Dehumidification Effect by Coupling an Electroosmotic Material with a Desiccant Interface

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Abstract

Separately dealing with the latent load, the load associated with moisture content in air, in air conditioning applications can lead to better efficiencies and better control of the indoor environment. This research studies a new method to separate the latent load from the sensible one. The method depends on coupling the electroosmotic force to pump water through a membrane, with the desiccant effect on one surface of the membrane.

The research consists of a variety of theoretical, numerical, and experimental investigations relevant to the proposed electroosmotic desiccant system. An ideal, generalized coefficient of performance, COP, for air conditioning processes is developed. Such a coefficient is a limiting case to evaluate the relative efficiency of any air conditioning process. The electroosmotic flow is modeled in porous membranes and the effect of capillary radius is examined. Bench-top experiments are performed to prove the concept of coupling the electroosmotic effect with the desiccant effect to transfer vapor against the vapor pressure gradient. Also, a new type of “thermal” desiccant is developed and experimentally characterized.

An electroosmotic dehumidifier system is modeled in order to estimate the area (size), voltage and power needed per unit mass flow of water to be transferred from a region. The operation of an A/C system with and without the electroosmotic dehumidifier is compared and situations where savings is possible are highlighted.
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List of Symbols

a capillary radius
A time coefficient s⁻¹
ai pore radius : i=1 desiccant material, i=2 electrokinetic material
COP coefficient of performance
cₚ specific heat at constant pressure [kJ/kg K]
D dielectric constant
D diffusion coefficient vapor in air [m²/s]
e electron charge
E electric potential [Volts]
Ex exergy (available energy) [kJ/kg]
g gravitational acceleration
Gr Grashof number
h micro-channel height
hm mass transfer coefficient
I₀ modified Bessel function from the first kind of order zero
k electric conductivity
Kb Boltzmann constant
L membrane height
M Mobility
m mass fraction
n number of ions
P Pressure
P* Non-dimensional pressure
P₁₀₀, Pᵥ, Pᵥ₀ vapor pressure at 100 relative humidity, Vapor pressure, initial vapor pressure
Pa air partial pressure [kPa]
Patm atmospheric pressure
Por Porosity
Pₛₐₜ saturation pressure [kPa]
Pᵥ vapor pressure [kPa]
Q heat transfer [kJ/kg]
Q volume flow rate
r radial coordinate
Rₐ, R ideal gas constant for air
Rᵥ, Rᵥ₀ air to desiccant surface flow resistance
Rᵥ₀, Rᵥ₁ flow resistance inside the desiccant layer
Re Reynolds number
Rₑ flow Resistance inside the electroosmotic layer
Rᵥ ideal gas constant of vapor (H₂O)
Sc Schmidt number
Sh Sherwood number
T Temperature
t Time
u Velocity
U₀ centerline velocity
$U_p$ Helmholtz-Smoluchowski electroosmotic velocity, $U_p = MY$

$W$ work [kJ/kg]

$X$ water content

$x$ flow-direction coordinate

$Y$ electric field gradient in flow direction

$Y$ cross-flow coordinate

$Z$ Valance

$\Delta x_i$ thickness of $i^{th}$ layer: $i=1$ desiccant layer, $i=2$ electrokinetic layer

**Greek letters**

$\rho_c$ charge density

$\rho_f$ fluid density

$\xi$ Non dimensional length in flow direction

$\alpha$ ionic energy parameter

$\beta$ non dimensional parameter relating the Debye-Huckel parameter to the ionic energy parameter

$\varepsilon$ dielectric constant of water

$\eta$ Non-dimensional length perpendicular to the flow direction

$\lambda$ Debye length

$\mu$ dynamic viscosity [kg/m-s$^2$]

$\mu_f$ fluid viscosity

$\nu$ kinematic viscosity [m$^2$/s]

$\rho$ density [kg/m$^3$]

$\omega$ Debye—Huckel parameter (inverse of Debye length)

$\psi$ electric potential of ions

$\psi_c$ centerline electric potential

$\psi_0, \zeta$ Zeta potential [volts]

**Subscripts**

$0$ Ambient

$in$ inlet conditions

$L$ Latent

$Out$ outlet conditions

$S$ Sensible

$av$ Average

$s$ Surface

$\infty$ bulk of the air of the conditioned space
Chapter 1. Introduction

Dealing with the latent load, the load associated with moisture content in air, separately in air conditioning applications can lead to better efficiencies and it also helps in better control of the indoor environment. This research studies a new method to separate the latent load from the sensible one. The method depends on coupling the electroosmotic force to pump water through a membrane, with the desiccant effect on one surface of the membrane. The chapters of this dissertation are written as independent topics addressing the issues related to conditioning air, exploring materials with electroosmotic and desiccant properties, and developing models for predicting the performance of an electroosmotic desiccant.

A generalized limiting coefficient of performance (COP) for conditioning air is developed in Chapter 2. The generalized COP takes into account the work needed to condition air from one state to another, by calculating the change in exergy level of each state. Beside the ambient temperature, the ambient humidity ratio (or vapor pressure) affects the performance of an air conditioning system. The chapter also uses the developed model to analyze a typical example and to study the effect of change in ambient conditions on the limiting COP of the system.

Chapter 3 reviews the “double layer” theory, the theory behind electroosmotic flow, EOF. Previously published works about modeling the flow in small geometries are also reviewed. A model that describes the EOF through a kaolin membrane is built based on relations and material properties reported by the open literature. The model is used to study the effect of pore diameter on the ratio between EOF and the pressure induced flow. It is concluded that the diameter of kaolin is suitable for such application. Finally, simplifications involved in the model that may cause deviations between experiments and the theory are described.

Experimental work investigating the electroosmotic flow phenomenon is described in Chapter 4. The materials investigated throughout the experimental period are presented. This chapter studies the effect of the imposed electric field and its orientation relative to the direction of the flow through membranes. The technique used to measure the zeta potentials of some materials is discussed. The goal and setup of each experiment is described. Sample results are presented with a discussion of the deviations from the theoretical cases. Experiments developed to demonstrate the electroosmotic desiccant effect are also included in this chapter.

Chapter 5 presents a model that simulates the combined electroosmotic and desiccant effects to achieve dehumidification. First, this model is described and then, the model is used to study the effect of different design parameters of the membrane. The area needed for an electroosmotic dehumidifier, EOD, is estimated as well as the power needed. The situations where this new dehumidification technique may have potential savings are evaluated. Conclusions and recommendations for future work are drawn from that model.

During the attempts to develop “electroosmotic desiccants”, some experiments revealed that combinations of salt and clay have beneficial “thermal desiccant” properties. Chapter 6 describes the use of kaolin-salt mixtures as a thermal desiccant material. This chapter reviews thermal desiccants and how thermal desiccant systems work. Finally, the results of the experiments performed with this new class of desiccant are presented and compared to the conventional thermal desiccant materials.

Chapter 7 gives overall conclusions of the previous chapters and presents recommendations concerning the feasibility of the process as a dehumidification technique.
Chapter 2. A Generalized Coefficient of Performance for Air Conditioning

2.1 Introduction

“Air conditioning”, in general, refers to a change of state of air from one condition to another, more desirable, condition. Willis Carrier’s (1911) paper laid the foundation for a simplified understanding of the energy changes that accompany changes of state for moist air. Of course, understanding work and heat transfer interactions is key to understanding the energy change for an air-conditioning process. For the simple cases of sensible heating or cooling of air, we have expressions for a “coefficient of performance” (COP) to describe the efficiency of a system used to change the state of air. When we are interested in the limiting case of “reversible” system performance, we are able to use the result from Carnot’s analysis to find ideal heat pump and air conditioning COPs for sensible air state changes between constant temperature thermal energy reservoirs (Stoecker, 1982). Although the psychrometric chart allows easy visualization of the combined sensible/latent heat processes, the amount of effort (work) required to achieve the desired change of state is not represented. In order to determine the effort required to change the state of air, second law considerations must be used.

2.2 Coefficient of Performance for Processes on Dry Air

The standard COP analysis assumes heat transfer with constant temperature reservoirs. Work driving a cycle can cause a heat transfer out of a low temperature reservoir and a heat transfer into a high temperature reservoir. The coefficient of performance, COP, similar to other performance parameters, is simply a ratio of the effect we want (a heat transfer) to the quantity that we must buy (work) in order to cause the desired effect.

\[
\text{COP} = \frac{Q}{W}
\]

(2-1)

Where Q is the heat taken out of the low-temperature reservoir in the case of refrigeration and is the heat added to the high-temperature reservoir in the case of heat-pump operation.

If the cycle is a reversed Carnot cycle, the heat transfers between the thermal energy reservoirs are related to the absolute temperatures of the reservoirs (an alternative way to state that entropy has been conserved as it is transported between the thermal reservoirs). Hence, the COP for the Carnot cycle will be the maximum between the given temperatures limits (Moran, 1999).

\[
\text{COP} = \frac{T}{|T - T_0|}
\]

(2-2)

The previous analysis is based on the assumption that the temperature of the conditioned space is constant. A more realistic approach is to assume that the air of the conditioned space changes temperature due to addition or rejection of heat. A schematic and T-s diagram are given in Figure 2-1, for an ideal refrigeration machine cooling dry air. This idealized machine can be imagined as an infinite-number of reversed-Carnot refrigerators, each working with isothermal heat absorption. The work needed, in this case, equals to the change in exergy between “out” and “in” states.
\[ W = C_p(T_{\text{out}} - T_{\text{in}}) - T_0 C_p \ln\left(\frac{T_{\text{out}}}{T_{\text{in}}}\right) \]  \hspace{1cm} (2-3)

The COP of such a process will be as in equation (2-4) which simplifies to equation (2-2) as \( T_{\text{in}} \) approaches \( T_{\text{out}} \).

\[ \text{COP} = \frac{T_{\text{out}} - T_{\text{in}}}{(T_{\text{out}} - T_{\text{in}}) - T_0 \ln\left(\frac{T_{\text{out}}}{T_{\text{in}}}\right)} \]  \hspace{1cm} (2-4)

Figure 2-1 Schematic and T-s diagram of an ideal refrigeration machine cooling dry air

The previous analyses and the analysis in this paper are based on the reversible limit. Klein (1992) describes limits based on finite-size heat exchangers and finite-rate of heat transfer for refrigeration cycles. The current approach is adopted to maintain complete generality, i.e. to avoid the specification of transfer processes.

