AN UNSATURATED FRACTURED ROCK SAMPLING TECHNIQUE BY IN SITU THERMOELECTRIC CONDENSATION OF WATER VAPOR

by

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STATEMENT BY AUTHOR

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APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below.

Daniel D. Evans, Professor of Hydrology and Water Resources

Date

Nov. 30, 1967
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With love and admiration,
this thesis is dedicated to
my parents
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ABSTRACT

Water vapor in the airspace of an unsaturated fractured rock may be sampled by reduction of the air temperature of the medium to its dew point and retrieval of the condensed liquid sample. The required temperature change was generated in this research by a thermoelectric cooling module, which operates according to the Peltier cooling effect. Laboratory studies of this technique involved the development of the module's heat sink system and calibration of the instrument for cooling temperatures and condensation rates obtained by variations in the applied current. Temperature and vapor density changes produced in the air space surrounding the instrument when operated in a moist environment were also evaluated. Field studies performed in an unsaturated, fractured, densely-welded tuff have shown the instrument to be capable of vapor collection, although at a rate lower than that established under laboratory conditions. Applications of this technique include evaluation of oxygen and hydrogen isotopes of moisture in unsaturated media and travel time studies of flow through the unsaturated zone using isotopes as tracers.
CHAPTER ONE

INTRODUCTION

Recent efforts toward the siting of high-level nuclear waste repositories in unsaturated fractured rock have lead to a need for accurate description of the transport of vapor phase constituents through such a medium. A number of radionuclides may be present in gaseous form in a high-level waste, including H-3, C-14, Kr-85, and I-129, which could potentially escape into the surrounding geologic medium in the event of a failed canister within the repository; hence, the need for development of a monitoring system capable of detecting vapor constituents is apparent. The ability of tritium, H-3, to readily combine with ordinary water vapor, a major constituent of the atmosphere of an unsaturated medium, is of considerable importance in this respect. If a method can be devised for extraction of a sample of water vapor from an unsaturated medium, a technique would be made available for monitoring the transport of tritium in this state. By in situ collection of water vapor from an unsaturated fractured rock in the area of a buried nuclear repository, and analysis of the tritium content by available laboratory techniques, a means would exist of determining if a failure of the repository has occurred. This is one example of the type of applications which this research is intended to address.

In situ collection of water vapor could be made possible through condensation of the vapor present in the air space of the unsaturated fractured rock by reduction of the air temperature to its
dew point and withdrawal of the liquid sample through a sampling tube to a collection vessel at the surface. The required temperature reduction has been accomplished in this research by the application of thermoelectric cooling techniques. This method makes use of the Peltier cooling effect produced by passing an electric current through a semiconductor junction. A thermocooling module is composed of a number of these junctions overlain by a thin ceramic plate, producing a surface on which condensation of water vapor may occur, once cooling to the dew point has been achieved.

This research involved:

(1) The application of thermoelectric cooling principles to vapor condensation;

(2) Investigation into effects on the liquid and vapor phase components of an unsaturated medium resulting from the use of the instrumentation;

(3) The development of a heat sink capable of dissipating the heat generated by the cooling process of the thermoelectric cooler;

(4) Laboratory studies of the range of temperature reduction and corresponding rates of condensation that may be expected;

(5) Field studies in which the apparatus was tested in a borehole located in an unsaturated, fractured, densely-welded tuff.
A number of sampling techniques have been devised for the extraction of both gaseous and liquid samples from unsaturated soils. There are two commonly-used methods for obtaining a sample of the soil atmosphere, referred to as the mass flow and diffusion techniques (van Bavel, 1965). The principal components of soil air commonly sampled by these means include nitrogen, oxygen, argon, and carbon dioxide.

In the mass flow method, a sampling tube of sufficient length is inserted into the soil to the desired depth, and soil air is removed by a hypodermic needle, or a vacuum pump for large samples removed from great depths. A difficulty arising from this method is the lack of knowledge concerning the actual depth from which the sample originated. It is probable that air withdrawn from a certain depth may have originated from a remote location due to preferential flow through large interconnecting macropores, channels, and fractures.

In the diffusion method, a sample container is connected directly through tubing to the depth of interest in the soil, and a pump is used to circulate air through the entire apparatus. Given sufficient time, the process of gaseous diffusion will cause the sample vessel to contain a gas mixture of a composition similar to the point where the sampling tube is open to the soil air. Although preferable to the mass flow technique, this method is complicated by the need to compute a dilution factor, as the soil gas will be diluted by the air present in the remainder of the apparatus during sampling. Another problem inherent to both these methods, as with any technique where gas samples are being handled, is the possibility of contamination of the sample with atmospheric air.
The most common method for extraction of liquid samples is the vacuum pressure lysimeter in which soil water is induced to flow into a porous cup by reduction of the potential energy of the water-filled pores of the cup to below the potential of the soil water, resulting in the movement of soil water down the induced potential gradient. A difficulty in application of this technique is the inability to withdraw a sample when the soil suction is greater than some critical value, slightly less than 1 bar, which is the upper limit for reduction of air pressure inside the porous cup. Amter (1987) has had some success with extending the range of application of the lysimeter by using an injection/recovery technique where a known amount of water is injected into the horizon of interest, thereby locally decreasing the soil water potential. A water sample is then collected by using the lysimeter in the conventional way, and the sample obtained will contain native soil water diluted by the injection water.

The major advantage of the proposed thermoelectric cooling method over other sampling techniques is that the water vapor sample is collected in situ and in liquid form, thus reducing the possibility of contamination with atmospheric air. Also, if properly designed with a sufficient power supply and heat sink apparatus, the instrument could be sealed and left in place for extended periods of time.

The capabilities of the technique are limited, in that information cannot be gained concerning the species or concentrations of solutes present in the rock water. This is because the method works essentially as a distillation process, whereby water vapor in the vicinity of the instrument is condensed along with water which has
first been evaporated from liquid moisture present in the rock frac-
tures and pores, with soluble salts left behind in the liquid phase
during the evaporation process. Therefore, water chemistry information
which can be obtained is limited to the isotopic content of the water
vapor, including tritium, deuterium, and oxygen isotopes.

In addition to the development of this sampling method as a
tool in examining the natural isotopic content of water in an unsat-
urated medium, and the monitoring of nuclear repositories sited in such
media, there is also the possibility of adapting the technique for use
in travel time studies of flow through the unsaturated zone. Water
labeled with an isotope such as deuterium or tritium added at the
surface or some other given point in the system may be recovered at a
deeper location by sampling with the proposed instrumentation and the
information used to describe movement of water through the zone of
interest.
CHAPTER TWO

BACKGROUND AND THEORY

Introduction

The collection of a water vapor sample from an unsaturated medium by the thermoelectric cooling technique is dependent upon the generation of a thermally-induced vapor gradient, so that vapor will tend to flow from a source toward a desired point of collection. When operated in a borehole in an unsaturated fractured rock, the sampling process may be divided into early and late time effects, corresponding to changes over time in the location of the source water and the mechanisms controlling its travel towards the instrument site.

At early time, the sampling procedure may be subdivided into four subprocesses: (1) condensation of vapor in the air space of the borehole due to the drop in temperature, (2) evaporation of water present at the borehole surface in response to the reduction in vapor density in the borehole air space, (3) diffusion of the vapor through the air under the generated vapor and thermal gradients, and (4) condensation of the vapor upon the cold surface of the instrument. During early time, thermal effects would be expected to be minimal due to the low thermal conductivity of air (0.024 J/s m°C), and vapor diffusion would be more greatly affected by the nature of the vapor gradient.

Over time, however, it is likely that the walls of the borehole will dry as moisture evaporates from them, so that the effects of the instrument operation will eventually extend into the medium. A
moisture potential gradient would thus be established within the fractured rock, causing flow in the liquid state from wetter regions toward the borehole. This liquid transfer mechanism would work in conjunction with transfer in the vapor state and in the same direction. If the cooling instrument was operated in place over an extended period of time, the rock surface near the instrument site would eventually experience a drop in temperature, so that thermal effects in the medium would also need to be accounted for in the moisture diffusion process during late time. The rate-controlling factors of this system include the moisture content, relative humidity and ambient temperature conditions of the medium, its porosity and permeability, the presence of soluble salts, the thermal conductivity of the medium through which moisture diffusion is occurring, and the nature of the temperature gradient established by the instrument.

The diffusion of water vapor through soils under isothermal and nonisothermal conditions has been a subject of extensive research for a number of years, with relatively few investigations devoted to the case of fractured rock. It is the combined purpose of this chapter to review previous work on the subjects of both vapor diffusion and liquid phase transfer of moisture in unsaturated media (since both mechanisms are expected to result from operation of the thermoelectric cooling technique), and to provide the necessary theoretical background pertinent to the above-mentioned processes and controlling factors.

As the chemical nature of the sample collected by the thermoelectric cooling technique will be that of distilled water, and the ultimate purpose for development of the proposed technique is the
collection of a sample of moisture for isotopic analysis, the behavior of hydrogen and oxygen isotopes and their use as tracers in unsaturated media will also be discussed in this chapter.

Properties of Moisture in Unsaturated Media

An unsaturated soil can be represented as a three-phase system, consisting of a solid phase (the soil matrix), a liquid phase (the soil water and any dissolved substances it may contain), and a gaseous phase (the water vapor and any other gaseous constituents of the soil atmosphere). Interaction between phases at their interfaces results in the phenomena of adsorption and surface tension, the importance of each depending on the magnitude of the interfacial area per unit volume of the soil system (Hillel, 1980), which is determined by the relative portions of the three phases in the soil at any given time.

The per mass or per volume fraction of water in a soil is used to express water content, while the physicochemical state of soil water is described in terms of its free energy per unit mass, or the soil-water potential. Soil-water potential is defined as the potential energy associated with a soil water relative to that of water at a standard reference state of pressure, composition, elevation, and temperature. The total potential of soil water is then the sum of the contributing potentials of these various factors, expressed as:

\[ \psi_r = \psi_g + \psi_o + \psi_p + ... \]  

(2.1)
where $\psi_T$ is the total water potential, $\psi_g$ is the gravitational potential, $\psi_o$ is the osmotic potential, and $\psi_p$ is the pressure potential. Terms for additional potentials may also be incorporated into the right-hand side of Equation (2.1) (Hillel, 1982).

When soil water is under a pressure lower than atmospheric, the pressure potential is considered negative and is generally referred to as matric potential ($\psi_m$). The negative sign is frequently dropped from the matric potential value, as a matter of convenience, and the absolute value $|\psi_m|$ is used instead which is referred to as matric suction (Marshall and Holmes, 1979). Matric potential results from the interaction of water with the solid particles of the soil which contain it. Water content and matric potential are related to each other for a particular soil by the soil moisture characteristic curve.

Moisture in the vapor phase in the airspace of an unsaturated porous medium is a function of the temperature and water content of the material. In evaluating the effect of water content (and hence the forces of adsorption and surface tension), consider a perfectly dry sample of soil and the changes which occur as moisture is added to the system by increasing the relative humidity of the soil atmosphere from 0 to 100% at constant temperature. Relative humidity, $h$, is defined as the ratio of the actual vapor pressure $e$ to the saturation vapor pressure $e_o$ at the same temperature, and may be related to matric potential at a given temperature under equilibrium conditions between the liquid and vapor phases and neglecting the effect of solutes, by the expression (Edlefson and Anderson, 1943):
\[
    h = \frac{e}{e_0} = \exp(\psi_m g/RT)
\]

(2.2)

where \( g \) (cm/s\(^2\)) is the acceleration of gravity, \( R = 4.615 \times 10^4 \) erg/gm\(^o\)K is the specific gas constant of water vapor, \( \psi_m \) (cm) is the matric potential, and \( T \) is temperature in degrees Kelvin. This relationship shows that matric potential must become very large to bring about a small drop in relative humidity; therefore, under most conditions, soils are generally considered to be saturated with respect to water vapor.

As \( h \) increases from 0, soil particles will begin to adsorb moisture, with the initial stage of adsorption occurring around active sites on the soil surface where exchangeable cations exist. The individual hydration envelopes surrounding these sites continue to grow with additional moisture until they coalesce, forming a monomolecular layer, with some multimolecular regions surrounding the active sites. According to Quirk (1955), who worked on the development of adsorption isotherms for water vapor onto various soils, a complete monolayer is adsorbed at a relative humidity of approximately 20\% for a clay soil. Adhesive forces between these initial molecular layers and the soil surface are very high, corresponding to soil suctions in the range of \( 1.0 \times 10^4 \) atm (1.0 x 10\(^4\) MPa) (Brady, 1974).

If there were no contact between individual soil particles, the thickness of the adsorbed film would be nearly uniform, since the attractive forces between the water molecules and solid surface (or adhesion) would be approximately uniform. However, at points of contact, the attractive forces of individual particles become
superimposed; hence, the film will tend to be thicker in these regions. As relative humidity is increased further, the film thickness continues to increase with overlap occurring at the contact points. Eventually, a level of humidity is achieved where layers of water molecules at the air-water interface are no longer strongly attracted to the solid surface. At this point, surface tension forces come into effect whereby a water molecule at the air surface undergoes a net inward force due to the cohesive force of attraction of the molecule for its neighbors (Kirkham and Powers, 1971). With the beginning of surface tension forces, the film of adsorbed water will tend to adopt a shape corresponding to the minimum surface area, particularly around the particle surface. This will result in the formation of a wedge-shaped meniscus of water around the point of contact, and the water vapor pressure of the air space over the liquid will be determined by the curvature of the liquid surface. The surface curvature of this water wedge is given by:

\[
\frac{1}{r} = \frac{1}{r_1} + \frac{1}{r_2}
\]

(2.3)

where \( r_1 \) is taken as being the radius of the water ring on the liquid side of the interface (and is considered positive), and \( r_2 \) is located on the air side of the interface and is considered negative. As a rule, \( r_1 > r_2 \); therefore, \( 1/r_1 < 1/r_2 \), so \( 1/r \) is negative, corresponding to a concave liquid surface.

