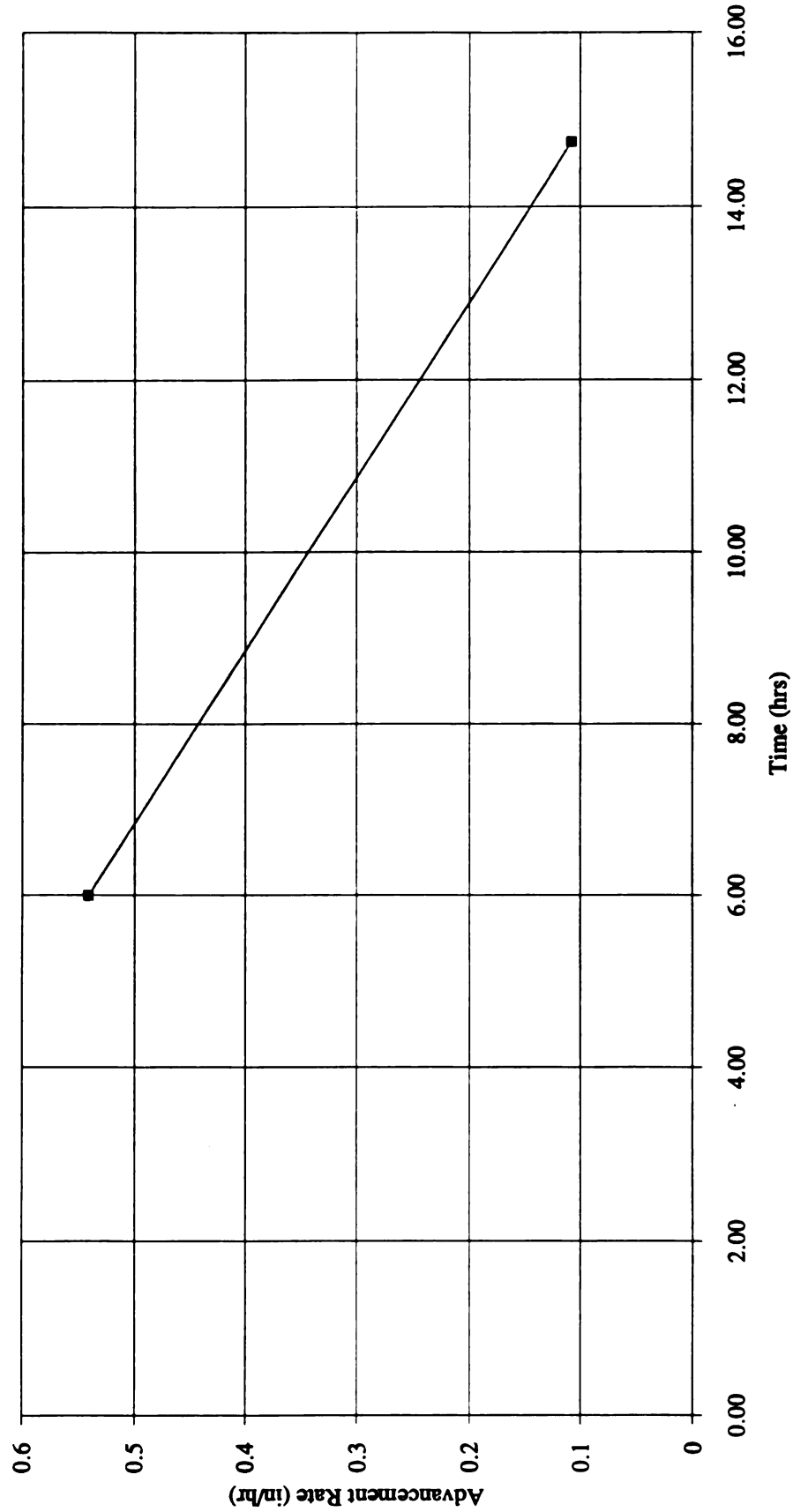


Figure B8.1: Advancement Rate vs Time for 65 ml/min With Dodecane