### 2.3 General Coefficient of Performance

Any change in the humidity ratio will affect both the air and water vapor partial pressure and hence the entropy and consequently their exergy. Considering the exergy of the ambient to be zero, we can write the following expressions for the exergy of air and water vapor per unit mass of dry air at any given state of temperature and vapor pressure (humidity ratio)

\[ E_{x_{\text{air}}} = c_{\text{p,air}} (T - T_0) - T_0 [c_{\text{p,air}} \ln\left(\frac{T}{T_0}\right) - R_{\text{air}} \ln\left(\frac{P - P_{\text{vapor}}}{P_{\text{vapor}}}\right)] \]  \hspace{1cm} (2-5)

\[ E_{x_{\text{vapor}}} = \left(\frac{0.622 P_{\text{vapor}}}{P - P_{\text{vapor}}}\right) \left[c_{\text{p,vapor}} (T - T_0) - T_0 [c_{\text{p,vapor}} \ln\left(\frac{T}{T_0}\right) - R_{\text{vapor}} \ln\left(\frac{P_{\text{vapor}}}{P_{\text{vapor}}}\right)]\right] \]  \hspace{1cm} (2-6)

The sum of these two contributions, for dry air and for water vapor, represents the minimum work needed to condition air from the ambient, dead state, to any other moist-air state. Figure 2-2 represents contours of this
minimum work property on a psychrometric chart for outdoor conditions of 25 C (dry bulb temperature) and 1 kPa (vapor pressure). Equations similar to (2-5) and (2-6) were developed by Moran (1989) to generate Figure 2-2.

The change in phase of water does not have an effect on the exergy of the system because the heat added to evaporate water is associated with an increase in entropy that equals the change in enthalpy divided by the temperature. However, the change in the humidity ratio does have a considerable effect on the heat added or rejected to change the state of air from the ambient state to any other state. This effect appears in the inclination of the enthalpy lines (Figure 2-2) (if this effect was not considered the constant enthalpy lines would have been almost vertical). The ASHRAE “Handbook of Fundamentals, 1985” gives equations to evaluate the enthalpy change associated with change in moist air states.

![Figure 2-2 Isenthalpic and isowork lines taking into account the change in enthalpy and entropy due to change in humidity ratio](image)

Figure 2-2 shows that conditioning a space can theoretically produce work when the initial space condition lies on a work contour of higher value than that of the final condition. One can also interpret this process as if the air to be conditioned drives a “heat engine” as it moves to the ambient conditions, and the work output from that process is used (plus or minus additional work) to drive a heat pump (or refrigerator) to condition the ambient air to the desired temperature and humidity ratio.
Figure 2-3 General Coefficient of Performance, COP, for systems conditioning air from the ambient to any point

With the analysis used in Figure 2-2, we can plot a contour for the maximum general COP associated with conditioning air from the ambient condition to any condition. As shown in Figure 2-3, for a process moving along the constant-enthalpy line the theoretical COP is zero -- meaning that no external heat is needed to condition the space because the sensible heat rejected equals the latent heat gained (or the latent heat loss is equal to the gain in sensible heat). Figure 2-3 also distinguishes between two different modes of operation based on the ambient conditions. If the final point has an enthalpy higher than the ambient the air conditioning machine has to operate in the heat-pump mode (even if the temperature is below the ambient). On the other hand, if the enthalpy of the final point is lower than that of the ambient the machine will work in the refrigeration mode.

2.4 Example on Cooling a Building

Many papers (Wepfer et al., 1979) for example) have invoked a second-law approach for evaluating thermodynamic processes. In this chapter, we avoid examining specific processes, and evaluate the conditioning system as a whole, treating it as a black box. In other words, the maximum COP for a given load is determined without specifying the components of the conditioning system.

During the design phase of a building or industrial process, energy loads (sensible and latent) must be determined in order to estimate the capacity of an air conditioning system. Various constraints must also be applied to the design, such as required comfort or process conditions (temperature and humidity), air velocities (comfort and noise), and fresh air requirements (health and safety).
As an example, consider a 250 m² house with a total volume of 1000 m³, that is required to be maintained at conditions of 22 °C and 0.0082 humidity ratio (50% relative humidity). The outside ambient is 35 °C and 0.0215 humidity ratio (60% relative humidity). The sensible and latent loads are 8 kW and 2.4 kW, respectively. The minimum supply temperature to the space is assumed to be 12 °C. For this load, the sensible heat ratio is equal to 0.77, and the supply air should be at 12 °C and 0.0072 humidity ratio (approximately 82% relative humidity). The air mass flow rate required for this process is 0.82 kg/sec.

Having $T_0$ and $\omega_0$ set, the work (kJ/kg dry air) produced by changing from room to ambient conditions, and the work needed to change from ambient conditions to the desired supply conditions can be determined. The difference is the work needed to condition air from “room” to “supply” conditions. In this case, the work needed is, approximately, 0.77 kJ/kg, and the thermal energy transferred to the ambient is 12.6 kJ/kg. Hence, the ideal COP is approximately 16.3. Amrane et al. (2003) reported COP values between 2.4 and 3.5 for real systems tested at the ARI conditions (the outdoor temperature 35 °C). They also reported that the sensible heat ratio was in the range between 0.59 and 0.79.

It is worth mentioning that there is no difference between the ideal limit in COP for cases in which the system uses return air or all fresh air, because room air is assumed to be reversibly equilibrated with the ambient air, and then reversibly conditioned to the supply condition. From the work point of view, it will not matter if the system uses fresh or re-circulated air.

### 2.5 Effect of Ambient Conditions on the Limiting Coefficient of Performance

For the example discussed above, the effect of changing ambient temperature and humidity ratio will be studied. Two cases will be considered. First, calculations will be performed with the assumption that the building is independent from the outside ambient environment. In the second case, the calculation will account for the change in the load due to a change in outdoor ambient conditions. The first case represents buildings that are “core” dominated, that is, in which the air conditioning load is due to activities within the structure such as in a large commercial building or an industrial process. The second case represents a load experienced by a domestic residence in which the outdoor conditions are the primary factors affecting the air conditioning load.

#### 2.5.1 Constant Load

In this case, the latent and sensible loads of the building will be considered as independent from the outdoor ambient conditions.

The limiting COP for the example discussed in the earlier section, under various ambient conditions is given in Figure 2-4. For the same ambient humidity ratio, the limiting COP decreases as the ambient temperature decreases. This behavior is because the higher the ambient temperature is, the larger the temperature lift and hence the ideal work needed to cool the air. The same effect is seen for the ambient humidity ratio. For the same temperature, the limiting COP decreases as the humidity ratio increases.
2.5.2 Load Varying With Ambient Conditions

In the second case, part of the load will depend on the ambient conditions. Part of the sensible load will be due to heat transfer from the ambient to the building through the overall heat transfer coefficient of the building. Similarly, part of the moisture and hence the latent load is assumed to be due to moisture transfer between the inside and outside ambient. The sensible load is assumed to be equal to $0.5 + UA (T_0 - 22)$ kW. The UA value of the building is assumed to be equal: 850 kJ/hr-K and $T_0$ is in Celsius. This loss coefficient is from measurements of a 250 m² floor area house with typical wood frame construction. Similarly, the latent load is assumed to be equal to $1 + MA h_{lg} (P_{V_0} - P_v)$ kW, where $MA$ is a parameter similar to the building UA, called building mass transfer coefficient. Both UA and MA were assumed based on experimental measurements from the same residence building with the dimensions mentioned in the example.

Figure 2-5 shows experimental measurements used to determine the overall mass transfer coefficient, MA, for the 250 m² house. Water condensate from the A/C unit of the house was collected and weighed, and the difference in vapor pressure between the inside of the house and outside ambient was measured. A linear regression analysis was used to fit the data. The slope of the line in Figure 2-5 is equal to the mass transfer coefficient of the building, and was found to be equal 1 kg/hr-kPa. This experimental technique for evaluating building moisture transport has also been used to determine the moisture transport in refrigerators and freezers (Stein, 2002). Note that zero vapor pressure difference shows a non-zero moisture load due to internal sources of moisture such as cooking, respiration of occupants, and other internal sources of water.

In this case, the work will be more sensitive to changes in the ambient conditions. Ambient conditions not only affect the exergy lift (as seen in case one, equivalent also to the temperature lift in Figure 2-1) but also affect
the load lifted. Figure 2-6 shows the change in work done (left) and the COP (right) for the example described under different ambient conditions.

Figure 2-5 Relation between the rate of condensate and the average water vapor pressure for the house specified in the example.

Figure 2-6 Ambient effect on the change in work done (left) and the COP (right)
2.6 Conclusion

This chapter has reviewed known expressions for calculating the coefficient of performance for dry as well as humid air. An expression that accounts for the change in energy and exergy due to change in water vapor content of the air (humidity ratio) was developed. The work and COP were plotted on the psychrometric chart to help visualize the work needed to reversibly condition air from one state to another.

An example implementing the expression developed was used to demonstrate the utility of the work chart. The analysis was also used to study the effect of the ambient conditions on the minimum work required by an air conditioning unit and also the limiting COP.
Chapter 3. Modeling of the Electroosmotic Flow

3.1 Introduction

This chapter presents the basic information about electroosmosis to familiarize the reader with the basic terminology used in this field. The chapter also covers modeling of the electroosmotic flow (EOF) in rectangular and circular capillaries. Some of the previous EOF works reported in the literature are mentioned to support ideas and assumptions made in this chapter. Finally, the model built to simulate the problem is described. Some insights are gained from the model, and the simplifications that can cause potential disagreement between the model and the experiments are described.

3.2 Background

3.2.1 Electric Double Layer

When an electrolyte is placed in contact with a solid that has electrokinetic properties, a layer of ions, approximately a single ion in thickness, is firmly adsorbed to the surface of the solid. An equal number of opposite ions will be in the electrolyte. The density of ions reduces as distance from the surface increases. The first layer consists of the part of the ions within the electrolyte near the surface together with the ions adsorbed into the surface. These ions effectively belong to the surface and do not move. The rest of the ions within the electrolyte, called the diffuse layer, are less attracted to the surface. The ions forming the diffuse layer can move with the application of an external electric field.