The pressure differential across the air-water interface is given by the capillary rise equation:
\[ \psi_m = 2 \gamma \cos \theta / r \] (2.4)

where \( \gamma \) is surface tension, \( \theta \) is the contact angle between the liquid-gas interface and the solid, measured through the water (generally assumed equal to zero), and \( \psi_m \) is the matric potential. Thus, capillary rise results from a combination of the adhesive forces between water molecules located near the solid surface of the soil particle and the surface tension of the water. The forces of surface tension and capillarity continue to control the water vapor pressure as long as concave menisci are present, or until the soil is completely saturated.

The effect of temperature changes at a given moisture content is to bring about a decrease in surface tension with an increase in temperature. As temperature rises, the density of the liquid will tend to decrease due to thermal expansion caused by an increase in kinetic energy of the water molecules. This reduces the cohesive forces between water molecules such that those located at the surface gain enough kinetic energy to escape into the soil atmosphere. Thus, a decrease in surface tension is also accompanied by an increase in vapor pressure.

The presence of dissolved substances in the soil water will also have an affect on surface tension, and therefore vapor pressure, depending on the species of solute molecule or ion. If the affinity of the solute for water molecules is greater than the affinity of the water molecules for one another (as in the case of a hydrophylic substance), then the solute will be drawn into the solution, causing an increase in surface tension and a lowering of vapor pressure. However,
if the cohesive attraction between the water molecules is greater than the attraction between water and the solute, as in the case of a hydrophobic substance, then the solute will tend to be pushed out of the water and concentrate at the air-water interface, thereby reducing surface tension.

**Vapor Diffusion in Unsaturated Media**

The process of gas diffusion is described in terms of the displacement of one gas by another such that equal flow of gases is taking place in opposite directions and the total pressure gradient remains zero (Penman, 1940). This may be written for the case of one-dimensional water vapor diffusion in air by Fick's law:

\[
q_v = -\frac{D_a}{\beta} \frac{dp}{dx}
\]  

(2.5)

where

- \(q_v\) = vapor flux density \((g/cm^2s)\);
- \(D_a\) = molecular diffusivity of water vapor through air \((cm^2/s)\);
- \(\beta\) = ratio of partial pressure to concentration \([mmHg/(g/cm^3)]\); and
- \(\frac{dp}{dx}\) = partial pressure gradient of water vapor in the \(x\) direction \((mmHg/cm)\).

When the inter-diffusion of water vapor and air is restricted to movement through a porous solid, the amount of vapor which can pass through a given cross section per unit time is reduced because of the
smaller area available and the tortuous nature of the interconnecting pores. Fick's law may thus be modified for application to a porous medium by (Penman, 1940):

$$q_v = -D_a \left[ \frac{P}{P - p} \right] t a \nabla \rho$$  \hspace{1cm} (2.6)

where

- $t$ = tortuosity factor;
- $D_a$ = molecular diffusivity of water vapor through air (cm$^2$/s);
- $a$ = volumetric air content of the mechanism (cm$^3$ air/cm$^3$);
- $\rho$ = water vapor density (gm/cm$^3$);
- $P$ = total air pressure (mm Hg); and
- $p$ = partial pressure of water vapor (mm Hg).

A number of investigators (see, for example, Gurr et al., 1952; Taylor and Cavazza, 1954) have attempted to describe vapor flow through soil columns under nonisothermal conditions using Equation (2.6) and found Fick's law to consistently underpredict net vapor movement.

The theory proposed by Philip and de Vries (1957) attempted to resolve the differences between observed vapor movement and that predicted by Fick's law, whereby water is assumed to move simultaneously in both vapor and liquid phases in response to both soil water potential and thermal gradients. The expressions they derived for net heat and moisture flow are:

$$q_h = -\lambda \nabla T - \rho L D_{vap} \nabla \theta$$  \hspace{1cm} (2.7)
where

\[ q_h = \text{soil heat flux density (cal/cm}^2\text{s)}; \]
\[ \lambda = \text{thermal conductivity (cal/s cm}^2\text{°C)}; \]
\[ T = \text{temperature (°C)}; \]
\[ L = \text{latent heat of vaporization (cal/gm)}; \]
\[ D_{\text{vap}} = \text{isothermal diffusivity of vapor (cm}^2/\text{s)}; \text{ and} \]
\[ \theta = \text{water content (cm}^3/\text{cm}^3). \]

and

\[ q = -D_T \nabla T - D_\theta \nabla \theta - K_i \]  \hspace{1cm} (2.8)

where

\[ q = \text{total flux density of water (gm/cm}^2\text{s)}; \]
\[ D_T = \text{thermal moisture diffusivity which is equal to the sum of} \]
\[ \text{the thermal diffusivities in the liquid and vapor states,} \]
\[ \text{or } D_{\text{liq}} + D_{\text{vap}}, \text{ (cm}^2/\text{s)}; \]
\[ D = \text{isothermal moisture diffusivity which is equal to the sum} \]
\[ \text{of the isothermal diffusivities in the liquid and vapor} \]
\[ \text{states, or } D_{\text{liq}} + D_{\text{vap}} \text{ (cm}^2/\text{s)}; \]
\[ K = \text{unsaturated hydraulic conductivity (cm/s)}; \text{ and} \]
\[ i = \text{unit vector in the positive z direction.} \]

The first term on the right of Equation (2.8) describes
moisture flow due to a thermal gradient; the second term describes
moisture flow due to the moisture gradient, and the third term that due
to gravity. In deriving the moisture flux density relationship, relative humidity was assumed equal to 100%, and the affects of soluble salts were neglected. The possibility of the transfer of moisture in the adsorbed phase by surface migration was also considered negligible in comparison to the volume of moisture transfer by other mechanisms.

It was further suggested by Philip and de Vries (1957) that enhancement of the vapor flux over that predicted by Fick's law was due to flow through "liquid islands", the term liquid island referring to water forming wedges or filling small pores at the points of contact between grains of the medium. By this mechanism, a vapor pressure gradient due to an applied thermal gradient leads to condensation of vapor on the warm side of the water filled pore, causing a decrease in curvature of the meniscus and evaporation on the cooler side, resulting in an increase in curvature. The changes in curvature generate capillary flow through the water wedge; thus, vapor flow is not restricted to the air-filled pore space of the medium alone. This transport process will operate only when the moisture content is below an amount where continuous liquid films exist within the medium. At moisture contents significantly above that required for liquid continuity, the radii of curvature of the menisci increase to the point where automatic adjustment of the vapor flux is not possible.

Philip and de Vries (1957) describe a second vapor transport enhancement factor as the generation of a localized temperature gradient within air-filled pores which is greater than the macroscopic thermal gradient of the material as a whole. This is due to the
thermal conductivity of water vapor being significantly lower than the thermal conductivity of the liquid and solid phases of the system.

With inclusion of these two factors, the specific expression for water vapor flux under a temperature gradient was written by Philip and de Vris (1957) as:

\[ q_v = -f(a) \left[ \frac{P}{(P-p)} \right] D_a \left( \frac{d\rho_s}{dT} \right) \eta \frac{dT}{dx} \]  

(2.9)

In this expression, \( \rho_s \) is the saturated vapor density, and \( f(a) \) is the enhancement factor, taking into account the increase in cross sectional area available for vapor transfer defined by:

\[ f(a) = \begin{cases} 
1, & a > a_k \\
\frac{a}{a_k}, & a < a_k 
\end{cases} \]  

(2.10)

where \( a_k \) is the value of \( a \) where \( \theta = \theta_k \), or the value of water content where liquid continuity begins.

The term \( \eta \) is the thermal gradient enhancement factor and is defined by the ratio of the volume averaged temperature gradient in the vapor phase to the volume averaged temperature gradient of the entire porous medium, with tortuosity effects taken into account.

Another theory describing soil-water movement in response to temperature gradients has been proposed by Taylor and Cary (1960), based on consideration of the principles of irreversible thermodynamics. In this approach, the irreversible phenomena are written as
a series of linear flow equations, one for each component of the system:

\[ J_i = \sum_{k=i}^{n} L_{ik} X_k \quad (i = 1, 2, \ldots, n) \quad (2.11) \]

where \( J_i \) is the flux of the \( i^{th} \) component, \( L_{ik} \) is the phenomenological coefficient due to the \( k^{th} \) driving force affecting the \( i^{th} \) flux, \( X_k \) is the driving force of the \( k^{th} \) component, and \( n \) is the number of driving forces.

For a closed system at steady state, the simultaneous flux of heat and water through a soil under a small temperature gradient may be written as:

\[ J_q = -L_{qq} \left( \frac{T}{T^2} \right) - L_{qw} \gamma \left( \frac{\mu_w}{T} \right) \quad (2.12) \]

and

\[ J_w = -L_{wq} \left( \frac{T}{T^2} \right) - L_{ww} \gamma \left( \frac{\mu_w}{T} \right) \quad (2.13) \]

where the subscripts \( q \) and \( w \) denote heat and water, respectively, and \( \mu_w \) is the chemical potential of the water. The interaction coefficients, \( L_{qw} \) and \( L_{wq} \), are identical according to Onsager's theorem, based on the principle of microscopic reversibility which requires that the variables of the system not deviate far from equilibrium.

As the fluxes of heat and water are coupled, the use of this system of equations for the prediction of soil water movement requires
measurement of the heat flux in addition to the net water flux in order to determine values for the interactive phenomenological coefficients. The theory was later modified by Taylor and Cary (1964) to eliminate this requirement so that the net moisture flux may be calculated by:

\[ J_w = -D_\theta [d \theta/dx + \beta^* d(ln T)/dx] \]  

(2.14)

where \( D_\theta = (D_{\theta \text{liq}} + D_{\theta \text{vap}}) \) and \( \beta^* = -d \theta /d(ln T) \), where \( T \) is the temperature in degrees Kelvin.

Both the analyses by Philip and de Vris (1957) and Taylor and Cary (1964) have been used by researchers in various studies of liquid and vapor state moisture transfer through soils and have found some degree of verification (Weeks et al., 1968; Cassel et al., 1969; Fritton et al., 1970).

Some modifications of the Philip and de Vris (1957) equations may be found in more recent literature. Groenvelt and Kay (1974) include a term for heat transport due to the heat of wetting of tightly-bound water. Nakano and Miyazaki (1979) have derived a similar equation to Philip and de Vris (1957) on the basis of soil water potential as opposed to water content, and include a term to account for the effect of change of temperature on relative humidity. Jury and Letey (1979) modified the water vapor transfer enhancement factor of Philip and de Vris (1957), which accounts for transfer through liquid islands, by showing that the presence of the liquid gap in the vapor continuum enhances vapor transfer by shortening the equivalent vapor path by the ratio of the effective vapor thermal conductivity to the liquid thermal
conductivity $\lambda_v / \lambda_1$, where $\lambda_1 > \lambda_v$. Milly (1982) has used the formulation of Nakano and Miyazaki (1979) to derive an expression for nonisothermal vapor flux in a heterogenous medium.

**Liquid Phase Transport in Unsaturated Media**

Unlike vapor transport, just described as resulting mainly from diffusion processes, water will move through an unsaturated soil by the process of convective flow. The driving force behind this mechanism is a gradient in hydraulic potential, resulting from a combination of gradients in gravity and water potential. Unsaturated flow processes are, in general, very difficult to quantify as they involve complex interrelations among the soil-water parameters of water content, matric potential, and hydraulic conductivity, which may vary both temporally and spatially in a soil. The analysis may be further complicated by the effects of hysteresis. Because of these complications, solutions of unsaturated flow problems often require the use of indirect techniques, such as approximations or numerical methods (Hillel, 1982).

The movement of water through an unsaturated medium may be described by Richards' equation (Marshall and Holmes, 1979):

$$q_1 = -K(\psi_m) \nabla H$$

(2.15)

where

$q_1$ = volume of water crossing a unit area perpendicular to the direction of flow per unit time (cm/s);
\( K(\psi_m) \) = unsaturated hydraulic conductivity, written as a function of matric potential (cm²/s); and

\( H \) = hydraulic head, which may include both matric potential and gravitational components.

The general flow equation can be derived by application of the continuity principle to Equation (2.15), yielding (Hillel, 1982):

\[
\frac{\partial \Theta}{\partial t} = -\frac{\partial}{\partial x} \left( K \frac{\partial \psi_m}{\partial x} \right) - \frac{\partial}{\partial y} \left( K \frac{\partial \psi_m}{\partial y} \right) - \frac{\partial}{\partial z} \left( K \frac{\partial \psi_m}{\partial z} \right) + \frac{\partial K}{\partial z} \quad (2.16)
\]

Philip and de Vris (1957) have written the liquid flux equation for a homogeneous, nonisothermal soil system as:

\[
q_l = -K \left( \frac{\partial \psi_m}{\partial T} \right) \nabla T - K \left( \frac{\partial \psi_m}{\partial \Theta} \right) \nabla \Theta - K z \quad (2.17)
\]

The first term on the right-hand side of Equation (2.17) accounts for liquid flow due to a temperature gradient, which results from an increase in surface tension with a decrease in temperature. This results in a decrease in the matric potential \( \psi_m \) in colder regions of a soil, as given by:

\[
\psi_m = 2 \gamma / r \quad (2.18)
\]

where \( r \) is the radius of curvature of the liquid surface. Since \( r \) is negative, an increase in surface tension corresponds to a decrease in \( \psi_m \). Therefore, flow occurs down the pressure gradient or in the
direction of decreasing temperature, as long as conducting liquid films are present (Gurr et al., 1952).

The second and third terms in Equation (2.17) correspond to liquid flow due to variations in water content through a soil and a vertical flow component, respectively.

**Countercurrent Theory**

One of the earliest studies of the effect of temperature on moisture movement through soils was that of Bouyoucos (1915), who found that moisture tended to flow from warm to cool ends of soil columns subjected to temperature gradients, and that a maximum thermal moisture transfer occurs at an intermediate water content, with less transfer at either higher or lower levels of saturation. He attributed these results to decreases in viscosity and surface tension with a rise in temperature, resulting in liquid flow towards regions of higher surface tension and viscosity, corresponding to cooler regions in the soil. Moisture transfer in the vapor phase was considered to be negligible.