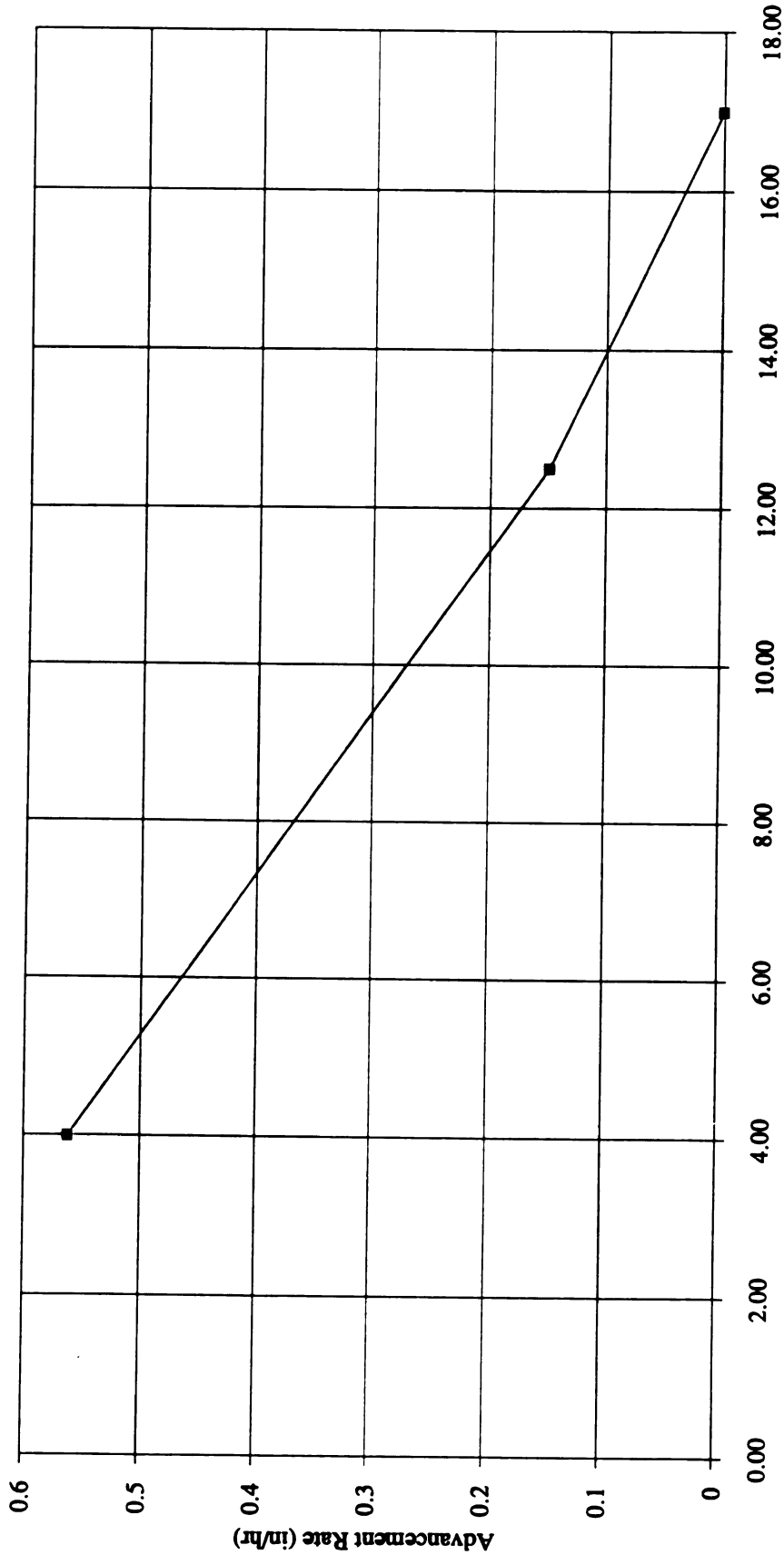


Figure B9.1: Advancement Rate vs Time for 65 ml/min Without Dodecane