3.2.2 Zeta Potential ($\psi_0 / \zeta$)

The zeta potential is the average potential in the surface of shear (an imaginary surface between the two layers of ions forming the double layer). This potential is used for characterizing the outer diffuse part of the double layer and hence valuable for discussing EOF. It is also the difference in potential between the plates of a hypothetical capacitor used to model the diffuse layer. Hunter (1981) gives detailed information about zeta potential. Investigators usually use the value of the zeta potential as the wall electric potential. In other cases (Shang, 1997) voltage at a fixed distance from the wall is assumed as the zeta potential.

3.2.3 Other Electrokinetic Phenomena

Electroosmosis is one of four related electrokinetic phenomena that depend upon the presence of an electric double layer at a solid liquid interface. The zeta potentials for three of them, (electroosmosis, electrophoresis, and streaming potential), are the same.

Electrophoresis, unlike the electroosmosis, describes the motion of charged solid particles with respect to the bulk fluid. For the case of an applied electric voltage on an electrolyte each charged particle moves with a certain velocity to the opposite electrode. The ratio between the particle velocity and the magnitude of the electric field is a characteristic number called the electrophoresis mobility.

The streaming potential is the electric potential generated across a membrane when a liquid is forced through its pores. The streaming potential is related to the zeta potential by the following relation,

$$\psi_0 = \frac{4\pi \mu K \Delta E}{D \Delta P}$$  \hspace{1cm} (3-1)

Measuring the streaming potential is one method used to evaluate the zeta potential.
The fourth electrokinetic phenomenon is the sedimentation potential. This phenomenon describes the movement of solid charged particles in a fluid. Pressure is applied on the liquid and voltage is resulted.

### 3.2.4 Debye Length and the Relation between the Zeta Potential and the Charge Density

If we consider simple electrolyte that ionizes into two equally charged ions of valence $z$, the net charge per unit volume $\rho_e$ is given by:

$$\rho_e = -2nez \sinh\left(\frac{\alpha \psi}{\psi_0}\right),$$

where $\alpha = \frac{ez\psi_0}{k_BT}$ is the ionic energy parameter.

The $\psi/\psi_0$ and the charge density $\rho_e$ are related by the following non-linear Poisson equation

$$\nabla^2 \left(\frac{\psi}{\psi_0}\right) = -\frac{4\pi D}{\psi_0} \frac{\rho_e}{\rho_e} = \beta \sinh\left(\frac{\alpha \psi}{\psi_0}\right),$$

where $\beta = \frac{(\omega h)^2}{\alpha}$.

Solution of equation (3-3) gives the electric potential distribution and hence helps to determine the electric double layer, where the most of the electric charge is concentrated. The electric double layer will have a Debye length, $\lambda$. According to Dutta et al. (1999), this length is function of the ionic density. At 25 °C, aqueous solutions with ion density 1 mol/m$^3$ and 100 mol/m$^3$ have $\lambda$ of 1 and 10 nm, respectively.

### 3.3 Distribution of Zeta Potential along the Cross Section

#### 3.3.1 Distribution in Rectangular Channels

Dutta et al. (1999) presented an integration of equation (3-3) to obtain an equation of the first derivative of the potential as:

$$\frac{d\left(\frac{\psi}{\psi_0}\right)}{dy} = \left(\frac{\omega h}{\alpha}\right) \sqrt{2 \cosh\left(\frac{\alpha \psi(y)}{\psi_0}\right) - 2 \cosh\left(\frac{\alpha \psi}{\psi_0}\right)}$$

(3-4)

They also reported that Burgreen and Nakache (1964) made a solution in terms of first kind integral equation. This solution shows the potential distribution for different $\alpha$ and $\beta$. A simple numerical solution is represented in Figure 3-1 and Figure 3-2. These figures show the distribution of zeta potential for different values of $\alpha$ and $\beta$, and hence, reflect Dutta’s idea which is as $\alpha$ and $\beta$ become larger the double layer becomes thinner. In typical “micro electro mechanical systems” (MEMS), the size of the channel is of the order of tens of micrometers wide which makes the effect of the wall negligible, (see Qiao and Aluru, (2002) for example).
Figure 3-1 Variation of the ratio of zeta potential to the wall zeta potential along the across section for various $\alpha$ values

Figure 3-2 Variation of the ratio of zeta potential to the wall zeta potential along the across section for various $\beta$ values
3.3.2 Distribution in Circular Capillaries

Rice and Whitehead (1965) studied the EOF in cylindrical capillaries and obtained a distribution of zeta potential, and consequently the charge density, along the radius.

\[ \psi = \psi_0 \frac{I_0(\omega r)}{I_0(\omega a)} \]  
\[ \rho_e(r) = -\frac{D\omega^2}{4\pi} \psi_0 \frac{I_0(\omega r)}{I_0(\omega a)} \]  

From equation (3-5) and (3-6), if the capillary radius is much larger than the Debye length, i.e. \( \omega a >> 1 \), then the potential and charge density will have an effect only in a small region near to the wall.

3.4 Modeling of the EOF

3.4.1 EOF between Two Parallel Plates

Dutta et al. (1999) analyzed the flow driven by electroosmotic force in microchannels. Their model applied to the almost uniform, plug like, flow with high \( \alpha \) and \( \beta \). They examined a case where the electroosmotic forces are imposed only on a middle section length of the channel while the inlet and exit length sections are pressure driven.

Applying the Navier Stokes equation in the flow direction and substituting for \( \rho_e \) in the body force term from equation (3-2)

\[ \frac{\partial p}{\partial x} = \frac{\mu}{\partial^2 u}{\partial y^2} + \frac{DY}{4\pi} \frac{\partial^2 \psi}{\partial y^2}, \]  

where \( Y = -\frac{dE}{dx} \) and \( E \) is the external (imposed) electric field potential.

The velocity distribution is determined by integrating equation (3-7) across the channel (i.e. with respect to \( y \)). Burgreen and Nakahe (1964) provided a method to perform this integration which resulted in

\[ u(y) = -\frac{h^2}{2\mu} \frac{\partial p}{\partial x} \left[ \frac{1}{4} - \eta^2 \right] + MY(1 - \frac{\psi}{\psi_0}), \]  

where \( M \) is the mobility \( (M = \frac{\psi_0 D}{4\pi\mu}) \) and \( \eta \) is the non-dimensional length in \( y \)-direction. The product of \( M \) and \( Y \) has the dimension of velocity and is called the Helmholtz-Smoluchowski electroosmotic velocity, \( U_p \) (Probstein, 1994). For the case of large \( \alpha \) and \( \beta \) the electrokinetic part of the velocity is represented by a constant velocity, \( U_p \). Qiao and Aluru (2002), for example, approximated the electroosmotic part of the flow by a constant velocity because their channel was of order of tens of microns wide.

The volume flow rate is given by integrating the velocity equation multiplied by a differential area over the height of the channel. This flow rate could be expressed in non-dimensional form as follows:

\[ \frac{Q}{U_0 h} = -\text{Re} \frac{dP^*}{12 \ d\xi} + \frac{U_p}{U_0} \]  

(3-9)
In the equation (3-9), \( P^* \) is the non-dimensional pressure \( \left( P^* = \frac{P}{\rho f U_0^2} \right) \), \( \text{Re} \) is the Reynolds number \( \left( \text{Re} = \frac{\rho f U_0 h}{\mu} \right) \), and \( \xi \) is the non-dimensional length in the flow direction \( \left( \xi = \frac{x}{h} \right) \).

In the pressure driven zone, there is no zeta potential \( \left( \psi = \psi_0 = 0 \right) \) and hence \( U_p = 0 \). Consequently equation (3-9) will take the following form in equation (3-10a)

\[
\frac{Q}{U_0 h} = \frac{\text{Re}}{12} \frac{dP^*}{dx}
\]

(3-10a)

From equation 2-8,

\[
\frac{dP^*}{d\xi} = -\frac{2}{\text{Re}}
\]

(3-10b)

at the duct centerline.

Dutta et al. (1999) combined equations (3-10a) and (3-10b) to reach

\[
\frac{Q}{U_0 h} = \frac{4}{3}
\]

(3-10c)

Using equations (3-9) and (3-10a, b, c), Dutta et al. (1999) predicted the pressure distribution along the channel studied for different discharge rates and Reynolds numbers. Based on their simulation results, for certain values of \( U_p \), the pressure increases in the direction of flow and hence the electroosmosis phenomenon could be used for micro pumping.

3.4.2 EOF in Circular Capillary

Solving the momentum equation with non-slip boundaries and centerline symmetry conditions (i.e., \( u = 0 \) at the wall and \( du/dr = 0 \) at the center) Rice and Whitehead (1965) obtained the following velocity distribution

\[
u(r) = \frac{dp}{dx} \left( a^2 - r^2 \right) - \frac{D \psi_0}{4\pi \mu} \left[ 1 - \frac{I_0(\sigma a)}{I_0(\sigma a)} \right].
\]

(3-11)

For the case of large \( \omega a \) (\( \omega a >> 1 \)) the electrokinetic uniform part of the velocity across the cross section is the Helmholtz-Smoluchowisky velocity. Cummings (1999) proved by his velocity measurement (using \( \mu \text{PIV} \)) that this assumption is often well approximated in microsystems. Also, Molho et al. (1998) used a caged fluorescence imaging technique in an effort to determine the mechanism that contributes to the fluid flow in microfluidic systems. Their pictures for a 75 \( \mu \text{m} \) diameter fused silica capillary with a 350 V/cm field exhibited a plug like flow.

Integrating the velocity multiplied by the differential area over the whole area gives the rate of volume transport \( Q \),

\[
Q = \left( \frac{dp}{dx} \right) a^2 \frac{A_e}{8 \mu} - \frac{D \psi_0}{4\pi \mu} \frac{dE}{dx} A_e \left[ 1 - \frac{2I_1(\sigma a)}{\sigma a I_0(\sigma a)} \right].
\]

(3-12)
Equation (3-12) reflects the physics of the process. The flow through the capillaries is divided into two terms. The first is due to pressure difference across the capillaries’ ends. This flow goes from the higher pressure to the lower pressure. The second is due to the application of an electric field. This flow direction depends on the zeta potential of the capillary material, which is toward the cathode for the case of cations present on the solution (as in the glass capillaries used in the Rice model). The resultant flow in some cases is against the pressure gradient; in this case the pumping effect discussed previously is achieved.