The experimental results of Smith (1940, 1943), Jones and Kohnke (1952), and Gurr et al. (1952) showed similar tendencies in thermal moisture movement. Smith (1940) at first attributed the moisture flow to vapor movement by convection, but in a later work (1943) supported the idea of liquid flow being the dominant transport process. Jones and Kohnke (1952) claimed that temperature-induced vapor pressure gradients were mainly responsible for moisture transfer.

Gurr et al. (1952) demonstrated that in a closed soil system subjected to a temperature gradient, vapor will tend to flow from warm
to cold ends of a soil column, while liquid flow occurs in the opposite
direction. The relative contributions of the liquid and vapor flow to
the net moisture movement were assessed in their experiments by meas-
uring changes in the distribution of a soluble salt added to the soil
water, with the assumption that soluble salts would be transported in
the liquid phase only. Experimental results from studies made on soils
of various textures and wetted to different uniform initial moisture
contents showed that a transfer of vapor had occurred toward the colder
ends of the columns (determined gravimetrically), while a transfer of
liquid occurred in the direction of increasing temperature (indicated
by an increase in chloride ion concentration). This was explained by
the generation of a countercurrent. By this mechanism, water vapor
evaporates at the warm end of the column because the saturation vapor
pressure of warm air is greater than that of cold; hence, the air can
hold more vapor. The vapor will then migrate down the vapor pressure
gradient toward the cold end of the column, where it condenses upon
encountering air at a lower temperature and, therefore, lower satura-
tion vapor pressure. At this stage of development of the countercur-
rent, during early time, there is also a net liquid phase flow in the
same direction, due to the decrease in surface tension with increasing
temperature, according to the mechanism described by Equation (2.18).
Over time, enough moisture will flow in the direction warm to cold that
the matric potential gradient is reversed, and liquid return flow
begins in the direction cold to warm. Within a closed system, a steady
state will eventually be established with equal flow rates in each
direction.
Most of the previous work concerning countercurrent theory has been done using soil columns. Some recent experiments, however (Matthews, 1986; Davies, 1987), have been carried out on porous rock. The sandstone cores studied by Matthews (1986), when subjected to a temperature gradient, and using fluorescein dye to monitor liquid phase transport, indicated a strong likelihood that countercurrent flow had been generated. The work of Davies (1987) concerning moisture flow in nonisothermal nonwelded and densely-welded tuff cores also showed evidence of countercurrent development.

The countercurrent phenomena would not be expected to develop by operation of the thermoelectric cooler. Liquid return flow will not be generated in the direction cold to warm within the medium, because moisture is continually being removed from the system when it reaches the borehole and is evaporated and recondensed onto the instrument's cold surface. Thus, a moisture potential gradient will not build up in the direction cold to warm as would occur in the case of a closed system.

Factors Affecting the Chemical and Isotopic Nature of the Sample

As stated in Chapter One, the thermoelectric condensation sampling technique is essentially a distillation process, consisting of the subprocesses of evaporation of a portion of the soil-water solution and the subsequent condensation of the vapor. The chemical nature of the vapor condensate will be that of a pure distillate, as only water and the volatile dissolved gases it contains will be capable of entering the vapor phase, while any dissolved salts present in the
original solution which are nonvolatile will remain behind. Important information concerning the nature of the moisture in the geologic setting from which the condensate is collected may be gained, however, from isotopic analysis of the sample. Evaluation of the stable isotopes of hydrogen and oxygen, deuterium (D), and oxygen-18, have often been used in hydrologic investigations as indicators of water source areas, while analysis of the radioactive isotope of hydrogen, tritium, has been used as a guide in evaluation the age of water in a system. The term age in this sense refers to the time elapsed since the water became isolated from the earth's atmosphere. The following sections review briefly some of the phenomena affecting the behavior of these stable and radioactive isotopes and their importance as tracers in unsaturated media.

Stable Isotopes

The naturally-occurring isotopes deuterium and oxygen-18 undergo fractionation whenever a change of state occurs in the water that contains them. Isotope fractionation is a consequence of the fact that the energy states of molecules depend on the masses of the atoms of which they are composed, such that the vibrational frequency of a molecule is inversely proportional to its mass. As a result, a given molecule containing the lighter of two isotopes has a higher vibrational frequency than a similar molecule containing the heavier isotope; hence, the bonds formed by the lighter molecule will be relatively weaker, making it the more chemically reactive of the two. In the case of evaporation, the vapor pressures of different isotopic
molecules of water are inversely proportional to their masses; therefore, evaporation of water will result in isotopic fractionation such that $^{16}$O and H will preferentially enter the vapor phase, while $^{18}$O and D will be concentrated in the liquid phase. This process is defined by the fractionation factor, $\alpha_{L/V}$ (Hoefs, 1973):

$$\alpha_{L/V} = \frac{R_L}{R_V}$$  \hspace{1cm} (2.19)

where $R_L$ is the ratio of the heavy to light isotope in the liquid phase, and $R_V$ is the same in the vapor phase. The fractionation factor for any given system is temperature dependent, decreasing toward unity with increasing temperature.

Stable isotope ratios measured by mass spectrometry are reported in per mil ($\delta/\omega$) differences of $^{18}$O/$^{16}$O and D/H ratios relative to a standard called SMOW (Standard Mean Ocean Water) (Craig, 1961) or:

$$\delta^{18}O = \left\{ \frac{[(^{18}O/^{16}O)_x - (^{18}O/^{16}O)_{SMOW})]}{^{18}O/^{16}O_{SMOW}} \right\} \times 10^3$$  \hspace{1cm} (2.20)

and

$$\delta D = \left\{ \frac{[(D/H)_x - (D/H)_{SMOW})]}{(D/H)_{SMOW}} \right\} \times 10^3$$  \hspace{1cm} (2.21)

where $x$ refers to the sample ratio. Positive values of $\delta^{18}$O and $\delta$D indicate enrichment of the sample in the heavier isotope with respect to SMOW, while negative values imply a depletion in the sample relative to the standard.
When water vapor condenses, the liquid condensate will be enriched in $^{18}O$ and D, relative to the vapor. The initial condensate to form will be enriched in heavy isotopes to a greater extent than later-forming condensate, as the air mass from which this later-formed condensate is derived has already been depleted in heavy isotopes (provided that the earlier-formed condensate has been removed from the system). Thus, as the condensation process continues, both the later-forming condensate and the vapor from which it forms become characterized by lower and lower concentrations of heavier isotopes. Also, since both condensation and isotope fractionation are temperature dependent, the isotopic composition of the condensate is temperature dependent.

The condensation of water vapor in equilibrium with water vapor and its subsequent removal from an air mass can be described by the Rayleigh distillation equation:

$$\frac{R}{R_0} = f\left(\frac{a_L}{V}\right)$$

(2.22)

where $R$ is the isotopic ratio of the remaining vapor, $R_0$ is the isotopic ratio of the vapor before condensation begins, $f$ is the fraction of vapor remaining, and $a_L/V$ is the isotope fractionation factor.

The result of isotopic fractionation during evaporation and condensation cycles in precipitation is that fresh water is generally depleted in $^{18}O$ and D compared to ocean water. On the basis of a large number of meteoric water samples collected at different latitudes,
Craig (1961) showed that del $^{18}O$ and del D values relative to SMOW can be linearly related by:

$$\text{del D} = 8 \text{ (del } ^{18}O \text{)} + 10 \quad (2.23)$$

The evaporation/condensation processes inherent to the proposed thermoelectric sampling technique present added complications to the evaluation of stable isotopes. The computation of a fractionation factor would be required in order to estimate the isotopic ratio of the soil water from which the vapor was evolved. However, this in itself would not be a straightforward procedure because of the Rayleigh distillation effect. Therefore, due to the uncertainties involved in evaluation of stable isotope data obtained by this technique, attention will be focused on the evaluation of tritium.

**Tritium**

Tritium is the naturally-occurring radioactive isotope of hydrogen. It is produced in the upper atmosphere by interaction of the fast cosmic-ray-produced neutrons with stable $^{14}$N according to the reaction:

$$^{14}_7\text{N} + ^1_0\text{n} \rightarrow ^3_1\text{T} + ^{12}_6\text{C} \quad (2.24)$$

Tritium readily combines with oxygen to form HTO which is subsequently dispersed throughout the hydrosphere. The concentration of tritium in various parts of the hydrosphere, particularly in the
northern hemisphere, has been greatly increased as a result of large-scale testing of thermonuclear bombs in the upper atmosphere from 1954 to 1963.

Tritium has a half-life of 12.26 years and decays to stable He by beta emission. It is detected by the energy spectrum of the emitted beta particles which is distributed over a range of $3 \times 10^3$ ev to a maximum of 18 Kev (Curran et al., 1949). Concentrations are reported in terms of the tritium unit (TU), which is defined as one atom of $^3$H for every $10^{18}$ atoms of $^1$H.

Although water molecules containing tritium are subjected to isotopic fractionation, this effect is generally considered to be negligible compared to variations in the rate of input and subsequent decay of tritium (Hoefs, 1973).

Measurements of tritium concentrations are useful in groundwater investigations concerning the residence time of water or its travel time through an aquifer. It has been estimated that prior to atmospheric testing, the natural tritium content of precipitation ranged from 5 to 20 TU; therefore, water that became isolated from the atmosphere (recharge water) prior to 1953 would be expected to have tritium concentrations of less than 5 tritium units. On the other hand, water containing tritium concentrations of one or two orders of magnitude greater than this value would indicate the presence of water added to the system since that time.

Applications also exist in the unsaturated zone. For example, Smith et al. (1970) determined the tritium concentration profile of a clay soil and used the location of the tritium peak produced by "bomb"
tritium to evaluate the velocity of soil water flow through the section. One of the goals of this research is to develop the thermo-electric sampling technique for applications such as this in unsaturated fractured rock.
CHAPTER THREE

THERMOELECTRIC COOLING SYSTEMS

It is only since the refinement of semiconductor materials in the early 1950's that thermoelectric cooling has become practical for most applications. The beginnings of the science, however, date back to the 1830's and the work of J. C. Peltier (Rowe and Bhandari, 1983), who noted in 1834 that a temperature change occurs in the vicinity of a junction between two dissimilar conductors when a current is applied. The effect was further evaluated by Lenz in 1938 (Rowe and Bhandari, 1983) who determined that heat may be produced or adsorbed between two dissimilar conductors depending on the direction of current flow. He demonstrated this by freezing water at a bismuth junction and then melting the ice by reversing the current direction.

The basic principles of thermoelectric cooling and the generation of thermal effects in semiconductors are reviewed in Appendix A. In this chapter, the entire framework that constitutes a thermoelectric cooling system is broken down into its components and subcomponents which are discussed individually. There are three main components of a thermoelectric cooling system including:

(1) The cooling module, which consists of a number of thermocouples joined electrically in series and thermally in parallel;

(2) The power supply, in this case a DC source; and

(3) A heat sink which discharges accumulated heat energy from the system.
In the following paragraphs, the functions of each of these elements, as well as other factors affecting the behavior of the total cooling system, will be examined more closely.

The Cooling Module

In the thermoelectric cooling module, semiconductor materials of dissimilar characteristics (n-type and p-type) are connected electrically in series and thermally in parallel in such a manner that two junctions, one hot and the other cold, are created by Peltier cooling when a current is passed through them. The arrangement is shown schematically in Figure 3.1. When the current is applied in the direction shown, heat is adsorbed at the cold junction as the charge carriers pass from the p- to n- semiconductors. The heat is pumped to the hot junction at a rate proportional to the carrier current passing through the circuit and the number of thermocouples in the module.

Cooling modules are available commercially in a variety of sizes and heat removal capabilities and in single or multiple arrangements. Single layer sizes typically range from 2.5 mm$^2$ to 50 mm$^2$ in cooling surface area and from 2.5 mm to 7.5 mm thick, with cooling capacities ranging from a few watts to greater than 130 watts. Any desired amount of cooling surface area may be created by combining a number of individual modules together in series. Multi-stage modules of up to 6 layers have also been developed that can generate several hundred watts of cooling capacity and provide cold junction temperatures as low as 125°C below ambient. The choice of module depends upon the intended application, and comprehensive data information sheets are
Figure 3.1. Schematic cross section of thermoelectric cooling module, showing arrangement of p and n semiconductors and location of the cold and hot junctions resulting from Peltier cooling due to an applied current (after Bosen et al., 1967).
available from manufacturers as an aid in determining the best module for a specific requirement. This procedure will be explained further in Chapter Four, where the specific cooling requirements for vapor condensation in a fractured rock system are determined.

The module used in this research contains 71 one p-n couples and measures 30mm X 30mm X 4mm. It has been developed by TECA, ThermoElectric Cooling America Corporation (Model No. 950-71) and specifications given throughout the remainder of this section are from the instruction manual and information brochures provided by the company (Bosen et al., 1967).

Because good thermoelectric materials are generally poor thermal conductors, the semiconductor elements are kept short to maximize heat removal from the cold junction (Smith, 1984). In conjunction with the use of shorter elements, heat removal in the module is improved by adding a material of good thermal and electric conductivities at the junction interfaces. The semiconductor elements in the cooling module used for these experiments are composed of bismuth telluride (BiTe₃), which has a thermal conductivity of only 0.015 W/cm °C. In comparison, the copper conductors located at element junctions have a thermal conductivity of 3.85 W/cm °C.