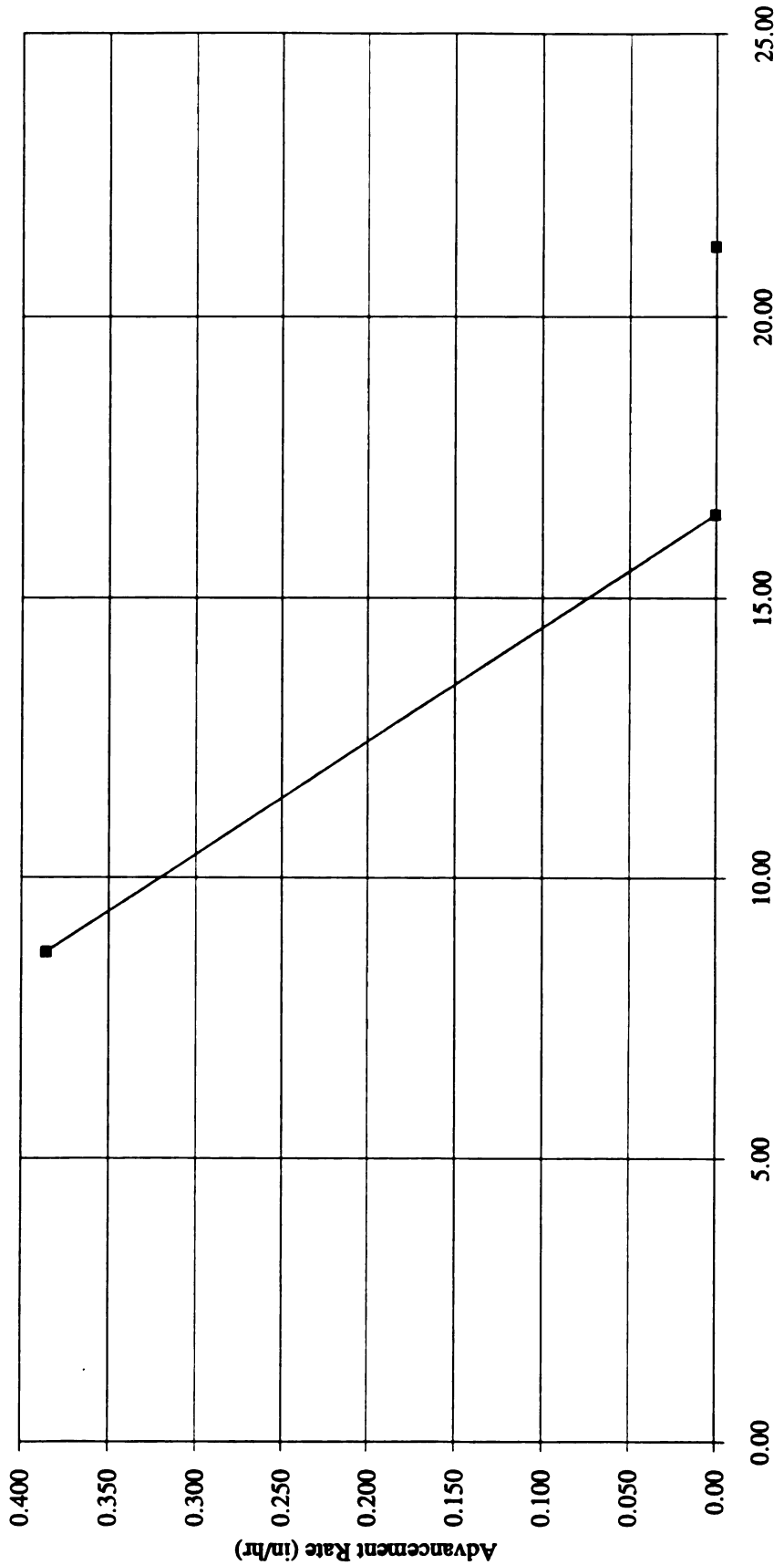


Figure B10.1: Advancement Rate vs Time for 79 ml/min With Dodecane