3.5 The Current in EOF

Rice and Whitehead (1965) have a good interpretation of the current. In their case of a single cylindrical capillary, they divide the current into two components. The first is the current associated with ion flow. The second is due to the conductivity of water. In our case, we are interested in a porous body, which could be imagined as a group of capillaries in parallel. Hence, another component may be the current conducted by the porous material itself.

It was noticed in the experiments performed that the resistance of the materials used varies dramatically with the percentage of water contained in the material. This means that the current associated with the ion flow and the water conductivity is considerably higher than the current flow through the material itself.

3.6 Modeling Vapor Transport between Two Chambers Separated by a Membrane

3.6.1 Model Description

An electroosmosis transport model is developed that describes the flow of water through an electroosmotic membrane. The model uses the equation of Rice and Whitehead (1965), equation (3-12), to calculate the flow rate through a capillary under the effect of electric potential and pressure gradients. Air is assumed not to diffuse through the membrane.

The EOF model is used to calculate the water flow through a 9cm-diameter, 2cm-thick, kaolin membrane, which is similar to dimensions used in experiments. Kaolin properties are assumed based on previous literature, such as: Acar et al. (1992), Bruell et al. (1992), Shang (1997), and Segall and Bruell (1992). Parameters such as zeta potential and Debye length varies with the chemical composition of the kaolin and the nature of the pore liquid (PH and ion concentration) and physical parameters such as the porosity and the pore size varies with the pressure applied on the specimen. Hence, the values from those references give guidelines to assume reasonable assumptions.

The simulation showed that an electric field applied on the membrane specified above will change the flow of water passing through it. The polarity of the electric field decides whether the electroosmotic flow will help or counteract the flow due to pressure drop. The pressure drop across the membrane is chosen arbitrary at this point of the research. Later chapters will take a close look to the membrane and calculate the pressure drop across it.

3.6.2 Effect of Capillary Radius

The EOF model is used to study the effect of the pore diameter on flow rate of vapor transferred. Figure 3-3 shows specific numbers for a membrane material with a Debye length of 1 nm (Rice and Whitehead, 1965, Dutta et al, 1999). The electroosmotic flow rate due to the electric field depends on the layer of mobile ions near the wall of the pore, and hence does not change after a certain pore size. The pressure induced flow, however, depends on the diameter of the pore. The graph compares the magnitude of both flows in case of a 9cm-diameter membrane with
reasonably assumed pressure and voltage gradients and porosity. Once the diameter is in the same order of magnitude of the Debye length the current equation will not apply to the case, (the dotted part of the curve).

![Graph showing the change in mass flow rate due to change in the applied electric potential on a kaolin membrane for an arbitrary pressure drop across the membrane.](image)

Figure 3-3 The change in mass flow rate due to change in the applied electric potential on a kaolin membrane for an arbitrary pressure drop across the membrane.

![Graph showing the effect of capillary diameter on electroosmotic flow and pressure driven flow (Poiseuille flow), a typical range of capillary diameter is between 10 to 100 nm](image)

Figure 3-4 Effect of capillary diameter on electroosmotic flow and pressure driven flow (Poiseuille flow), a typical range of capillary diameter is between 10 to 100 nm

### 3.6.3 Deviation of the Model

The idealized capillary tube model of Rice does not take into account variations of the material composition and geometry as found in clay or other porous materials. Some of these considerations are described below.

**Impurities:** An important factor to take into consideration with some materials is purity. Clays, for example, consist mainly of silicon dioxide with other oxides such as aluminum, iron, and manganese. The presence of such oxides will affect the charge distribution along the pore wall. Because the nature and the number of these
oxides are not well defined for clay membranes, experimental measurements are required in order to define parameters for modeling electroosmotic characteristics.

**Non-homogeneity:** An important factor that is not accounted for in the present model is the non-homogeneity of the material porosity. Experimental determination of effective porosity can be used to determine this characteristic of real materials.

**Pore Tortuosity:** As noted by Shang (1997) the pores’ “tortuosity” may be an important reason for deviation of the model from the reality. This tortuosity effect not only increases the capillary length, but it can also change dramatically the direction of flow as the external field is not oriented parallel to the solid walls (a non-streamwise electric field has been simulated for the control of flow within complex microgeometries (Dutta, 2000). The “Laboratoire de Physico-Chimie Théorique” has examined a similar case but in a flat plate. They showed that: “the net flow may not be the one inferred from the simple consideration of the surface net charge, and the electroosmotic flow can be at some angle to the applied field (even 90 degrees)” (Ajdari, 1999 and Long et al., 1999).

### 3.7 Conclusion

This chapter introduced the basic information about the double layer theory, the underlying theory behind the electroosmosis phenomenon. Models that characterize the charge distribution as well as the electroosmotic flow were reviewed. This knowledge was used to develop an electroosmotic flow model. The EOF model was used to gain some insight about the effect of capillary size on the relative magnitude of the pressure induced flow and the electroosmotic flow. Some deviations between the model and the real application were highlighted.

The next chapter will deal with the experimental work performed to study the electroosmotic flow in materials considered to be candidates for an electroosmotic desiccant. More detailed comparison between the model and the experimental setups with the experimental materials will be conducted.
Chapter 4. Experimental Investigation of Electroosmotic Flow

4.1 Introduction
This chapter presents experiments performed to study the electroosmotic phenomena and to implement the EOF in the dehumidification process. First, the materials chosen for experimental investigation will be discussed. Then, experiments with flow through a membrane with and without a voltage imposed are presented. Then, the Electroosmotic flow coupled with a desiccant effect on the membrane surface layer will be described with a discussion of results. Finally, experiments to determine the zeta potential of some candidate EOF materials will be described.

4.2 Previous Investigations of Electroosmosis
This section discusses some applications of electroosmosis. First, a sample of research activities related to EOF in soil is presented. Then, some recent experimental research in the mechanical engineering field is discussed. Finally, research dealing with different types of membranes and fluids other than water is reviewed.

Electroosmosis was used as a soil consolidation technique in applications such as strengthening pile foundations and stabilization of earth dams. It was also used in driving hazardous materials out of the soil (Shultz, 1997). Also working with electroosmotic flow (EOF) in natural soil, Chen et al. (1999) used a low voltage DC source to drive water through natural soil (field test). This research aimed to study the effect of electroosmosis on soil properties such as PH and electrical conductivity. They used a layer of granular graphite as their lower electrode and a metallic mesh as their upper electrode. Their results showed the feasibility of using horizontal electrodes at shallow depth. They reported also a difference of 40 times between the results of the field test and the experiments done on kaolinite in the laboratory.

Fujiwara and Kitoh (2002) studied (experimentally) the effect of microchannel size, pressure gradient, and electric field on the electroosmotic flow. They reported that the EOF is proportional to the size of the channel which is a very surprising result. They also found that sometimes the EOF is not proportional to the electric field and linear to the pressure gradient.

Morf et al. (2001) described theoretically the behavior of EOF in complex microgeometries, by considering the equivalent hydraulic resistance and the equivalent electrical resistance. They verified their results with a flow rate and back pressure of a microfabricated electroosmotic pump.

Yao and Santiago (2003) developed a theoretical model that predicts the performance of a porous glass electroosmotic pump. Their model discusses porosity, tortuosity, pore size, bulk ionic density, and the non-uniform conductivity distribution over charge layers.

The use of electroosmosis to transfer fluids was not restricted to soils and glass microchannels. Investigators have also studied flow through biological membranes such as skin and blood veins. Pikal (1992) studied experimentally the effect of electroosmosis on drug delivery through the skin. Hsu (2002) studied the electroosmotic flow in elliptical channels such as blood veins. The fluids studied were not restricted to water. Lee (2003) studied EOF of toluene while Touchard (1990) investigated EOF with petroleum.
4.3 Materials Used

4.3.1 Concrete/Plaster
A research project conducted by a U.S. Army research lab (Hock et al., 1998) reduced water transport into basements by using electroosmotic “pulse” technology. The project succeeded not only to move water through their basement foundations, but also reduced the relative humidity inside the building. The water level in a water-well installed just outside the building was higher than the floor level of the basement. These results developed our idea that a material, such as concrete, may act as a desiccant as well as an electrokinetic material suitable to pump water through against a water vapor pressure gradient.

First concrete was used as a membrane. The results were not promising as the EOF was not detectable. Due to these results, membranes were manufactured from plaster instead.

4.3.2 Kaolin (Clay-Like Materials)
Kaolin, also called china clay, is used in diverse applications due to its properties. Besides manufacturing China and porcelain, kaolin is used as a filler in paints, cardboard, chalk and rubber products. It is the base material for cosmetics and the carrier for active ingredients of some pharmaceutical tablets. Kaolin is also an important ingredient of concrete, electrical insulators and magazine papers.

In recent years, electroosmosis has been extended to geoenvironmental engineering applications such as dewatering and consolidation of soil. The success of these research activities indicated that clay is a possible material of interest to our studies. Hamed and Bahadra (1997), for example, have conducted research on kaolinite (\([\text{Si}_4\text{Al}_4\text{O}_{10}\text{(OH)}_8]\)) to study the effects of the PH and the current density on EOF in kaolinite. Their results showed promising water transport rates over a wide range of current densities. Beside previous research, Preliminary experiments done on kaolin showed a significance of the electroosmotic flow. The next section describes this experiment and discusses its results.

4.3.3 Other Materials
Beside clays and plasters, other materials were tested for potential use as membranes. The materials investigated, consisted mainly of silica (SiO₂). Some of the materials showed a good potential to be used as electroosmotic membranes.

Silica-gel is a material known for its use as a solid thermal desiccant. Slabs of water glass were manufactured to be tested as membranes by adding sodium hydroxide to a slurry of silica-gel and water. The mixture was then cast into circular membranes of 5-cm diameter. Electrodes of carbon fibers were implanted on both sides of the paste. When the material solidified, the mixture gave a semi-transparent membrane. The membrane shrank in a manner that surface became concave and the sides detached from the plastic ring containing the mixture. This problem caused no further investigation to be done.