Attached to the copper conductors at both hot and cold junctions are thinly layered ceramic-metal laminate plates that furnish a continuous surface area upon which cooling takes place. The purpose of the layering is to provide electrical insulation (through the ceramic material) while maintaining good thermal contact (by means of the metal layers) with the environment to be cooled.
Power Supply

The power supply is usually the largest component in the thermoelectric cooling system. Its function is to convert the available AC current, which actually drives the system, to the DC required by the module as shown schematically in Figure 3.2. The current regulator must be capable of removing, as much as possible, the fluctuation (or ripple) inherent to the alternating current which leads to variability in the performance of semiconductor elements as the current flows through them. Maximum cooling capacity of the module is obtained when the current ripple is reduced to less than 10 percent (Egli, 1960). This is illustrated in Figure 3.3, which shows the ratio of temperature difference obtained with zero ripple against the percentage of current ripple remaining after passing through the filtering system of the DC converter. This relationship may be expressed as (Bosen et al., 1967):

$$\frac{\Delta T_R}{\Delta T_{MAX}} = \frac{1}{1 + N^2} \quad (3.1)$$

where

- $\Delta T_R$ = temperature differential with current ripple ($^\circ$C);
- $\Delta T_{MAX}$ = temperature differential with zero ripple ($^\circ$C); and
- $N$ = percent current ripple.

The Heat Sink

The heat being removed from the environment at the module's cold junction is subsequently deposited at the hot junction. If this
Figure 3.2. Schematic representation of thermoelectric cooling system, showing power supply arrangement (after Bosen et al., 1967).
Figure 3.3. Current ripple effect on temperature differential obtained at thermocooler cold junction (after Egli, 1960).
heat is not dissipated in some form of a heat sink, it will tend to be conducted back through the module to the cold junction (i.e., from the higher to lower energy state). The performance of a cooling module is therefore highly dependent on the rate of heat dissipation by the heat sink. Heat sinks fall into three general categories: (1) natural convection, (2) forced convection, and (3) liquid cooled, and their capacities for heat dissipation are measured in Kelvin per watt. The type of heat sink required for a given application depends on the heat load to be dissipated. Natural convection has the advantage of no moving parts and consists of blocks of massive or finned material soldered directly onto the hot plate. This method can be employed when the cooling load is moderately low but is generally inadequate for most thermoelectric applications (Rowe and Bhandari, 1983). Forced air cooling, consisting of a finned heat sink and blower, may be used in situations where cooling with a liquid is not possible, although it is generally not as effective. For most applications, the liquid cooled system is the preferred choice (Rowe and Bhandari, 1983), although it has the disadvantage of requiring tubing and a pump, which defeat the small size advantage of using a thermoelectric system.

Factors Affecting Cooling Performance

A number of related thermoelectric effects have been found to influence the ability of a cooling module to absorb heat by Peltier cooling. These factors need to be given consideration in the design of a thermoelectric cooling system. One of the primary relationships established in the description of cooling system performance is that
defined by Lord Kelvin between the Peltier effect and Seebeck effect, given by (Elgi, 1960):

\[ Q_p = \pi I = -aI T \]  \hspace{1cm} (3.2)

where

- \( Q_p \) = heat energy removed per unit time at the cold junction by Peltier cooling (W);
- \( I \) = current (Amps);
- \( \pi \) = Peltier coefficient (W/A or V);
- \( T \) = absolute temperature (K); and
- \( a \) = Seebeck coefficient, or thermoelectric power of the junction (V/K).

The Peltier effect is thoroughly discussed in Appendix A. The Seebeck effect is the voltage developed across a thermocouple junction when the two junctions are maintained at a temperature difference of 1°C, and is given by (Elgi, 1960):

\[ V = a(T_H - T_C) \]  \hspace{1cm} (3.3)

where \( T_H \) is the temperature of the hot junction, \( T_C \) is the temperature of the cold junction in Kelvin degrees, and \( a \) is the Seebeck coefficient.
The direction of the Seebeck voltage development across the junction and that of the external power supply are such that the two potentials tend to compensate each other.

Another factor involved in determining overall cooling capabilities is the conductance of heat down the potential energy gradient, or from the hot to the cold junction. This is given by:

\[ Q_c = K(T_H - T_c) \]  (3.4)

where \( K(W/°K) \) is the thermal conductance of the two thermocouple branches in parallel.

A third factor influencing the cooling performance of the module is the Joule heat resulting from the internal resistance of the semiconductor elements and is given by (Elgi, 1960):

\[ Q_j = 1/2(I^2R) \]  (3.5)

where \( R \) is the sum of the resistances within the two branches of the thermocouple.

The total heat energy removed from the surrounding medium by the cold junction is therefore given by the sum of the three terms:

\[ Q_T = \alpha IT - 1/2(I^2R) - K(T_H - T_c) \]  (3.6)

The total power input to the thermocouple is given by (Elgi, 1960):
\[ P_T = IV_T \quad (3.7) \]

where \( V_T \) is the total potential drop across the thermocouple and may be written as (Elgi, 1960):

\[ V_T = IR + a(T_H - T_C) \quad (3.8) \]

where the first term is the voltage drop across the thermocouple, and the second term is the Seebeck voltage.

The coefficient of performance, \( C \), of the cooling junction is used as an indication of the efficiency of the system and is defined as the ratio of the total heat absorbed at the cold junction to the amount of power supplied (Elgi, 1960):

\[ C = \frac{Q_T}{P_T} \quad (3.9) \]

or:

\[ C = \frac{\alpha IT - 1/2I^2R - K(T_H - T_C)}{[IR + Q(T_H - T_C)]/I} \quad (3.10) \]

As the coefficient is a function of the current running through the module, the current for which \( C \) is a maximum can be found by setting the derivative \( \partial C/\partial I \) equal to zero and solving for \( I \). With the optimum current value substituted into Equation (3.10), the maximum coefficient of performance becomes (Elgi, 1960):
\[ C_{\text{MAX}} = \frac{T_{c}}{T_{H} - T_{c}} \cdot \frac{(1+ZT_{m})^{1/2} - (T_{H}/T_{c})}{(1+ZT_{m})^{1/2} + 1} \]  

where

\[ T_{m} = \frac{(T_{H} - T_{c})}{2} \]  

and

\[ Z = Q^{2}/RK \]  

The coefficient \( Z \) is defined as the figure of merit for the thermocouple and indicates the lowest cold junction temperature which can be achieved with a given thermocouple for a prescribed hot junction temperature. This is given by the set of equations (Elgi, 1960):

\[ (T_{H} - T_{c})_{\text{MAX}} = 1/2(ZT_{c}^{2}) \]  

for the maximum temperature drop, and

\[ (T_{c})_{\text{MIN}} = [(1 + 2ZT_{H})^{1/2} - 1]/Z \]  

for the minimum cold junction temperature.

Other extraneous heat sources may also reduce cooling efficiency, such as convection of higher temperature air across the lower temperature cold plate. Convection losses have been determined by the
manufacturer of the modules used in these experiments (Bosen et al., 1967) to be on the order of 1 mW per cm² surface area of cold face, per °C temperature difference between cold plate and ambient.
As indicated in Chapter Three, there are a number of parameters to be evaluated when attempting to develop a thermoelectric cooling system for a particular application. These include:

1. The total heat load (number of watts to be pumped from the heat source area);
2. Module current and voltage;
3. Required cold junction temperature;
4. Ambient temperature; and
5. Heat sink requirements.

In the following discussion, each of these elements will be addressed in the context of designing a cooling system for the condensation of water vapor as a sampling technique in an unsaturated medium. Because a number of system parameters were not precisely known in advance such as the amount of time cooling must be applied to achieve a desired amount of sample and the total amount of moisture available for condensation, the operational cooling current and voltage as well as heat sink and power supply requirements were determined experimentally before field work was attempted. The laboratory setting was designed to simulate field conditions as closely as possible and was based on the following proposed situation.

A 10-ml sample of vapor condensate is to be collected from an isolated section of borehole (4.5 cm diameter) in a fractured, densely-
welded tuff. The interval of interest is located in the unsaturated zone where the relative humidity under normal conditions may be expected to vary from no less than 98 to 100 percent (Hillel, 1980). The air temperature in the borehole is assumed to be 25°C.

Estimated Heat Load

The amount of heat energy to be removed from the sampling area for the condensation of water vapor may be estimated as the sum of the energy required to change the temperature of the vapor to below the dew point (where condensation will take place) plus the energy released from a phase change at that temperature, or:

\[ Q_c = m c \Delta T + m L \]  

(4.1)

where

- \( Q_c \) = total cooling energy required (J);
- \( m \) = mass of water condensed (approximately 10 gm at 25°C);
- \( c \) = specific heat of water at 25°C (4.18 J/g°C);
- \( L \) = latent heat of vaporization of water at 25°C (2440.7 J/g); and
- \( T \) = temperature (°C).

When water undergoes a phase change from the vapor to liquid state, latent heat of condensation is released into the surroundings from the water, while when changing from a liquid to a vapor, latent
heat of vaporization is added to the evaporating water from the environment. The two types of heat energy are numerically equivalent (2440.7 J/g); only the direction of energy transfer is reversed. The latent heat of condensation is added to the right-hand side of Equation (4.1) in this case because the heat energy given off by the condensing vapor must be compensated for by the cooling surface of the cold junction.

Given that 10 gm of water vapor is to be condensed, the only unknown in Equation (4.1) is the change in temperature required to bring about condensation, which may be estimated from the vapor pressure of the air in the borehole. The saturation vapor pressure of water as a function of temperature may be obtained from psychrometric tables (Lindsay et al., 1972), and at 25°C is given as 31.67mbar (3.167kPa), which yields an actual vapor pressure of 31.04 mbar at 98% relative humidity.

The relationships between temperature, saturation vapor pressure, and vapor density are illustrated in Figure 4.1. The volume of air under consideration in this problem is initially close to saturation, having a temperature and vapor pressure corresponding to point A in the diagram. Under these conditions, cooling of less than 1°C will be enough to bring the air to its dew point, located by the intersection of the horizontal line indicating isobaric change in temperature with the water vapor equilibrium curve (point B). The dew point is defined as the temperature to which air must be cooled to become saturated with the vapor it contains, and additional cooling beyond this point will result in the condensation of excess moisture. Once
Figure 4.1. Saturation vapor pressure and water vapor density as functions of temperature.
condensation begins, the temperature drops much more slowly because the loss in heat energy is partially compensated by the release of latent heat of condensation; thus, cooling takes place along the line BC until the final temperature (point C) is reached. The total amount of condensation is given by the change in vapor pressure $\Delta e$ and, as the graph indicates, the greater the temperature change, the greater the amount of moisture released.

For the purpose of collecting a sample of vapor condensate from a natural rock vapor system, it is important to reduce the temperature at the sampling point as much as possible. This will generate a steep temperature gradient in the system which in turn will produce a steep vapor pressure gradient.

The actual temperature drop and time required to establish evaporation from liquid surfaces in the system must be determined experimentally; however, a temperature change of 15°C was selected as a rough estimate for evaluating the present hypothetical case. For a temperature change of 15°C, the total heat energy to be removed from the sample area for extraction of 10 ml vapor sample [from Equation 4.1)] is 25,034 J.

### Cooling Module Selection

The number of watts of heat to be removed at the module cold junction for the condensation process (a value important in cooling module selection) may be considered a variable at this point inasmuch as the amount of time needed to condense the vapor is not fixed. Because power is inversely related to time (the units are energy per
unit time, or Watts = Joules/sec), increasing the amount of time allowed for removal of the 25 kJ of heat energy will decrease the power load at the cold junction. The relationship between heat removal and condensation was examined experimentally in the laboratory to establish probable sample collection rates for the field situation; however, for the preliminary selection of a cooling module for testing purposes, a time limit of one hour was assumed, yielding 6.95 watts of heat to be removed from the sampling area for collection of the 10 ml sample.

Once the operating temperatures (cold junction and ambient) and heat load are determined, estimates may be made of power supply and heat sink requirements using graphical relationships derived by thermoelectric companies for the specific cooling modules they manufacture. Examples for TECA's model 950-71, which was used in this work, are shown in Figures 4.2a-b. Locating the intersection point of the assumed temperature differential of 15°C with the predicted heat load of 6.95 watts yields an operating current of approximately 1.75 amps. Figure 4.2b is then entered at 1.75 amps, and the halfway point between $\Delta T = 0$ and $\Delta T = \text{MAX}$ is located. A horizontal line projected to the y axis indicates a power supply voltage of approximately 3.0 V.

An additional heat load is generated by the power input $P$ to the cooling module, and this is given in Equation (3.7). Thus, the heat load generated by the power input is 5.25 watts for this situation.

The total heat load to be dissipated by the heat sink is then the sum of the heat removed from the sampling area plus the heat generated by the power input, or 12.2 watts.
Figure 4.2. Thermoelectric relationships for determining cooling module performance. (a) Heat load verses ambient-cold side temperature differential for various operating currents, and (b) voltage estimation based on current and temperature differential. Modified from TECA Corp. data sheets for TECA Model No. 950-71.
After similar studies were made of thermoelectric cooling modules produced by several manufacturers, it was decided that the Model 950-71 produced by ThermoElectric Cooling America Corporation (described in Chapter Three) was best suited for the needs of this study.
CHAPTER FIVE

LABORATORY STUDIES

Heat Sink Design

The design of the heat sink is one of the most critical aspects of the thermoelectric cooling system. If it is not capable of dissipating the required heat load from the sampling area, the temperature of the entire system will rise and condensation will not occur. In typical situations where thermoelectric cooling modules are used, heat exchange systems are fairly simple to devise, as the environment to be cooled and the environment into which heat is rejected are usually physically separated. For example, when used for cooling a constant temperature bath, the body of water to be cooled is held within a container with one surface in contact with the thermoelectric cold junction, while the hot junction and heat exchange system are located outside the container in the ambient environment. The present situation is complicated by the fact that the entire cooling module and heat sink must be placed together in the borehole, where the heat-losing and heat-gaining environments are not completely separable. In relation to this complication, one of the major problems involved in using the thermoelectric system for this application is inherent to its basic design, in that the cold junction surface and hot junction surface are separated by a distance of only a few millimeters, or the length of the semiconductor elements. Therefore, it is essential that the heat sink design be as efficient as possible.
Thus, it was a major task of this research to determine if the shortcomings of the heat exchange system may be overcome to the extent that thermoelectric cooling may be considered a viable sampling technique in unsaturated media. Several alternatives were evaluated in the laboratory, and the most effective method was chosen for testing in the field.

Preliminary Testing of Cooling Modules

The cooling modules were first tested for instrument response in the absence of a heat sink, by measuring temperature differentials from ambient produced at both hot and cold junctions under various applied currents. The purpose of these experiments was to evaluate temperature changes produced by the power input to the cooling module alone, and to gain a better understanding of the amount of heat to be dissipated by the heat exchange system.

This was accomplished by attaching a thermistor to the center of each hot and cold surface using an epoxy adhesive. The modules were placed inside an insulated chamber while testing to avoid extraneous effects from changes in laboratory conditions. The chamber was also airtight, so it could be assumed that the cooling module was interacting with a constant volume of air. The cooling module leads were connected to a DC power regulator which was plugged into an AC wall outlet. Temperature changes over time were recorded for applied currents ranging from 0.1 A to 1.0 A at increasing increments of 0.1 A. Testing for currents greater than 1.0 A was not attempted because of the excessive amounts of heat generated. Hot and cold surfaces were
allowed to return to the initial ambient temperature reading between each current test. Thermistor output was in resistance (ohms) and was converted to temperature in Celsius using the calibration technique provided by the thermistor manufacturer. This procedure was repeated for each of three cooling modules (all of the same model) obtained from TECA Corp. to check for response variability.

Results and Discussion

Responses for the individual units (with respect to temperature changes relative to ambient) were all found to be similar for similar applied currents. Some slight variability may be attributed to thermal gradients produced within the insulated chamber by excessive heating at the thermocooler hot side, and also to variability in the DC regulator which was difficult to control accurately to within +/- 0.1 A current. Because responses for individual modules were fairly consistent, it was not considered necessary to repeat procedures for each module in subsequent experiments. The data for one of the modules are plotted as temperature (°C) versus time (minutes) for the first 15 minutes of testing in Figures 5.1 and 5.2.

The important features of the response curves are summarized in Table 5.1, including initial and final temperatures ($T_i$ and $T_f$, respectively), total temperature change ($\Delta T_{f-i}$), time when final temperature was reached ($t_f$), minimum temperature attained ($T_m$), maximum temperature drop from ambient ($\Delta T_{m-i}$), and time required to reach minimum temperature ($t_m$). Negative signs indicate a temperature decrease below ambient.
Figure 5.1. Module no. 1; cold junction temperature versus time for various applied currents in absence of heat sink.

Figure 5.2. Module no. 1; hot junction temperature versus time for various applied currents in absence of heat sink.
Table 5.1. Cooling Module Response for Various Applied Currents

<table>
<thead>
<tr>
<th>Current</th>
<th>$T_i$ **</th>
<th>$T_f$</th>
<th>$T_{f-i}$</th>
<th>$t_{f}$ ***</th>
<th>$T_m$</th>
<th>$T_{m-i}$</th>
<th>$t_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>25.40</td>
<td>24.80</td>
<td>-0.60</td>
<td>43.0</td>
<td>24.21</td>
<td>-1.19</td>
<td>2.0</td>
</tr>
<tr>
<td>0.2</td>
<td>26.23</td>
<td>25.50</td>
<td>-0.73</td>
<td>39.0</td>
<td>24.80</td>
<td>-1.43</td>
<td>1.5</td>
</tr>
<tr>
<td>0.3</td>
<td>23.64</td>
<td>23.83</td>
<td>0.19</td>
<td>11.5</td>
<td>21.61</td>
<td>-2.03</td>
<td>1.0</td>
</tr>
<tr>
<td>0.4</td>
<td>23.46</td>
<td>25.40</td>
<td>1.94</td>
<td>9.5</td>
<td>21.27</td>
<td>-2.19</td>
<td>1.0</td>
</tr>
<tr>
<td>0.5</td>
<td>22.91</td>
<td>25.60</td>
<td>2.69</td>
<td>8.0</td>
<td>21.03</td>
<td>-1.88</td>
<td>1.0</td>
</tr>
<tr>
<td>0.6</td>
<td>23.09</td>
<td>26.55</td>
<td>3.46</td>
<td>5.0</td>
<td>20.30</td>
<td>-2.79</td>
<td>0.75</td>
</tr>
<tr>
<td>0.7</td>
<td>22.82</td>
<td>25.30</td>
<td>2.48</td>
<td>3.0</td>
<td>20.30</td>
<td>-2.52</td>
<td>0.50</td>
</tr>
<tr>
<td>0.8</td>
<td>23.09</td>
<td>26.02</td>
<td>2.93</td>
<td>3.0</td>
<td>20.78</td>
<td>-2.31</td>
<td>0.75</td>
</tr>
<tr>
<td>0.9</td>
<td>22.73</td>
<td>25.91</td>
<td>3.18</td>
<td>2.0</td>
<td>19.91</td>
<td>-2.82</td>
<td>0.50</td>
</tr>
<tr>
<td>1.0</td>
<td>23.00</td>
<td>25.00</td>
<td>2.00</td>
<td>2.0</td>
<td>20.46</td>
<td>-2.54</td>
<td>0.50</td>
</tr>
</tbody>
</table>

*Current = amps; **$T$ = Temperature (°C); ***$t$ = time (min.)
The data reveal that as expected, greater temperature drops are achieved in shorter time periods with increasing applied current; however, this effect is severely limited by the amount of heat produced at the module hot junction. In fact, a stable lowered temperature was maintained at the cold junction only when very low currents of 0.1 and 0.2 A were applied. At currents above this range, return heat flow from the hot to cold junction caused the cooling surface to heat up to temperatures above ambient at rapidly increasing rates.

This series of tests indicates that in order to achieve and maintain sufficient temperature differentials for the condensation of water vapor to occur, some type of heat exchange system must be attached to the thermocooler hot junction, as the temperature drops obtained in the absence of a heat sink would be insufficient to produce any significant condensation. This was supported by the results from a subsequent test, where the module was suspended in a high humidity environment (consisting of a sealed 1-liter beaker containing 250 milliliters of distilled water) and operated at a cooling current of 0.2 A. Although the current was maintained continuously for 8 hours, no significant condensation occurred. Very small beads of moisture were noted to appear on the cooling surface after a period of approximately one hour; however, no droplets large enough to collect as a sample were formed. This would indicate that the combined vapor density/temperature gradient established by the slight temperature change was not steep enough to draw vapor from very great distances or to stimulate evaporation from the free water surface.
Natural Convection Heat Sinks

An important characteristic in choosing a material for a heat sink is its thermal conductivity, which is defined by the Fourier Law as:

\[ H = - \lambda A \frac{dT}{dx} \]  

(5.1)

where \( H \) is heat flow in J/s or W, \( \frac{dT}{dx} \) is the thermal gradient in the x direction (°C/m), and \( A \) is the surface area of the material (m²). The thermal conductivity \( \lambda \text{(J/sm°C)} \) is not a constant but increases with increasing temperature for most materials. This relationship reveals that, for a large value of \( \lambda \), the amount of heat flow will be greater, all other factors being equal, and this is a desirable quality of the material chosen for a heat sink. A substance with a large value of thermal conductivity would be capable of pulling the heat away from the hot junction rapidly and redistributing it quickly and evenly throughout its mass.

An equally important consideration is the heat capacity of the material which is defined as the quantity of heat energy \( dQ \) (J) required to raise the temperature of a mass \( m \) (g) of the substance by an amount \( dT \) (°C), or:

\[ c = \frac{1}{m} \frac{dQ}{dT} \]  

(5.2)

where \( c \) is the specific heat capacity in (J/g°C). The relationship shows that, for a given amount of thermal energy added, a material
having a high heat capacity will undergo a lower temperature increase than a similar mass of material having a lower heat capacity. A high heat capacity is thus another desirable characteristic of the material to be used for a heat sink, as it is important to contain the heat within the mass of material as much as possible without increasing its temperature or that of the surrounding air space, which could be a deterrent to the vapor condensation process.

Equation (5.2) may be used to determine the mass of material required to dissipate the heat generated by the condensation of a 10-ml sample of water vapor. This was calculated in Chapter Four as being equal to the sum of the energy required to cool the air to the dew point plus the energy given off as latent heat of condensation plus the energy generated by the module itself, or 12.2 watts. For a 1-hour cooling period, the amount of heat energy \( Q \) to be removed would be 43,920 J. The temperature differential \( \Delta T \) in this relationship is the temperature difference between the material at \( t = 0 \), or the initial borehole temperature and the temperature at the end of the sampling period, assumed to be one hour. In order to prevent a reversal in the vapor pressure gradient in the sampling area, the heat sink must not be allowed to increase to a temperature much greater than that of the ambient environment; otherwise, vapor would be driven away from the region to be sampled and would condense upon encountering an area of lower temperature at some distance from the desired point. For this reason, a limit of 3°C was set for \( \Delta T \).

Table 5.2 lists the specific heats (J/g°C), thermal conductivities (W/cm°C), and densities (g/cm³) of some common substances. By
Table 5.2. Thermal Conductivities, Specific Heats, and Densities of Some Common Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>$k$ (J/m°C)</th>
<th>$c$ (J/g°C)</th>
<th>$25,C$ (g/cm³)</th>
<th>$m$ (g)</th>
<th>$V$ (cm³)</th>
<th>$L$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>201</td>
<td>0.912</td>
<td>2.7</td>
<td>16,053</td>
<td>5,946</td>
<td>473</td>
</tr>
<tr>
<td>Iron</td>
<td>80.3</td>
<td>0.460</td>
<td>7.8</td>
<td>31,826</td>
<td>4,080</td>
<td>325</td>
</tr>
<tr>
<td>Copper</td>
<td>384</td>
<td>0.389</td>
<td>8.9</td>
<td>37,635</td>
<td>4,229</td>
<td>336</td>
</tr>
<tr>
<td>Mercury</td>
<td>8.3</td>
<td>0.138</td>
<td>13.6</td>
<td>106,087</td>
<td>7,801</td>
<td>621</td>
</tr>
<tr>
<td>Lead</td>
<td>34.7</td>
<td>0.130</td>
<td>11.3</td>
<td>112,615</td>
<td>9,966</td>
<td>793</td>
</tr>
<tr>
<td>Glass</td>
<td>0.8</td>
<td>0.837</td>
<td>2.6</td>
<td>17,491</td>
<td>6,727</td>
<td>535</td>
</tr>
<tr>
<td>Water</td>
<td>0.6</td>
<td>4.184</td>
<td>1.0</td>
<td>3,499</td>
<td>3,499</td>
<td>278</td>
</tr>
</tbody>
</table>
rearranging Equation (5.2) and solving for m, the mass of material needed to dissipate the 43,920 J of heat for each of these substances was calculated, as well as the volume of material required, which was determined from dividing the mass by the density of the substance.

Given a borehole diameter of 4.5 cm, the radius of the heat sink material, or of the vessel containing the heat sink in the case of water, should be no greater than approximately 2.0 cm. Knowing the volume of material required from the previous calculations, the length of the heat sink was determined by rearrangement of the formula for the volume of a cylinder:

\[ L = \frac{V}{\pi r^2} \]  

(5.3)

Values determined for volume and length are also recorded in Table 5.2.

The results of these calculations show that, for most of these substances, the volume of material required to dissipate the heat generated in one hour would preclude their use as a heat sink in this situation, especially those materials having relatively low thermal conductivities, such as mercury, lead, and glass. Aluminum and copper would be possible alternatives because of their high thermal conductivities; however, exceptionally long sections of material are required due to the borehole diameter restrictions, making their use impractical.

An attempt was made to verify these findings by attaching a small aluminum heat sink having a mass of 375 gm and dimensions of 11 cm x 3.5 cm x 3.5 cm to the hot junction and recording temperature
changes with time at both ends of the heat sink and cold junctions for cooling currents of 0.2, 0.4, 0.6, 0.8, and 1.0 A. Results are shown in Figure 5.3 and 5.4 and summarized in Table 5.3.

**Results and Discussion**

The cold junction temperature versus time curves in Figure 5.3 demonstrate that significant temperature drops can be obtained using the aluminum heat sink; however, the minimum temperatures could be maintained for significant periods of time only for the 0.2 A current. The temperature curves for each of the applied currents ranging from 0.4 A through 1.0 A appeared to be slowly approaching a steady value; however, return heat flow had already increased the cold junction temperatures.

Figure 5.4 shows the hot side temperature changes over time at points 0.5 cm and 9.0 cm from the hot junction. The close proximity of the two curves reveals the ability of the material to distribute the heat energy quickly throughout its mass due to the high thermal conductivity of aluminum. The temperature increase of the total mass, however, is close to the stated acceptable limits of 3.0°C for the 0.2 A and 0.4 A cases only. Equilibrium temperatures had not yet been reached for the 0.4 A to 1.0 A applied currents by the end of the experiment, although they appear to be approaching constant values and should not achieve significantly higher temperatures over longer periods of time.

These tests indicate that a massive aluminum block could be a potential option as a heat sink for the thermocooling system, provided
Figure 5.3. Temperature versus time at cold junction for various applied currents with massive aluminum heat sink.
Figure 5.4. Temperature versus time at two points along massive aluminum heat sink for various applied currents. Solid line = 0.5 cm from hot junction; dotted line = 9.0 cm from hot junction.
Table 5.3. Module Response with Massive Aluminum Heat Sink

<table>
<thead>
<tr>
<th>Current (Amps)</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cold Side</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_i$ (°C)</td>
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<td>22.92</td>
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<td>24.15</td>
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<tr>
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<td>17.26</td>
<td>18.97</td>
<td>19.89</td>
</tr>
<tr>
<td>$T_{f-i}$ (°C)</td>
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<tr>
<td>$T_{m-i}$ (°C)</td>
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<td>-7.31</td>
<td>-9.76</td>
<td>-11.94</td>
<td>-14.90</td>
</tr>
<tr>
<td>$t_m$ (min.)</td>
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<td>3.0</td>
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<td>2.5</td>
</tr>
<tr>
<td><strong>Hot Side (d = 0.5 cm)</strong></td>
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<td>22.95</td>
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<td>3.27</td>
<td>5.43</td>
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<td>12.06</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$T_i$ (°C)</td>
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<td>22.64</td>
<td>23.00</td>
<td>24.93</td>
<td>24.15</td>
</tr>
<tr>
<td>$T_f$ (°C)</td>
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<td>25.91</td>
<td>28.23</td>
<td>31.97</td>
<td>34.98</td>
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<tr>
<td>$T_{f-i}$ (°C)</td>
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<td>7.04</td>
<td>10.83</td>
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<tr>
<td>$T$ (°C) along length of heat sink:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>0.13</td>
<td>0.04</td>
<td>0.15</td>
<td>0.25</td>
<td>1.29</td>
</tr>
</tbody>
</table>
the block was large enough to absorb the required amount of heat energy, so that minimum cooling temperatures could be maintained for longer periods of time. This type of heat sink would be particularly adaptable to the use of the thermoelectric technique in soils, where a larger access hole could be more easily drilled for insertion of a system having a relatively larger heat sink.