Another silica-based material used is diatomaceous earth. This material is an earthy deposit of fine, grayish, powder composed chiefly of the remains of diatoms. It may occur as a powder or as a porous, rigid material. The material, in the form of fine powder was pressed into a piece of PVC with electrodes on both sides. The zeta potential was measured, and will be described later.
Fiber glass is a material widely used in insulation. This material was investigated for potential use as an Electroosmotic membrane. The zeta potential of the fiber glass was measured. Efforts were also made to incorporate it in a membrane with a silica gel desiccant layer on the surface to be dried.

4.4 Preliminary Clay Electroosmotic Experiments
Diagnostic experiments were performed on some types of clay to check the effect of an electric field on the water flow inside these materials. Small specimens of both china clay (kaolin) and red art clay were left to dry out in the same environment (see Table 4-1 for approximate composition of the clays used). Three equal-weight samples were made from each material. Each sample was placed on a shallow plastic cup with aluminum screen on each side of the clay. One of the specimens was subjected to a positive voltage on the upper electrode. The other had a negative voltage applied to the upper electrode. No voltage was applied to the third specimen. The loss in weight was studied by recording the weight of the three specimens periodically.

As the ions carrying the current are cations, the sample having the negative electrode up was expected to dry the fastest and the one having the negative electrode down was expected to dry the slowest. The results obtained showed that the samples with the applied voltage differences lost weight faster. The samples with opposite polarity showed exactly the same behavior. The test was repeated on the kaolin and red clay. Both clays showed the same trends. A sample of the results is shown in Figure 4-1.

Table 4-1 Approximate composition of clay

<table>
<thead>
<tr>
<th></th>
<th>China Clay (kaolin)</th>
<th>Red art</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>44.72</td>
<td>64.27</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>39.20</td>
<td>16.41</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.36</td>
<td>7.04</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.76</td>
<td>1.06</td>
</tr>
<tr>
<td>CaO</td>
<td>0.22</td>
<td>0.23</td>
</tr>
<tr>
<td>MgO</td>
<td>0.01</td>
<td>1.55</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.01</td>
<td>4.07</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.01</td>
<td>0.40</td>
</tr>
<tr>
<td>So₄</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>F₂</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>L.O.I¹</td>
<td>13.55</td>
<td>4.78</td>
</tr>
<tr>
<td>Others</td>
<td>0.22% moisture</td>
<td>-</td>
</tr>
</tbody>
</table>

¹ Loss on ignition
A possible interpretation of the unexpected results is one based on observations. In the case of a positive lower electrode, water was pumped up, as expected, so that the upper screen became wet and loosened. For the case of a negative upper electrode, water was percolating near the connecting wire and the container edges. This could be interpreted as the water pumped downward (the expected direction) to the container bottom and then seeping up due to its higher pressure to the top through the cracks created around the wire and around the container walls. Figure 4-2 shows a schematic of the process.

A reduction in the pore size can cause similar results due to squeezing water out of the pores. In both cases, having more water sites on the surface causes a higher water evaporation rate and a faster reduction in the specimen weight, consequently. The fact that the difference happens on the first few hours promotes this explanation.

The Joule-Thomson heating effect was checked and the electric power input was not sufficient to evaporate water and cause the significant difference in weight loss. After 15 hours for example the specimens with voltage

Figure 4-1 Percent reduction in weight with time for kaolin specimens with and without voltage applied. Error bars are too small to represent O(10^{-5}).

Figure 4-2 Interpretation of the clay behavior with different polarity voltage applied based on observations. The white arrows represent the water flow direction.
applied lost about 0.4 grams of water more than the one with no voltage input. The energy input will evaporate 0.001 grams in the worst case. The effect of heating was checked also on the temperature of the specimen. The electric power supplied was not enough to raise the temperature of the specimen significantly (less than 0.2 °C for the whole experiment).

4.5 Effect of Voltage on Water Vapor Transfer Across a Membrane

An experiment was designed to test a membrane’s ability to transmit water through its pores. The experiment consists of two cylindrical chambers separated by a 1.6 mm (1/16 inch) thick kaolin membrane. Electrodes are erected on the opposite sides of the membrane so that an electric field could be applied. Each of the two chambers is fitted with either a thermocouple and a relative humidity sensor or a thermocouple and a container of water, as shown in Figure 4-3. The vapor pressure is measured on either side of the sample and recorded with time. The difference is plotted against time for forward, reversed and no voltage cases. Figure 4-4 shows the results obtained from these experiments. The flow is retarded by the application of a voltage across the membrane. The polarity of the voltage field did not affect the flow through the membrane. The mass flux of water through this membrane was $10^{-7}$ kg/sec.m$^2$ at the beginning of the experiment. (Approximately 1.5 hr was required to move 1/100 gram of water through a membrane of this size.)

An important question arises: why is there no difference in flow rate due to polarity change? The answer is that the electroosmotic flow is overshadowed by the pressure induced flow. And the deceleration of the flow is due to a change in the Debye length due to the voltage application may have occurred blocking all the transversal pores and leaving only the ones in the flow direction (i.e. changing a grid system in case of no voltage to an array of parallel pipes in case of voltage application). A large Debye length with respect to the radius may cause the clay to act as a semi-permeable membrane, (see Keijzer, 2000)
An experiment was designed to check that some of the pores can be blocked by the expansion of their wall dominance on the ions due to voltage application. The experiment was performed on a plaster membrane with an electrode in the center and the other on the circumference. The electric field applied is perpendicular on the average flow direction. The membrane separates two well sealed chambers. One chamber had a fixed vapor pressure by having a small cup of water to maintain a 100% relative humidity, while the other chamber had the temperature and relative humidity recorded every minute. The difference in vapor pressure between the two chambers is plotted with time. The rate of change of the pressure difference is an indicator of the water flow rate through the membrane (i.e. the faster the difference in pressure decreased, the faster the water flow between the chambers).

The expected result is that the flow will get decelerated by the application of the electric field up to a certain limit. The membrane diameter is about 5 cm and the voltage varied from 0 to 5 volts. Because the flow of vapor depends on the vapor pressure difference across the membrane, the difference in pressure is expected to follow an exponential decaying function with time.

\[ P^* = \frac{P_{100} - P_v}{P_{100} - P_{v0}} = (1 - const)e^{(-at)} \]  

In Equation (4-1), \( P_{100} \) is the vapor pressure in the 100% relative humidity chamber, \( P_v \) is the vapor pressure in the other chamber at any time, \( t \), \( P_{v0} \) is the vapor pressure at the beginning of the experiment \( (t=0) \) when the voltage was applied and the water cup was placed in the other chamber. The constant in equation (4-1) should be ideally zero, so here it is taken as a measure of error. Experiments with constant more than 4% (0.04) are rejected from the analysis. Figure 4-5 shows the experimental data collected in case of an applied potential of 2.4 volts. In this case, the coefficient “A” is 0.00002 sec\(^{-1}\) and the constant is 0.01 (1%).
Figure 4-5 Experimental data and curve fit of the non-dimensional pressure dependence on time

For each experiment a curve as in equation (4-1) is fit to the data collected. The constant “A” is plotted verses the voltage applied in each case (Figure 4-6). As the voltage applied increases the A coefficient decreases. This means that the decay with time is slower because the vapor flow through the membrane is slower. This confirms the conclusion that the electric field applied in a direction other than the axis of the pore will cause a partial blockage in it.

Figure 4-6 Variation of the time coefficient, A, with the voltage applied perpendicular on the average flow direction

4.6 Combined Desiccant and Electroosmotic Effect (Moving Water Vapor against a Pressure Gradient)
This experiment consists of two cylindrical chambers separated from each other by a membrane. The two chambers are well sealed so that they do not exchange moisture with ambient. One of the chambers is maintained at
constant relative humidity of 13 %, approximately, by adding a saturated lithium chloride (LiCl) solution. As the temperature is kept constant during the test, this chamber has a constant vapor pressure of 370 Pascal (as measured by the thermocouple and the relative humidity sensor). The other chamber is equipped, as well, with a thermocouple and a humidity sensor. But its humidity is allowed to vary freely.

The membrane was manufactured from plaster of Paris, a commercial name for a type of plaster* that solidifies quickly. The membrane was cast in a plastic ring. The membrane has a diameter of 5 cm and a thickness of 1 cm. The electrodes were cut from carbon fiber cloth and were connected to the external circuit with carbon fibers too. One face of the membrane, the one facing the low vapor pressure, is covered with silica gel crystals. The silica gel has cobalt carbonate in it as a color indicator of moisture. As the membrane was solidifying, its electrical resistance increased and the color of crystals was turning from rose (hydrated) to blue (dehydrated).

After the membrane was put in place few droplets of water were added to its surface to lower its electrical resistance. As time passed, the vapor transferred through the membrane and both sides were adjusting to an equilibrium condition of 13 % relative humidity. When the salt solution side reached its equilibrium condition, a voltage was applied to drive water out of the low-humidity zone to the high humidity one.

The application of 5 volts across the membrane drove the high-humidity side to a vapor pressure of about 600 Pascals. The average rate of water flow was calculated to be 2.31 grams/m²hr. The voltage difference managed also to keep pumping water at high enough rate to balance the counter pressure induced flow for 300 minutes. The total time where the water was pumped forward enough to increase the difference in vapor pressure was about 900 minutes. After that time, the vapor pressure on the high-humidity side began to decrease. Figure 4-7 shows the current drawn by the membrane during the experiment, and consequently the power used to pump water. Figure 4-8 represent the change of vapor pressure in both chambers before and after the voltage application.

![Figure 4-7](image)

Figure 4-7 The current drawn and the power consumed to pump water through a membrane of plaster of Paris

* calcium carbonate, calcium sulfate and silica
The same experiment was repeated on the same membrane as well as one with a lithium chloride coating on the surface as desiccant and a solution of calcium chloride on the low humidity side (23-26%), and the same trend was observed but with a smaller pressure rise.