Liquid Cooled Heat Sinks

In the liquid cooled system, a circulating fluid is used to carry heat away from the hot junction as it is produced. The high heat capacity of water makes it an excellent choice as a heat sink medium, but the relatively low thermal conductivity limits its use unless a circulating system is devised to move the heated water away from the hot junction and replace it with cooler water. This system would be less desirable than the massive heat sink because of the additional tubing and pumping equipment required for circulating the water and because of the potential for leakage from the circulating system once emplaced in the borehole which could lead to sample contamination. However, as this was the only practical heat sink available at present, whereby heat energy is actually carried away from the sampling environment, it was decided to test it with the understanding that if a preferable technique becomes accessible in the future, it may be substituted for this method.

Procedure

In these experiments, the heat sink was attached to the thermo-cooler hot junction as shown in Figure 5.5. An aluminum plate having
Figure 5.5. Thermoelectric cooling module with attached water cooled heat sink.
the dimensions 1 cm x 3.8 cm x 3.8 cm was joined to the hot junction using a high-temperature resistant adhesive. The plate served to promote rapid removal of heat energy away from the hot surface. Copper tubing of 0.64 cm outer diameter was attached to the aluminum plate for circulation of the cooling water from the hot junction to a cold water reservoir, in this case, a constant temperature bath in which the temperature was maintained to within one or two degrees of ambient. The water was pumped through the system at a rate of approximately two liters per minute. The entire heat sink was also covered with a thin layer of insulating foam to minimize transfer of heat into the surroundings. The instrument was tested in an insulated chamber as in previous experiments to reduce environmental effects. Thermistors were connected to the cold surface, and the center of the aluminum plate and temperatures were recorded over time for two-hour test periods for cooling currents ranging from 0.1 to 1.0 A. Results of these experiments are summarized in Table 5.4 and illustrated as temperature versus time curves for cold and hot junctions, respectively, in Figures 5.6 and 5.7.

Results and Discussion

The temperature versus time curves reveal the ability of the liquid cooled system to establish and maintain an equilibrium cold temperature for longer periods of time and at greater applied currents than for the module used alone or in conjunction with a massive aluminum heat sink. Although the massive heat sink technique was able to produce greater temperature drops, the lowest temperature could not
**Table 5.4. Module Response with Liquid Cooled Heat Sink**

<table>
<thead>
<tr>
<th>Current (Amps)</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
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<tr>
<td><strong>Cold Side</strong></td>
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<td>$T_i^{\circ C}$</td>
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<td>22.38</td>
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<tr>
<td>$T_f^{\circ C}$</td>
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<td>17.61</td>
<td>15.94</td>
<td>14.77</td>
<td>16.46</td>
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<tr>
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<td>-6.64</td>
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<td>15.81</td>
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<td>16.39</td>
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<td>-6.57</td>
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<td>-6.71</td>
</tr>
<tr>
<td>$t_m$ (min.)</td>
<td>20.0</td>
<td>40.0</td>
<td>40.0</td>
<td>23.0</td>
<td>90.0</td>
</tr>
<tr>
<td><strong>Hot Side</strong></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>$T_i^{\circ C}$</td>
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<tr>
<td>$T_f^{\circ C}$</td>
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<td>23.37</td>
<td>24.90</td>
<td>26.34</td>
<td>29.81</td>
</tr>
<tr>
<td>$T_{f-i}^{\circ C}$</td>
<td>0.27</td>
<td>0.0</td>
<td>2.43</td>
<td>4.10</td>
<td>6.72</td>
</tr>
<tr>
<td>$T_m^{\circ C}$</td>
<td>23.37</td>
<td>23.93</td>
<td>24.90</td>
<td>26.34</td>
<td>29.81</td>
</tr>
<tr>
<td>$t_m$ (min.)</td>
<td>2.0</td>
<td>1.5</td>
<td>90.0</td>
<td>60.0</td>
<td>95.0</td>
</tr>
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</table>
Figure 5.6. Temperature versus time at cold junction for various applied currents with water cooled heat sink.

Figure 5.7. Temperature versus time at hot junction for various applied currents with water cooled heat sink.
be maintained for more than a few minutes. The liquid cooled system, using this configuration, appears to reach its maximum cooling capabilities at an applied current of 0.7 A ($\Delta T = -7.22 \, ^\circ C$). Above this level, return heat flow from the hot junction prevents the cold surface from achieving greater temperature drops, and cold side temperatures begin to increase beyond this point.

Based on the findings of this set of heat sink experiments, it was decided to continue further research with the modules using the liquid cooled system.

**Condensation Rate Tests**

Having established that the thermoelectric cooling module with a liquid cooled heat sink was capable of maintaining reduced temperatures over an extensive period of time, experimentation was required to determine the volume of condensate that could be collected for the various cooling currents at which the system might be operated. The experiment was designed so that at the same time, the temperature and vapor density gradients resulting from operation of the thermocooler could be evaluated.

**Procedure**

These experiments were conducted in the manner illustrated in Figure 5.8. Three hundred ml of water were ponded in the bottom of a horizontal, 80-cm long, 6-cm diameter plexiglas tube, sealed with rubber stoppers, and allowed to come to vapor equilibrium with the air space in the tube. This was done to simulate conditions of nearly 100% relative humidity within the borehole which should exist in the actual
Figure 5.8. Schematic arrangement of laboratory equipment for evaluation of condensation rates.
field case. The system was allowed to equilibrate for several hours before beginning the experiment to ensure that high relative humidity and uniform temperature conditions existed within the tube. Along the top of the tube, holes had been drilled at 12-cm intervals, and thermocouple psychrometers were inserted and sealed in place with silicon rubber to prevent air leaks. The psychrometers, used in conjunction with a microvoltmeter, had been previously calibrated over expected potential and temperature ranges by both dew point and psychrometric methods (Brown et al., 1971) according to well-established techniques. For a detailed discussion of the psychrometer calibration procedure, see Anderson (1986). The psychrometers were used in this experiment to monitor changes over time in relative humidity and air temperature with distance from the instrument. The data were then used to evaluate the vapor and thermal gradients generated over time by the cooling module when operated under typical cooling currents.

Before subjecting the thermocooler to the humid conditions of the simulated borehole, the module was modified by sealing the semiconductor elements, which are exposed along the edges of the module, with an epoxy adhesive. The entire assembly, with attached heat sink apparatus, was inserted into one end of the tube with the copper water circulation tubing and electrical leads extending through holes drilled in the rubber stopper. The electrical leads were connected to a DC regulator and AC source, and the water circulation tubing was connected to a constant temperature bath equipped with a pump. Thermistors were attached to both the condensing plate and heat sink and connected to a
resistivity meter to monitor temperature changes at these surfaces throughout the experiment.

Cooling water was circulated through the system at an average rate of two liters per minute and at a temperature no lower than 3°C below ambient. This lower limit was set because it was found that if the circulating water was at a temperature much lower than ambient, vapor would tend to condense on the surface of the tubing as well as on the module's cold plate, leading to a loss of sample. It was occasionally necessary to decrease the temperature of the water to below this limit at various points during the experiment, especially when the module was operated at higher currents, in order to carry off the excessive heat produced at the hot junction. Therefore, temperature was carefully monitored and adjusted when necessary throughout the experiment to prevent both overheating of the hot junction and overcooling of the circulating water.

The thermoelectric cooler was also modified for collection of a sample by attaching a small cup to the cold surface and inverting the unit, so that as water condensed, it would drip into the cup. Teflon microbore tubing of .025-cm inner diameter was run from the bottom of the sample cup to a sample bottle outside the borehole. Small diameter tubing was used so that a sample could be drawn off after only a few drops of water had collected in the cup by application of a slight vacuum. Teflon material was chosen because it would offer the least resistance to flow of water through the tubing and would be unlikely to contribute to sample contamination because of its non-reactive properties. Samples were withdrawn through the tubing by a small
hand-operated vacuum pump connected to the sample bottle. A detail of the sample collection part of the system is shown in Figure 5.9.

The experiment was run for a 24-hour period at a cooling current of 1.0 A, and again at 2.0 A, 3.0 A, and 4.0 A for 10-hour periods. Results and conclusions for each of these experiments are discussed in the following section.

Results and Discussion

The experiment was aborted during the first three trials because of problems in the instrument design. In the first attempt, it was found that the heat sink, which consisted of an aluminum block attached on one side to the thermocooler hot junction and on the other to the water circulation tubing, was inefficient. The aluminum block tended to heat up faster than the water flowing through the copper tubing could carry the heat away. This resulted in a reversal of the thermal gradient such that moisture in the air of the "borehole" would diffuse away from the thermocooler, as was evidenced by the condensation of moisture along the walls of the "borehole" at a distance of 15 to 20 cm away from the instrument site. Decreasing the temperature of the cooling water in an attempt to remove the heat from the aluminum block lead to the condensation of moisture onto the surface of the circulation tubing, resulting in a further loss of sample.

To improve the heat removal capacity of the cooling system, the heat sink was redesigned by attaching a small water reservoir, constructed of thin (1/32-inch) brass sheeting, to the circulation tubing and attaching this assembly to the thermocooler hot junction as shown
Figure 5.9. Schematic detail of sampling procedure for condensation rate experiments.
in Figure 5.10. The water would flow through one tube into the reservoir and out a second tube so that the cold water was brought into direct contact with the entire surface of the thermocooler hot junction and could thus more effectively carry the heat away. In subsequent testing, this design proved to be capable of removing the heat from the hot junction without the generation of additional thermal gradients in the sampling region. It was also found that this design permitted greater temperature drops from ambient than the previous design as may be noted by comparison of Figures 5.6 and 5.11.

In the second attempt, condensation began to occur on the outside surface of the sampling cup rather than on the cold junction surface and would then drip back into the "borehole" instead of into the cup from which it could be collected. This was most likely due to the cup being in direct thermal contact with the cold surface, whereby the thermal conductivity of the cup material was high enough that it would experience a temperature decrease along with the cold plate when the cooling current was applied. Moisture diffusing toward the sampling site under the thermal and vapor density gradients would condense upon the nearest cold surface encountered, in this case, the sample cup. To alleviate this problem, the instrument was modified by suspending the cup below the cold plate so that thermal contact between the two surfaces was avoided.

A third attempt was terminated because, although moisture was noted to condense on the cold plate until a thin film of liquid water had covered the surface, droplets large enough to fall into the cup did not form, although the experiment was continued for six hours. It
Figure 5.10. Redesigned water cooled heat sink, whereby cold circulating water is brought into direct contact with the hot junction, allowing for more efficient heat removal.
Figure 5.11. Temperature versus time at hot and cold junctions applying 1.0 A current, with redesigned heat sink.
appears that the forces of adhesion created by the ceramic surface of the thermocooler are greater than the cohesive forces between the water molecules which should have caused the water film to coalesce into droplets as condensation continued. Furthermore, the presence of this strongly-sorbed layer of water seems to slow down the condensation process so that no further noticeable liquid moisture develops. This may be attributed to the formation of a vapor gradient in the direction opposite that of the thermal gradient. That is, the presence of the liquid water on the cold plate may have lead to the development of a high water vapor pressure directly over the film surface which decreases in the direction away from the cold plate. If this reversal in the vapor pressure gradient became stronger than the thermal gradient operating in the opposite direction, then moisture could be forced to diffuse away from the cold plate, and further condensation would not be possible.

Adhesion of liquid moisture to the cold plate was avoided by covering the surface with a hydrophobic substance such as Teflon. For such a material, the forces of cohesion between water molecules would be strong enough to overcome the negligible adhesion to the solid surface, allowing the water film to coalesce into droplets and fall into the collection cup, once they became large enough to be overcome by the force of gravity.

Results from the fourth condensation rate test, using the Teflon-coated surface, operated at 1.0 A cooling current and 1.5 V voltage are illustrated in Figure 5.12, which plots both cumulative volume of condensate and rate of condensate formation against time for
Figure 5.12. Cumulative volume condensate and condensation rate versus time for 1.0 A applied current.
the 24-hour testing period. The rate of collection appears to reach a steady state after the first four hours of testing, when an equilibrium rate of 0.4 ml/hr is achieved. Variations above and below this level may be attributed to errors in reading values from the collection vessel which was marked in 0.2-ml increments.

The graph also reveals that no condensate was collected until the end of the first hour of testing, and then only 0.15 ml was withdrawn, or the equivalent of 2 or 3 drops of water. The initially slow response of the system may be attributed to the establishment of the vapor density gradient. Sufficient moisture must be removed from the air space in the borehole to induce evaporation from the free liquid surface. Once this gradient has been established and evaporation has begun, the system continues to operate at a steady state as long as a free surface of water is available as a source of moisture.

It may be noted that the equilibrium rate of condensation obtained in the lab is much lower than the 10-ml/hr rate assumed in the calculation made in the previous chapter for collection of a 10-ml sample when the thermocooler is assumed to operate under similar conditions. One of the factors which may influence the rate at which sample is collected is the amount of cold junction surface area available for condensation to take place. This was limited in these experiments to 9 cm² by the borehole diameter and the configuration of the instrument when placed in the borehole. A second factor is the diffusivity of water vapor through air, which has been determined to be 0.274 cm²/sec (Philip and deVries, 1957). Related to this is the distance separating the thermocooler from the liquid water which serves
as the source for the sample. In these experiments, the instrument was suspended directly above a free water surface, where the distance of separation between the two was less than 3 cm. This close proximity to the source may actually have served to enhance the condensation rate over what may be expected under field conditions; however, the source was limited to the surface area of the ponded water in the bottom of the tube, while in the field (depending on the water content of the rock), the instrument would be inserted into a borehole within a medium which completely surrounds it with a source of water for evaporation. Another limiting factor is the rate at which water may be evaporated from a liquid surface, which is itself limited by the temperature and vapor density conditions which exist in the air space above the surface of the liquid. Finally, a given amount of time is involved in the formation of droplets large enough to drip into the cup under the force of gravity.

The moisture potential versus time curves for the thermocouple psychrometer readings are plotted in Figure 5.13. Two sampling points, those located at distances 10 cm to the front and rear of the instrument, are not shown because no steady readings could be obtained after the initial values while the thermocooler was operating. This indicates that the vapor density and temperature gradients are very steep in this region, causing nonsteady environmental conditions in which the psychrometer cannot be operated accurately. This effect eventually extends as far as the measuring point at 22 cm after the first 1.5 hours; however, conditions appear to remain steady at the other four more distant measuring points throughout the remainder of the test.
Figure 5.13. Moisture potential versus time at various distances from cold surface for 1.0 A applied current.
Changes in moisture potential over the length of the borehole do not appear to be related to a vapor density gradient produced by the instrument. Instead, they appear to relate more to temperature changes along the borehole (shown in Figure 5.14) which varied with ambient room temperature during the experiment. Greater changes in potential appear to roughly correlate with rapid changes in room temperature, while a leveling out in potential occurs during times when the room temperature is relatively stable. Another conclusion drawn from the temperature versus time curve is that temperature changes are related more to ambient conditions rather than the temperature of the cold plate. Although the temperature of the instrument decreased to a low of nearly 16°C, cooling effects along the borehole were insignificant (Figure 5.15). A notable depression in temperature occurred only at the 10-cm measuring point, which tended to remain 0.5 to 1.0 °C cooler than the remaining points throughout the experiment. Moisture potential is also plotted against distance from the cold plate for various times in Figure 5.16. These curves show that moisture potential was greater at every point along the tube at all times after initial conditions, indicating that some drying has occurred, possibly due to removal by the condensation process; however, a definite trend over time is not apparent.

The data may be converted to units of vapor density (gm/cm³) by first calculating relative humidity from the relationship given by Equation (2.2). Vapor pressure can then be solved for, using values of $e_o$ determined from psychrometric tables. Vapor density, $\rho_v$, can then
Figure 5.14. Temperature versus time at various distances from cold surface for 1.0 A applied current.
Figure 5.15. Temperature versus distance from cold surface for various times at 1.0 A applied current.
Figure 5.16. Moisture potential versus distance from cold surface for various times at 1.0 A applied current.
be calculated from the values obtained for vapor pressure by the relationship:

\[ \rho_v = 0.622 \frac{e}{R_g T} \]

where 0.622 is the ratio of the specific gravity of water vapor to that of dry air at the same temperature and pressure, \( R_g \) is the specific gas constant for dry air \((2.87 \times 10^3 \text{ cm}^2/\text{s}^2\text{K})\), and \( T \) is the temperature in degrees Kelvin. If these results are plotted as vapor density versus distance for various times and vapor density versus time for each sampling point, as in Figures 5.17 and 5.18, it may be seen that actual changes in vapor density are fairly insignificant, on the order of \(10^{-6} \text{ gm/cm}^3\). Again, no trends over time or distance which could be caused by cooling at the location of the instrument are readily apparent.

When the experiment was repeated at a 2.0 A cooling current, which produced an average cold surface temperature of approximately 3.0°C, the sample was found to freeze upon the condensing surface. In order to collect a liquid sample, it was necessary to heat the surface by reversing the current direction until the crystals melted and dripped into the collection cup. Before switching the electrical leads, the current was lowered to 0.5 A to assure that the sudden increase in temperature would not be great enough to re-vaporize the sample. The entire collection process required approximately 2 minutes.
Figure 5.17. Vapor density versus distance from cold surface for various times at 1.0 A applied current.
Figure 5.18. Vapor density versus time at various distances from cold surface for 1.0 A applied current.
The average condensation rate achieved with the 2.0 A current was 0.56 ml/hr. (Figure 5.19). As in the case of the 1.0 A current, temperature effects produced by the instrument's cold surface were minimal, with a 0.5°C temperature depression occurring at the 10-cm sampling point relative to the more distant points. Temperatures at all points increased by nearly 3.0 °C during the 10-hour testing period, corresponding to changes in room temperature, as shown in the plot of temperature versus distance for various times in Figure 5.20. Figures 5.21 and 5.22 plot vapor density versus distance for given times and vapor density versus time for each measuring point, respectively. The only notable trend is a steady increase in vapor density over time along the borehole, which can be attributed to the increases in room temperature over the course of the experiment.

The 3.0 A cooling current, corresponding to a -3.4 °C average cold surface temperature, produced a slightly greater condensation rate of 0.66 ml/hr., as shown in Figure 5.23. Results for temperature versus distance and vapor density changes over time and distance are similar to the two previous experiments and are plotted in Figures 5.24, 5.25 and 5.26, respectively.

Increasing the cooling current to 4.0 A produced a temperature drop of only - 0.94 °C at the condensing plate, although the temperature of the circulating water was dropped to approximately 5 °C below ambient in an attempt to remove the heat energy more effectively. The average condensation rate of 0.64 ml/hr (Figure 5.27) was also slightly less than that produced by the 3.0 A current. Figures 5.28, 5.29, and 5.30 show results for temperature change over time, vapor density
Figure 5.19. Cumulative volume condensate and condensation rate versus time for 2.0 A applied current.
Figure 5.20. Temperature versus distance from cold surface for various times at 2.0 A applied current.
Figure 5.21. Vapor density versus distance from cold surface for various times at 2.0 A applied current.
Figure 5.22. Vapor density versus time at various distances from cold surface for 2.0 A applied current.
Figure 5.23. Cumulative volume condensate and condensation rate versus time for 3.0 A applied current.
Figure 5.24. Temperature versus distance from cold surface for various times at 3.0 A applied current.

Figure 5.25. Vapor density versus distance from cold surface for various times at 3.0 A applied current.
Figure 5.26. Vapor density versus time at various distances from cold surface for 3.0 A applied current.
Figure 5.27. Cumulative volume condensate and condensation rate versus time for 4.0 A applied current.
Figure 5.28. Temperature versus distance from cold surface for various times at 4.0 A applied current.

Figure 5.29. Vapor density versus distance from cold surface for various times at 4.0 A applied current.
Figure 5.30. Vapor density versus time at various distances from cold surface for 4.0 A current.
changes over distance, and vapor density changes with time respectively. Results are similar to those of the previous experiments.

It may be concluded that, under this set of experimental conditions (ambient temperature 25 °C to 27 °C, high humidity environment with a source of liquid water), and with this specific heat sink design, the 3.0 A current provides the highest vapor condensation rate and the most efficient use of energy.

As a general conclusion, these tests reveal that the effects in both temperature and vapor density produced by operation of the thermoelectric cooler in an environment of high relative humidity are near-range phenomena, and sample collection is dependent more upon the availability of liquid water as a source from which moisture may be evaporated than upon the generation of long-range vapor or thermal gradients in the air space of the system.
CHAPTER SIX

FIELD STUDIES

The main objective of the field work was to determine if the thermoelectric cooling system could be operated efficiently under field conditions. Laboratory tests of the instrument had been executed under such conditions that a free surface of water was available as a sample source which was in close proximity to the instrument's condensing surface. When emplaced in a borehole in an unsaturated fractured rock, it is possible that the condensation rate for a given temperature reduction may be lowered, depending on such factors as the water content of the rock and the distance of separation between the cold plate and the source of water for the sample.

A second objective was to determine if the liquid sample obtained was chemically pure, or if contamination had occurred. Possible sources of contamination could be liquid moisture dripping directly from the rock surface into the sample cup without first entering the vapor phase, or leakage of water from the heat sink system.

Field Site Description

Field investigations were performed in the abandoned Queen Creek road tunnel near Superior, Arizona, on the western edge of the Pinal Mountains in central Arizona (Figure 6.1).

The climate of this region is semi-arid, receiving less than 510 mm of rain per year. Seasonal variations occur in rainfall, with
Figure 6.1. Location of Queen Creek road tunnel site, Superior, Arizona.
localized, convective, high-intensity storms occurring in the period from July through September, while widespread, frontal, low-intensity storms are common from December through March. Summer temperatures typically range from 10 to 40 °C, while winter temperatures vary from -5 to 15°C.

The geologic deposit in which the study area is located is a dacitic ash-flow sheet described by Peterson (1961) as consisting of an undetermined number of individual flows that erupted close enough together in time to cool as a single unit. The units at one time covered an area of approximately 1000 km$^2$ in the region, but have since been reduced by erosion to an area of around 250 km$^2$. The average thickness of the sheets is 150 m, but is greater than 600 m in the area east of Superior. The flows have been dated to 19.9 +/- 0.9 million years (middle Miocene). Peterson (1968) divided the ash flow sheet into five units based on the degree of welding and classified it as a quartz latite based on chemical composition, although it has been referred to as a dacite because of the presence of large phenocrysts in the ground mass (Rasmussen and Evans, 1987).

Experiments were performed in a horizontal borehole (5 cm diameter, 15-m length) located in the densely-welded unit, also referred to as the brown unit (Peterson, 1968). The bulk density of this unit has been calculated from core samples as approximately 2.42 gm/cm$^3$, with a matrix porosity of about 9.0 percent (Davies, 1987). The fracture density, also determined from core data, is three fractures per meter. The fracture porosity is 0.1 percent based on an estimated aperture of 300µm; therefore, the total porosity of the brown zone is 9.1 percent.
Procedure

A schematic diagram of the thermoelectric cooling system when emplaced in the borehole is shown in Figure 6.2. The cooling module was attached to a packer assembly by the copper tubing extending from the water reservoir of the heat sink system. The inflatable packer was used to isolate the sampling region from the atmosphere. The cooling water for the heat sink was circulated from a water supply at the surface through the center of the packer by means of a peristaltic pump. Electrical leads running from the cooling module to a DC power regulator at the surface (which was supplied by a small portable generator) fit tightly between the packer and borehole wall when the packer was fully inflated. The sample collection system was the same as that used in the laboratory experiments (Figure 5.9); however, a sturdier Teflon tubing (0.4 cm OD, 0.2 cm ID) was used to prevent the tube from collapsing when the packer was inflated.

After emplacement, the thermocooler was operated at a cooling current of 3.0 A (5.0 V), as this provided the highest condensation rates in the laboratory setting. Because this level of current produces a temperature drop below freezing, the sample was collected on an hourly basis by reversing the current direction through the cooling module in order to heat the surface and melt the frozen sample, which would then be withdrawn through the vacuum tubing to the container at the surface.
Figure 6.2. Schematic diagram (not to scale) of thermoelectric sampling system when emplaced in a borehole within the densely welded tuff unit at the Queen Creek road tunnel site. Depth of packed off borehole is approximately 3 m.
Results and Discussion

In the initial test, the experiment was terminated after four hours because no sample had been recovered. Upon removing the packer assembly from the borehole, it was discovered that moisture had condensed along the packer and on the surface of the tubing and water reservoir of the heat sink, indicating that the temperature of the circulating water had been too low. This is apparently a very critical aspect in the overall design of the thermoelectric condensation technique. If the temperature of the heat exchange system is not carefully controlled, temperature gradients may be generated which can overpower that produced by the module's cold surface and influence the direction of the vapor flux in the sampling area. To eliminate this problem, the temperature of the circulating water was controlled by a constant temperature bath. The temperature at the level to be sampled in the borehole was measured with a thermistor prior to inserting the instrument. The thermocooler and packer assembly were then inserted into the borehole, and the temperature of the circulating water was maintained to within 1°C of the borehole temperature by the constant temperature bath.

A second test was also terminated when a leak developed in the circulation system. When removed from the borehole, it was found that a crack had developed in the water reservoir attached to the hot side of the thermocooler module. The epoxy used to seal the edges of the reservoir was evidently not strong enough to withstand the pressure due to the circulation water. A new reservoir was constructed with the edges welded together, rather than sealed with epoxy, which when tested
by applying water pressures in excess of those required in the field showed no signs of leakage.

In the following test, the system was operated for eight hours, during which an average condensation rate of 0.2 ml/hr was achieved. Electrical conductivity measurements performed on the sample showed a conductivity of $1.5 \times 10^{-6}$ mhos, while a sample of distilled water read $1.15 \times 10^{-6}$ mhos, indicating the sample had not been contaminated during the collection process.

The rate of condensation was approximately 0.5 ml/hr lower than that obtained in the laboratory under the same applied cooling current which could be explained by a number of factors.

The small diameter of the borehole and the packer arrangement placed restrictions on the amount of monitoring equipment that could be emplaced in the borehole with the cooling module; therefore, thermistors were not used to monitor the temperatures at the cold surface and heat sink on a continual basis as was done in the laboratory. Temperature drops maintained by the cold surface could possibly have been less in the field than in the laboratory because the temperature of the circulating water was about three degrees higher than in the laboratory, which would result in a lower condensation rate, since the rate at which heat was removed from the hot junction would be less.

A second reason for the lowered rates may be related to the water content of the rock. In studies of vapor diffusion through soil columns (Philip and de Vries, 1957), it was found that vapor diffusion was greatest in soils wetted to an intermediate volumetric moisture content in the range of 0.03 in the case of a sand, to 0.105 for a loam
soil. Information necessary for computation of the level of water content resulting in maximum vapor transfer was not available for the tuff studied in these experiments; however, it could be that the moisture level was higher or lower than this maximum transfer value, resulting in a lowered condensation rate.