After the experiment, the membrane was broken open. The volume between the electrodes was dry and the layer on the side of the electrode was wet as shown in Figure 4-9. This means that the water was not moving from the desiccant as fast as it is moving under the electric field in the plaster, and not as fast as it is moving from the air to the desiccant. This indicates that the water flow rate through from the desiccant to the electrode is an area that needs improvement.

4.7 Measuring the Zeta Potential

This section describes experiments done on membranes to measure the zeta potential. The experiments measure the streaming potential which is the potential produced when pure water is forced to flow through a
capillary or a porous solid. The value of this potential is independent of the size and thickness of the membrane and the water flow rate through its pores (Quincke, 1859\textsuperscript{2}). The streaming potential is related to the pressure imposed on the membrane by the following relation involving the zeta potential.

\[
\Delta E = \frac{D\zeta}{4\pi\mu k} \Delta P
\]

where, \(D\), \(k\), \(\mu\), and \(\zeta\) are the dielectric constant, specific conductance, viscosity of the fluid inside the pore and zeta potential, respectively.

Szymczyk \textit{et al.} (1998) compared the values of zeta potential obtained from electroosmosis and streaming potential and found that the one obtained from the electroosmosis is always higher (from the graphs they presented 1.4 to 2 times higher for ionic strength from 0.0001 to 0.01 molar respectively). This led them to the conclusion that the plane of shear is nearer to the surface during electroosmosis.

The first trial was to measure the zeta potential of "plaster of Paris" (the membrane that gave the best result in transferring vapor). The setup used is described in details in appendix A. The method depended on measuring \(\Delta E\) for a given constant \(\Delta P\) and hence calculating zeta potential. Results were not consistent enough to rely upon. Therefore, another approach, described in the next paragraphs, was considered.

An alternative method of measuring the zeta potential is through measuring the relation between the streaming potential and the pressure difference across the membrane as that difference in pressure changes (rather than depending on one single point). Figure 4-10 shows the setup used for this purpose. The setup consists of an elevated, sealed water tank connected to a compressed air line, from one side, and to the membrane from the other side. The pressure of the air could be changed and hence the pressure acting on the membrane. This pressure is measured by a manometer connected to the high pressure side of the membrane. The electrodes on both sides of the membrane are connected to a voltmeter to measure the streaming potential.

After a new membrane is placed in place, the water tank is connected to the membrane through a universal joint. The valve connecting the pressurized air to the tank is opened and the pressure above the water is controlled through adjusting the release valve opening. For each pressure, read with the manometer, the voltage produced across the membrane sides is read from the voltmeter.

Membranes made out of plaster of Paris were tested first. The change in voltage noticed due to the increase in pressure was of the order of the normal voltage change with time, and hence, the results were not reliable enough to use in zeta potential calculation.

\textsuperscript{2} McGraw Hill encyclopedia of chemistry
Figure 4-10 Setup of measuring the zeta potential by measuring the relation between the pressure and the streaming potential across the membrane

Figure 4-11 A picture of the flange, shown in Figure 4-10, used to hold the cartridge membrane
Figure 4-12 A plaster membrane(left) and the carbon fiber electrodes (right)

Figure 4-13 Plaster membranes deteriorating due high pressure water

Figure 4-14 A picture of the diatomaceous earth membrane

Materials with silica base such as diatomaceous earth and fiber glass were tested next and showed a reasonable, measurable, streaming potential change with the pressure change.

Results similar to the one shown in Figure 4-15 are used to get the slope of the function between the voltage and the applied pressure. Equation 4-2 is used then to calculate the zeta potential. The zeta potential is calculated for diatomaceous earth and fiber glass and the values obtained are in the order of 1 mV. The values for the zeta potential obtained are less than the expected (the reported value for Kaolin is 100 mV and specimens of
diatomaceous earth and fiber glass showed a higher voltage change than a specimen of kaolin for the same pressure applied), most likely, because of using the values of the conductivity of pure water rather than an electrolyte.

![Graph showing streaming potential variation with pressure](image)

Figure 4-15 Streaming potential variation with pressure

### 4.8 Conclusion

This chapter presents the experimental work to investigate the electroosmotic effect as well as the combined effect of a desiccant and electroosmosis. The materials used during the research were reviewed. Finally, a method to measure the zeta potential using the streaming potential effect is described.

The chapter shows the necessity of the compatibility of all the processes involved in transferring the vapor from one side of the membrane to the other. The next chapter will model the processes involved and examine the relative importance of each transport effect.
Chapter 5. Modeling the Combined Desiccant Electroosmotic Effect

5.1 Introduction
Dehumidification using an electroosmotic desiccant is described in this chapter. An overall system model is developed that combines the desiccant vapor adsorption process with the electroosmotic transport of moisture through a membrane. The electroosmotic dehumidifier (EOD) model is developed within the context of residential air conditioning. The model’s main goal is to decide the scale and configuration of an EOD as well as the power it uses and the savings it can provide.

The EOD model is first described then a parametric study is performed to show the sensitivity of the phenomena to certain parameters. The model also estimates the area needed to for a given load. The power consumed by the device in order to achieve dehumidification is also estimated. The potential savings in operating cost of an A/C system with an electroosmotic dehumidifier (EOD) is studied at different weather conditions. Finally, shortcomings in the model are highlighted and suggestions for better simulations are discussed.

5.2 Description of the Electroosmotic Model
The model describes the flow of vapor in three stages. First, the vapor flows from the bulk of the conditioned space to the surface of the desiccant layer. Once condensed on the surface, water flows through the desiccant layer due to a pressure difference. Finally, water is pumped from the one electrode to the other through the electrokinetic material by the electroosmotic force. Figure 5-1 represents the pressure of vapor along the different stages of the model.

Vapor is attracted to the surface of the desiccant because of the low vapor pressure at the surface of the desiccant. The driving force will be the difference in vapor mass fraction (difference in specific humidity) between the bulk of the room air and the surface of the desiccant. The mass flux of vapor from the conditioned space to the surface is calculated by multiplying the mass transfer coefficient by the difference in mass fraction of vapor as given in equation (5-1)
Given the water content inside the desiccant layer, the relative humidity is given as a function of the water mass per dry desiccant mass (called water content). In case of the relative humidity at the surface can be calculated using equation (5-2) Pesaran (1987).

\[ \text{RH} = 0.078 - 0.0579 \times 24.165 \times X^2 - 124.48 \times X^3 + 204.226 \times X^4 \]  

where RH is the relative humidity and X is the water content of the desiccant, in this case, silica-gel. The saturation pressure of water, \( P_{Sat} \) (kPa), at any temperature, T (Celsius), is given by equation (5-3) (a curve fit for \( 0 < T (°C) < 100 \)).

\[ P_{Sat} = 0.61138 + (4.4053 \times 10^{-2}) \times T + (1.4594 \times 10^{-3}) \times T^2 \]
\[ + (2.6092 \times 10^{-5}) \times T^3 + (2.8332 \times 10^{-7}) \times T^4 + (2.7316 \times 10^{-9}) \times T^5 \]

And hence, the vapor pressure, \( P_v \), at the surface of the desiccant is calculated by multiplying the saturation pressure by the relative humidity. The vapor pressure is used to evaluate the mass fraction, \( m \), of vapor using equation (5-4) where \( P_a \) is the air partial pressure.

\[ m = \frac{P_v}{P_a + P_v} \]

Equations (5-3) and (5-4) are used to evaluate the mass fraction of vapor at the bulk conditions of the room air in a similar manner. Figures 5-2 and 5-3 represent equations (5-1) and (5-2), respectively.

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* This equation was used by many researchers in the solar energy field with temperatures in the ambient range as well as in the exhaust gases range. No difference in accuracy was reported by the literature covered.
The mass transfer coefficient can be calculated using the heat and mass transfer analogy. The analogy is considered for both natural and forced convection regimes. Natural convection regimes take place when the dominant driving force is the buoyancy caused from the difference in density between the air in the close vicinity of the wall and the room air. The heat transfer coefficient in such cases is usually between 5 to 25 W/m²K. Forced convection is the dominant regime when air is forced to flow past the wall by an external means (fan for example). The heat transfer coefficient varies widely in this regime depending on the flow regime (laminar/turbulent), and the wall structure.

For natural convection, the flow will be governed by the Grashof number which is a ratio between the buoyancy force (driving force) and the viscous force. Grashof number is defined by equation (5-5), where, L is the characteristic length of the surface and ν is the kinematic viscosity. The density difference in this case is caused by the composition difference as well as the temperature difference between the room air and the surface. However, the effect of composition difference is not considerable with respect to that of the temperature difference (equivalent to about 0.5 °C temperature difference).

\[
Gr = \frac{g \Delta \rho L^3}{\nu^2}
\]

For the range of Grashof number in this problem (10^4 – 10^9), the Nusselt number is related to the Grashof number by equation (5-6)

\[
Nu = \frac{hL}{k} = c[Gr Pr]^{1/4}
\]

where c = 0.59 in case of vertical wall, h is the heat transfer coefficient, k is the thermal conductivity.

In the mass heat analogy, the Sherwood number, Sh, replaces the Nusselt number and Schmidt number, Sc, replaces the Prandtl number, Pr. For a membrane placed vertically with a rectangular surface, the Sherwood number is related to the Grashof number, Gr, and the Schmidt number by the following relation (5-7) (Çengel, 1997)
where \( h_m \) is the mass transfer coefficient, and \( D \) is the diffusion coefficient of water vapor in air.

From equations (5-6) and (5-7) the mass transfer coefficient can be related to the heat transfer coefficient by equation (5-8):

\[
\frac{h}{h_m} = \frac{k}{D} \left[ \frac{Pr}{Sc} \right]^{1/4}
\]

(5-8)

For temperature conditions near ambient, the \( Pr \) number and \( Sc \) number are comparable and the ratio between them is near unity. The ratio between the heat diffusion coefficient and the mass diffusion coefficient is roughly 1000:1. And hence, the relation between the heat and mass transfer coefficient can be written in the following form (5-9):

\[
\frac{h[W/m^2K]}{h_m[m/s]} \approx 1000\left[ J/m^3K \right]
\]

(5-9)

For the case of forced flow, the flow is described by the Reynolds number. The Nusselt number is a function of the Reynolds number and the Prandtl number. The Sherwood number will have the same function but with the Schmidt number instead of Prandtl number. The heat and mass transfer coefficients are related with equation (5-10):

\[
\frac{h}{h_m} = \frac{k}{D} \left[ \frac{Pr}{Sc} \right]^{1/2}
\]

(5-10)

Because the ratio between Prandtl number and Schmidt number is near unity, the relation between the heat and mass transfer coefficients, for the case of forced convection, will also be given by equation (5-9).