A third possible explanation concerns the amount of air space separating the cold plate from the water film lining the tuff matrix and fracture surfaces. The thermal conductivity of air is low enough that it essentially acts as an insulator to the system; therefore, if the air thickness over which the temperature gradient must act was greater than that of the laboratory setting, the rate of condensation could be lowered. This effect can be seen in the equation describing heat flux under a temperature gradient:

\[ q_h = -\lambda_a \frac{dT}{dx} \]  

(6.1)

where \( q_h \) is the heat flux generated by a temperature difference \( \Delta T \) (given by the temperatures of the cold plate and rock surface) acting over the distance through air separating the two surfaces, \( \Delta x \), and \( \lambda_a \) is the thermal conductivity of air. As \( x \) is increased, the heat flux decreases, and because the heat and vapor density fluxes operate in the same direction, the vapor flux will be lowered and the rate at which a sample may be collected will be less.
CHAPTER SEVEN

CONCLUSIONS AND RECOMMENDATIONS

This research into the application of thermoelectric cooling as a sampling method for water vapor in unsaturated fractured rock has shown the technique to have some potential use.

Laboratory tests have shown that collection of the condensate is not dependent upon the generation of thermal gradients, or on diffusion of vapor, over long distances through the medium being sampled. The main source for the sample will be liquid surfaces close to the cold plate of the instrument, from which vapor will evaporate, diffuse toward the cold surface, and subsequently recondense.

Electrical conductivity analysis of the field sample collected in an unsaturated, fractured, densely-welded tuff has indicated that it contained a dissolved salt content similar to distilled water (1.5 x 10^{-6} mhos for the sample versus 1.15 x 10^{-6} mhos for distilled water); hence, contamination of the sample was not likely. As the chemical nature of the condensate is that of distilled water, the usefulness of the technique is centered around isotopic analysis of the sample collected, particularly tritium, which may be used to indicate travel time of moisture through the unsaturated profile.

A number of improvements must be made in the technique before it may be practically used in field situations.

The heat sink design in these experiments consisted of a water cooled circulation system, which necessitated the addition of tubing, a pump, and a source of water at the surface. Additional avenues of
research should include the use of different types of heat sinks, such as massive substances having high thermal conductivities and heat capacities, which could remove heat from the hot junction more efficiently.

More laboratory work should be done in determining the effects of matric and osmotic potential on the system and the rates of condensation resulting from variations in these parameters.

Laboratory studies should also be performed to verify the ability of the sampling technique to collect isotopic information and to evaluate the extent of fractionation of isotopes. This could be done using laboratory apparatus similar to that designed for measuring condensation rates in this research (see Chapter Five), by spiking the source water with a known concentration of an isotope such as deuterium or tritium and comparing the sample and initial concentrations.

Rather than designing the instrument to be used in conjunction with a commercially available packer, as was done in these experiments, a packer should be designed specifically for accommodating the thermo-electric cooling system, allowing room for the electrical leads, sample tubing, and other monitoring equipment (such as thermistors and thermocouple psychrometers) to run through the center of the packer.

Experimentation in the field should be carried out for longer periods of time to determine the long-term capabilities of the sampling system. Information on late time effects on the medium being sampled could be gained by emplacing monitoring equipment (such as thermistors and thermocouple psychrometers) in the sample borehole as well as in
parallel boreholes, which could also serve as neutron probe access holes, at varying distances from the instrument site.

Condensation rates obtained thus far have been prohibitively low, requiring exceptionally long times to collect sufficient sample volumes for isotopic analysis. Improvements may be made in the rates obtained by increasing the surface area of the cold surface onto which condensation is occurring. This parameter was limited in these experiments by the narrow diameter of the borehole in the media sampled. It may be of interest, in this respect, to test the device in an unsaturated soil where a larger diameter access hole may be drilled for insertion of an instrument having a greater cold plate surface area.
APPENDIX A

PRINCIPLES OF THERMOELECTRIC COOLING

In this appendix, the basic principles of thermoelectric cooling pertinent to the objectives of this study will be examined, beginning with a review of the theory describing electrical conduction in solids and semiconductor materials and concluding with an examination of how these mechanisms contribute to the thermal effects observed in semiconductor materials.

Electrical Conduction in Solids

Electrical conduction in solids is generally classified into the three categories of insulators, conductors, and semiconductors. Insulators have a very high resistivity on the order of $10^6$ ohm-cm or greater and a dielectric constant between 1 and 10. Conductors, which include most metals, exhibit very low resistivities in the range of $10^{-2}$ ohm-cm or less. Semiconductors have resistivities in the intermediate range between conductors and insulators, and the dielectric constant is usually in the range of 5 to 50 (Greiner, 1961).

The electric conductivity of a material may be explained on the basis of the energy-band structure of solids. According to quantum mechanics theory, a specific, quantized, energy state is associated with an orbital around an atom, and each energy level can be occupied by no more than two electrons in pairs having opposite spin orientation. When atoms come together to form a solid, a multitude of electronic energy states become available because of the large number...
of atoms present. These energy states form essentially continuous bands of allowed energy which the electrons can occupy and that control the motion of electrons through the material (Greiner, 1961).

An energy band diagram (Figure A.1) is often used to illustrate the band scheme, where the position of an electron is located along a one-dimensional scale of energy. The scale is oriented so that electrons tend to move downward into the lowest possible energy state. The energy axis can be divided into forbidden bands, where no electrons exist having those energy states, and allowed bands, which may be occupied by electrons. The allowed bands may be further subdivided into conduction bands at higher energy levels which are normally vacant and valence bands which are normally filled with electrons. The lowest energy bands consist of electrons located deep within the atomic structure of the material and are therefore tightly bound and not free to move (Fraser, 1983).

The band scheme is useful for examining the differences between the various types of conductors as shown in Figure A.1. Metals are distinguished from semiconductors and insulators by the existence of a partially-filled conduction band. Electrons present in these bands represent excess mobile electrons which are not tied up in interatomic bonds and are hence relatively easy to mobilize under an applied electromotive force (emf). Semiconductors and insulators, on the other hand, have a completely filled valence band separated from an empty conduction band by a forbidden band or energy gap. The difference between the two materials is a matter of degree, with insulators having larger energy gaps on the order of 3eV or more, while semiconductors
Figure A.1. Energy-band diagrams for (a) conductors, (b) semiconductors, and (c) insulators (after Fraser, 1983).
have band gaps ranging from 2.5eV down to 0.1eV (Fraser, 1983). For
the semiconductor case, as temperature is increased from absolute zero
to room temperature, some electrons become thermally excited enough to
move into the conduction band, where an applied emf can produce current
flow. In the case of insulators, electric conduction is generally not
possible because the energy gap is so large that thermal excitation is
not enough to raise electrons into the conduction band (Inokuchi,
1965).

Conduction in Semiconductors

A better understanding of the conduction mechanism in semicon-
ductors may be gained from investigating the nature of the bonding
between atoms in these materials. In semiconductors, all or nearly all
electrons are tied up in covalent bonds between neighboring atoms, as
occurs with the elements of groups III and IV of the periodic table
(Holden, 1969). Taking the element germanium as an example, it is seen
in Figure A.2a, that each Ge atom has four valence electrons which are
tetrahedrally bound to four neighboring Ge atoms. All electrons are
used in covalent bonding and no excess mobile electrons are found in
the crystal, so at low temperatures Ge will act as an insulator.

When heated, thermal excitation releases electrons from the
interatomic bonds as shown in Figure A.2b, and electrons are free to
move through the solid in the conduction band (Holden, 1969). When an
electron is released from an interatomic bond, a vacancy exists at that
site which may combine with an electron in an adjacent bond, leaving a
vacancy in the new site as it does so (Figure A.2c). In other words,
Figure A.2. Conduction mechanism of intrinsic semiconductors. (a) Tetrahedral bonding in germanium crystal. (b) Ejection of electron from covalent bond under thermal excitation. (c) Movement of positive charge carrier through crystal lattice by successive transfer of electrons into vacancies (after Holden, 1964).
a vacancy, usually referred to as a hole, is effectively a positive-charge carrier that is free to wander through the valence band of the crystal (Holden, 1965). This essentially random motion of the hole through the valence band will acquire a drift velocity in the direction opposite the flow of electrons in the conduction band when an emf is applied. The combined motions of these two oppositely-charged carriers is the mechanism responsible for conduction in semiconductor materials (Kip, 1962).

In its path through a semiconductor crystal, an electron may eventually encounter a hole, where they will recombine and both charge carriers disappear. The conductivity in the material will remain constant, however, because excitation of the electrons into the conduction band and recombinations in the valence band are occurring at the same rate. Semiconductors with an equal number of electrons and holes, as in the situation described above, are called intrinsic semiconductors (Inokuchi, 1965).

A second class of semiconductors is brought about by the addition of impurity atoms to intrinsic semiconductors. For example, consider the effect of replacing a Ge atom in a pure germanium crystal lattice with an atom from group V of the periodic table such as arsenic as shown in Figure A.3a. Four of the valence electrons of the As atom will be shared with four neighboring Ge atoms, while the fifth electron will be only loosely bound to the impurity atom by the coulomb force of attraction to the nucleus. As a result, extra electrons contributed by group V impurity atoms can be raised into the conduction band by the adsorption of much lower energies than those required for raising
Figure A.3. Conduction mechanism of n-type semiconductors. (a) Substitution of an arsenic atom into a germanium crystal, creating an additional electron. (b) Energy-band diagram for n-type semiconductor, showing extra "donor" energy levels supplied by impurity atoms (after Fraser, 1983).
electrons from the valence band to the conduction band (Fraser, 1983). Impurity atoms such as these, which contribute extra electrons to the conduction band without the formation of a complementary hole are called donors. The type of semiconductor produced is referred to as an n-type (negative) extrinsic semiconductor (Holden, 1964). The energy-band diagram for this case is shown in Figure A.3b. The energy-band levels produced by impurity atoms are shown near the top of the forbidden energy gap. At low temperatures, electrons occupy these levels; however, relatively low energies of excitation will lift them into the conduction band (Fraser, 1983).

If, on the other hand, a group III element such as indium is introduced into sites normally occupied by Ge atoms (Figure A.4a), the situation is reversed. The three valence electrons of the In atom form chemical bonds with three of the four adjacent Ge atoms, while the fourth remains a one-electron bond. In this case, the introduction of In has produced a hole, or positive-charge carrier, in the valence band without the formation of a compensating electron. These extrinsic semiconductors are referred to as p-type (positive), and the impurity atoms are called acceptors (Holden, 1964). The energy-band diagram for this case is shown in Figure A.4b. The energy states associated with the holes produced by the impurity atoms (acceptor levels) are located close to the valence band and are empty at low temperatures. When the acceptor levels of the impurity atoms are filled with excited electrons at higher temperatures, conduction occurs primarily by holes in the valence band (Fraser, 1983).
Figure A.4. Conduction mechanism of p-type semiconductors. (a) Substitution of an indium atom into a germanium crystal creating an extra positive charge carrier. (b) Energy-band diagram for p-type semiconductor, showing additional "acceptor" energy levels supplied by impurity atoms (after Fraser, 1983).
Thermal Effects

Thermoelectric effects in semiconductors are generated by the formation of a p-n junction. When two sections of a semiconductor material are joined, one containing an acceptor impurity (p-type) and the other containing a donor impurity (n-type), a p-n junction is created (Smith, 1984). As shown in Figure A.5a, a concentration gradient will exist along the line of contact between the two sections. This will lead to a diffusion of mobile holes from the p-side to the n-side where they will tend to recombine with mobile electrons. The reverse process occurs in the case of the mobile electrons which diffuse across the junction to the p-side where they will tend to recombine with holes (Figure A.5b). A net negative charge will be produced on the p-side of the junction due to the immobile acceptor ions left behind; similarly, a net positive charge will develop on the n-side because of the donor ions (Figure A.5c). The formation of these bound charges along the junction prevents the further diffusion of mobile charge carriers by creating a potential barrier, or hill, for holes moving into the n-region and electrons into the p-region, as shown in Figure A.5d. Only charge carriers possessing sufficient energy to cross the potential barrier will pass through the junction. The sum of these two potential differences yields a total potential difference, $V_o$, at the interface (Smith, 1984).

If an emf is applied as shown in Figure A.6a, so that the potential gradient of the battery is opposite that of the junction, the junction potential $V_o$ will be effectively reduced by the amount of the battery potential, $V$. In other words, the amount of energy a charge
Figure A.5. Generation of potential energy barrier at a p-n junction. (a) P-n junction, showing excess charge carriers. (b) Diffusion of charge carriers across junction. (c) Net charges created at interface by bound ions. (d) Potential barriers (hills) oppose further diffusion and create potential difference $V_0$ at junction (after Smith, 1984).
Figure A.6. Development of thermoelectric effects at a p-n junction. (a) Application of external emf as shown reduces the potential barrier by the amount of the battery voltage. (b) Reversing direction of applied emf increases the potential barrier by the amount V, resulting in the removal of heat energy from surroundings (after Smith, 1984).
carrier needs to cross the junction is reduced due to the "push" given by the battery potential (Smith, 1984).

Applying an emf in the opposite direction, as shown in Figure A.6b, increases the potential barrier by the amount V and decreases the probability of a charge carrier possessing sufficient energy to pass through the interface. In order to cross the junction, energy must be supplied to the charge carriers, and this will occur by removal of heat from the surroundings. The result is a decrease in temperature at the junction known as the Peltier cooling effect (Smith, 1984), named after the discoverer of the phenomenon.

The rate of heat absorption accompanying the passage of a given current is given by the relationship (Rowe and Bhandari, 1983):

\[ Q = \pi_{ab} I \]  \hspace{1cm} (A.1)

where

- \( Q \) = rate of reversible heat absorption (watts);
- \( I \) = current (amps); and
- \( \pi_{ab} \) = Peltier coefficient of the junction (watts/amp, or watts).

By convention, \( \pi_{ab} \) is taken as positive when current flows through a junction from a to b and an amount of heat \( Q \) is removed from the surroundings. The Peltier effect is the basic phenomenon on which the field of thermoelectric cooling has developed.
LIST OF REFERENCES


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