Once vapor is “condensed” on the desiccant surface, the water flows under a pressure gradient from the surface to the first electrode. The pressure drop at this stage has to be recovered in the following stage (the electroosmotic pumping section of the membrane). The pressure drop depends on the effective length of the passage, the average pore size as well as the water flow rate pumped per cross section area. Equation (5-11) describes the water mass flux as a function of these parameters.

\[
m^* = \frac{\rho a_1^2 \Delta P}{8 \mu \Delta x_1}
\]

(5-11)

This pressure drop has to be recovered by electroosmotic pumping while the flow is between the two electrodes. The pumping effect happens because of the material electrokinetic properties as well as the electric field applied. Equation (5-12) describes the relation between the electric field the pressure gradient and the flow rate. In this model silica, with a 0.1 volt zeta potential is assumed

\[
m^* = \frac{\rho a_2^2 \Delta P}{8 \mu \Delta x_2} + \frac{\epsilon \psi \rho \Delta E}{\mu \Delta x_2}
\]

(5-12)
5.3 Governing Phase of the Flow through the Membrane

This section studies the individual flow resistance of each of the three regions of the flow. The flow rate of moisture through the EOD is governed by the sum of resistances of the three regions. Studying the individual resistance of each region helps identify the region with the highest resistance. Figure 5-4 represents all the interactions between surfaces and shows the flow resistance of each phase.

Node 1 refers to the ambient air where the vapor pressure is the partial pressure. Node 2 refers to the surface of the desiccant. This surface is represented by two pressures. First the depressed vapor pressure on the surface of the desiccant. The second pressure is the atmospheric pressure that acts on the water once condensed. The resistance between the air and the desiccant surface is a mass convection resistance. From equations (5-1) and (5-4), the resistance between the air and the surface could be represented by equation (5-13):

$$R_{air-Desiccant} = \frac{R_v}{Ra} \frac{P_{atm}}{h_m} = \frac{1.63 \times 10^5 [Pascal]}{h_m}$$

(5-13)

For a membrane installed in a room as a wall with natural convection, the mass transfer coefficient, $h_m$, is about 0.005 kg/m$^2$.s. The resistance to the flow is $3.3 \times 10^7$ Pascal-m$^2$.s/kg, from equation (5-13). The value of this resistance should not be compared blindly with the resistances of the other two stages since the flow of vapor from the air to the surface is governed by the partial pressure difference while the flow of water through the membrane is governed by pressure difference.

Figure 5-4 Flow resistances: an analog circuit to the flow circuit.
Node 3 refers to the electrode surface. The resistance between nodes 2 and 3 is a wall friction resistance as the water is flowing through the desiccant. Rearranging equation (5-13) the desiccant resistance can be written as:

\[ R_{\text{Desiccant}} = \frac{8\mu \Delta x_1}{\rho a_1^2 \text{Por}} \]  

For a desiccant layer of 5 mm (pore diameter of 20 nm and porosity of 50%) the resistance to the flow is \(2 \times 10^8\) Pascal-m\(^2\)-s/kg. Similarly, the resistance between nodes 3 and 4 (the two electrodes) is calculated. The thickness of this layer is assumed to be 12 mm and the pore size is assumed to be 100 nm. The resistance based on these values is \(10^7\) Pascal-m\(^2\)-s/kg.

Node 5 represents the outside air. Because the water leaves the membrane in the liquid state, the evaporation rate from the surface does not need to be compatible with the rest of the flow. Any excess water can be drained from the surface in the liquid form.

Although the values of the different resistances calculated for this membrane suggest that the desiccant layer is the one causing the highest resistance (one order of magnitude higher than the others), the resistance to the vapor flow from the air to the surface of the desiccant is the highest. If we consider the flow of 1 g/m\(^2\)-s, for example, the pressure drop needed for that flow in the desiccant layer is 4 bars (difficult to achieve: a high voltage is needed). On the other hand, the drop in partial pressure is 40 kPa (impossible to achieve with ambient air, saturation pressure in the order of 1 kPa).

Another way to simplify comparing the different resistances is to multiply the pressure at nodes 1 and 2 (in Figure 5-4) by a constant to make the pressure curve at point 2 continuous. The resistance to the flow is given by equation (5-13’)

\[ R_{\text{air-Desiccant-Modified}} = \frac{\Delta P_{\text{air}}}{\rho a_1^2 \text{Por}} + \frac{0.622 + \omega_s}{\omega_s} \]  

where, \(\omega_s\) is the humidity ratio at the surface of the desiccant. In this case the resistance between the room air and the surface of the desiccant is \(2 \times 10^9\) Pascal-m\(^2\)-s/kg.

The electroosmotic effect is represented as a fluid pump that recovers the pressure drop in both the desiccant layer and the electroosmotic layer. The required voltage relates to the pressure drops by the following equation.

\[ \Delta E = \left[ \frac{\Delta P_{\text{desiccant}}}{R_{\text{desiccant}}} + \frac{\Delta P_{\text{electrokinetic}}}{R_{\text{electrokinetic}}} \right] \frac{\mu \Delta x_2}{\varepsilon \psi \text{Por}} \]  

5.4 Effect of Water Content of the Desiccant on the Membrane Performance

The desiccant content of water is assumed to be uniform over the desiccant layer thickness. This implies that the flow of water through the desiccant layer is driven only by the pressure difference between the surface of the membrane and the electrode. The flow through the membrane and from the ambient to the membrane surface may not be equal due to transient effects. There are limiting conditions in both ways: If the water builds up to certain limit (40% of the dry desiccant mass in the case of silica-gel) the desiccant becomes saturated and cannot take any
more water in its pores. On the other hand if the membrane is dry initially, the process will not begin because of lack of water in the pores.

Figure 5-5 shows that the mass concentration on the surface increases with its water content which reduces the driving force of the flow (i.e. reduces the amount of vapor condensing). The desiccant water content also affects the composition (mass fractions) on the surface and hence the difference in density between the air on surface and the room air.

![Figure 5-5 Bulk, and surface mass fraction at several desiccant water contents](image)

Air temperature 21°C, air relative humidity 50 %, and desiccant temperature 21 °C.

### 5.5 Effect of Voltage on the Mass Flux through the Membrane

Voltage is the input to the system and the mover of the process. The input DC voltage affects the electroosmotic flow, the flow in the desiccant, and the flow of vapor from the air to the surface of the desiccant. This section discusses the effects of the voltage, and estimates the required range of voltage needed to run the process.

For a given configuration every voltage applied will have a corresponding flow, and hence, corresponding water content in the desiccant. The membrane discussed has the following specifications: a desiccant layer 5 mm thick with 20 % water content and 21 °C surface temperature, an electroosmotic layer 12 mm thick with a DC volt applied. The ambient is the same as described before assumed to be 21 °C and 50 %. Figure 5-6 represents the mass flow rate variation with the applied voltage. The corresponding water content of the desiccant is also plotted on the same graph.

From Figure 5-6, the mass flux increases linearly with the voltage applied. The voltage calculated from the model is in the range desired by this research (this research targets the development of a dehumidification material compatible with low DC voltage, such as generated by photovoltaic cells, batteries, and fuel cells). Because of the simplifications in modeling the flow through the pores, the voltage required in real cases may be higher. However, even with two orders of magnitude (Shang, 1997) the actual voltage is still in a reasonable range. It is also concluded that, the higher the voltage applied, the lower the steady state water content of the desiccant.
5.6 Effect of Membrane Thickness

The thicknesses of both the desiccant layer and the electroosmotic material have a significant effect on the characteristics of the membrane. Both must be minimized as much as possible. A smaller desiccant layer thickness leads to a lower pressure drop through this layer, and for a given flow rate will lead to a smaller pressure drop to be recovered in the electroosmotic layer. A thinner electroosmotic layer means a higher voltage gradient (electric field) for a given voltage difference which increases the flow rate.

5.7 Power and Area Requirements

The area required per kg/hr of vapor removed from the room air depends on two factors. The first factor is the difference in mass fraction between the air and the surface of the desiccant. For the case of a room at 25 °C and 50 % relative humidity and a surface consisting of silica gel at the same temperature with 20 % steady state water content, the difference in mass fraction is 0.0027 kg-water/kg-air. For the case of natural convection, the mass transfer coefficient multiplied by the average air density is approximately 0.01 kg/m²-s. The area needed for these conditions is 10 m² per kg/hr. For the case of forced convection, the mass transfer coefficient mass transfer coefficient is higher. The mass transfer coefficient multiplied by the average density is typically 0.1 kg/m²-s. This mass transfer enhancement will decrease the area needed per kg/hr to 1 m². The higher surface mass transfer rate, however, will cause a higher pressure drop in the desiccant layer and consequently, will need a higher voltage to be applied on the electrokinetic layer.

For a house of 250 m² of floor area with 6 occupants on average, the rate of vapor generation is approximately 0.5 kg/h (ASHRAE Handbook, Fundamentals, 1985). If this house has an infiltration rate of 1 kg/hr for each kPa vapor pressure difference between the outside and the inside, and is located at a humid city (such as Orlando, Florida (34°C/26°C dry and wet bulb temperatures)), the difference in vapor pressure will be 1.8 kPa. The
The total latent load will be 2.3 kg of vapor per hour. The area of the electroosmosic dehumidifier needed for such house is 23 m² for natural convection conditions, and 2.3 m² for a mass exchanger that depends on forced convection.

The theoretical voltage needed to pump this amount of water across the membrane of 5 mm of desiccant layer thickness and 12 mm of electrokinetic layer is 0.75 volts for natural convection (low mass flux) and 7.5 volts for forced convection (high mass flux). In both cases, the current is the same. Assuming that each ion drags one water molecule on average, the current needed for 2.3 kgwater/hr can be calculated using Faraday’s law (Equation 5-15).

\[ m^* = \frac{I M}{F} \]  

The current required is 3.5 Amperes. Consequently, the theoretical power needed is 2.5 watts for a natural convection surface and 25 watts for a forced flow mass exchanger.

Another estimate of the power needed to pump the humidity load is based on the efficiency reported by Chen et al (2000) for their electroosmotic pump. Although the efficiency reported Chen is very small, it will be considered for two reasons. First, it is an experimental prototype that validates the feasibility of such a process. Second, it will be considered attainable efficiency.

For the case of natural convection, the pressure needed to be overcome in the membrane is 10 kPa with a volumetric water flow through the membrane of 6.3 \(10^{-7}\) m³/s. Using Chen’s efficiency of 0.01%, the power supplied to the electroosmotic pump is 64 watts. Similarly, for the case of a forced convection system, the power needed is 640 Watts.

From the estimation of the power needed to pump water out of the EOD, it appears that the amount needed is 1-27.5 W/(kg/hr) in case of low mass flux and 10-275 W/(kg/hr) in case of high mass flux, and hence there is the ability for energy savings, as will be discussed in the next section.

5.8 Potential Energy Savings

Using electroosmotic dehumidification does not directly reduce the load on the air conditioning system, as shown in Figure 5-7, because the heat released from vapor condensation is supplied back to the room air. However, as this heat returns to the room in the form of sensible heat, many advantages are gained.

The lower the latent load (that is, the higher the sensible heat ratio for the same cooling load), the higher the required evaporator surface temperature. Consequently, the pressure lift on the refrigerant compressor is smaller and the compressor’s isentropic efficiency is higher (Boewe et al, 1999) Lower pressure lift and higher isentropic efficiency reduces the overall work needed for the same load.
For a house of 250 m$^2$ with 6 occupants in Orlando, Florida, the latent load is 1.625 kW and the sensible is 7.125 kW, approximately. To maintain comfort conditions of 25°C and 50%, as mentioned in the previous section, the evaporator temperature is 11.9°C. A system with typical configuration will need 1.821 kW of compressor power. Incorporating an EOD with the system will make it possible to raise the evaporator to about 15°C (5°C logarithmic mean temperature difference, LMTD), and hence reduce the compressor power to 1.576 kW, which means a saving of 245 W. On the other hand, the EOD will use 64 W to pump the water for the case of a low mass flux membrane (natural convection mass flow), or will use 640 W for the case of a high mass flux membrane (Forced convection mass transfer).

Figure 5-8 represents the power used by a 10 kW air conditioning unit to maintain a room at 25°C and 50% relative humidity using supply air at 16°C at different sensible heat ratios. The thick solid line is the power used by the unit for the case of normal operation (i.e. without EOD). The dotted lines represent the power used by a system with a high flux EOD. The lower line is based on a theoretical estimate of power needed to pump the water through the membrane. The higher line is based on an assumed low efficiency for the electroosmotic pump.

Similarly, the thin solid lines represent the power used by a system with a low mass flux EOD integrated into the air conditioning system.
Figure 5-8 shows that in general, the higher the sensible heat ratio, the lower the power used to remove the same load. The integration of a low mass flux EOD will save in the power used by the system. On the other hand, the savings achieved by converting the latent load to sensible one may be overshadowed by the power used by a high mass flux EOD depending on its pumping efficiency.

The supply temperature plays an important role in the savings because the higher the desired supply air temperature the greater the difference between the evaporator temperature for both cases of operation (with and without the EOD). Moreover, if the supply air temperature is very low, the evaporator temperature will be low regardless of the sensible heat ratio in order to maintain a reasonable temperature difference between the refrigerant side and the air side. The room temperature has the same effect on energy savings. The higher the room temperature setting, for the same room humidity ratio, the lower the evaporating temperature and consequently, the work needed to operate the compressor is greater. For the case of an EOD integrated to the system, the change in the room temperature does not cause a significant change in the evaporator temperature. Consequently, the power required by the system does not change with small changes in room temperature. Therefore, the energy savings due to an EOD installation will be more pronounced in higher room temperatures.

5.9 Model Shortcomings

The model formulated assumed the pores in the membrane materials are manufactured as straight flow passageways with a fixed diameter. The model did not consider pore orientation which may affect the resulting fluid flow.

A factor that proved to be important in the model analysis results is the membrane resistance to flow. The model did not assign a value for the pressure drop across the electrodes. The pressure drop across the electrodes may
vary dramatically depending on the electrode type and size of the electrode mesh. The mesh size should be sufficiently large relative to the pore size of the membrane in order not to throttle the flow.

It was assumed that the pores are full with water with no air present in the pores. Some air voids may exist in the pores, and the water flow may be affected by the presence of a gas core.

5.10 Conclusion
This chapter describes the flow of vapor to a desiccant surface and its flow in the liquid form in the desiccant layer (under the pressure difference) and the electroosmotic layer due to pressure and voltage gradients.

An electrical analogy is described to help in studying the transport processes, namely identifying the stages that govern the flow of the water. The analogy shows that, for the resistances studied, the air to desiccant surface mass transfer resistance is the highest. The enhancement of the surface of the membrane increases the mass transfer coefficient, and hence increases the capacity of the membrane to transport water.

Other parameters are also studied with the help of the EOD model. The effect of desiccant water content, and the applied voltage and thickness of different layers of the membrane on the performance are investigated.

The model is used to estimate the area needed to achieve a desired water transport rate. The use of a natural or forced flow mass transfer changes the area needed dramatically. The power required to pump water is estimated based on two assumptions. The first uses the Faraday equation and the second uses the reported efficiency of pumping water with an electroosmotic pump (Chen et al, 2000).

A simple system simulation is used to study the effect of integrating the EOD to an A/C system. Converting the latent load to a sensible one reduces the power needed to operate the system. The amount of energy needed to pump the rejected humidity is always lower than the savings in case of low mass-flux membranes. The energy required is sometimes greater than that of a conventional A/C system for the case of a high mass-flux membrane depending on the efficiency of the pumping.
Chapter 6. Use of Kaolin-Salt Mixtures as Thermal Desiccant

6.1 Introduction

While conducting experiments with kaolin, it was found that adding salts to the mixture (water and kaolin powder) results in a solid that has desiccant characteristics when it dries. This chapter gives a background about desiccant systems especially solid desiccants, and presents results showing the desiccant effect seen in different kaolin salt mixtures.

A desiccant is a substance that has a high affinity for water. The physical phenomenon associated with dehumidification varies from one type of desiccant to another. Adsorbent desiccants such as silica gel or zeolites, dehumidify air by adsorbing water (surface absorption) like a sponge. On the other hand, absorbents such as salts or their solutions (calcium chloride, calcium bromide or lithium chloride) or chemicals such as triethylene glycol, depend on absorbing vapor to their bulk.

Water is attracted to the surface of a solid desiccant because of the non-uniform charge distribution on the surface (Roberson, 1991). Every desiccant has an equilibrium vapor pressure that determines the amount and direction of the vapor exchange between one unit area on its surface and the ambient. This equilibrium vapor pressure is a function of the temperature and the water content of the desiccant. As the moisture condenses, it diffuses into the pores allowing it to attract more moisture. The speed of diffusion depends on the radius of the pores in the desiccant and is usually characterized by the diffusion coefficient.

Figure 6-1 represents different dehumidification cycles on the psychrometric chart. Solid desiccant systems work by dehumidifying the air and then evaporatively cooling it. The dashed line shows how the solid desiccant system works. Liquid desiccant systems can be represented by a straight line from the initial to final point. On the other hand, a conventional dehumidification using a refrigeration system depends on the condensation that occurs on the cooling coil as a result of its low temperature. This air will need a reheat to return the air to the desired supply temperature. The solid line in figure 6-1 represents this system. (ASHRAE Systems and Equipment, 2000)

![Figure 6-1](image-url)

Figure 6-1 Solid and liquid desiccant systems, compared to a conventional system, represented on the psychrometric chart
In order for a desiccant system to function continuously, the desiccant should be regenerated. Most desiccant systems currently used depend on thermal regeneration of the desiccants. Solid desiccants, often installed in a desiccant wheel or a packed bed, use a stream of hot air to get rid of their water. For liquid desiccants, a cooling tower, called a regenerator, (where liquid desiccant is in contact with hot dry air that absorbs moisture), is used to close the liquid desiccant cycle.

6.2 Desiccant Characteristics of Kaolin-Salt Mixtures

Salt solutions of lithium chloride and calcium chloride are often used as liquid desiccants. Those two types of salt turn into a liquid solution once left in an environment with a relative humidity higher that their saturated salt solution (11-13 % for lithium chloride, and ~25% for calcium chloride, depending on the temperature).

During experimentation to develop an electroosmotic desiccant, various salts were mixed with kaolin to improve its electrokinetic characteristics. Some mixtures showed dependence between its water content and the relative humidity of the ambient air in equilibrium with the mixture. Experiments were repeated with different ambient temperatures at the same relative humidity, and the water content showed no dependence on the temperature at the same relative humidity.

The salt-clay moisture content dependence on the ambient relative humidity increases with salt percentage in the clay mixture as seen in figures 6-2 to 6-4. In all three figures the pure kaolin is also plotted and showed no change in its water content with the change in the equilibrium relative humidity. Figure 6-2 represents the results of an experiment performed with several specimens of kaolin-calcium chloride mixture. Each set of specimens (with different compositions) was kept in an insulated container with constant relative humidity and the weight of each specimen was monitored until all the specimens reached equilibrium with the imposed environment. The water content is defined as the ratio between the mass of water in the desiccant to the mass of the other materials.

![Figure 6-2](image-url)  
Figure 6-2 The relative humidity for a different compositions of kaolin-calcium chloride mixture, compared to the silica gel
Figure 6-3 represents the equilibrium relative humidity dependence on the water content of a kaolin-lithium chloride mixture. The salt to kaolin ratios are 0, 9.5%, 14.7%. Similar to kaolin-calcium chloride mixtures, as the percentage of salt in the kaolin-lithium chloride increases, the water content of the mixture under the same equilibrium relative humidity increases.

![Figure 6-3 The relative humidity for a different compositions of kaolin-lithium chloride mixture, compared to the silica gel](image)

6.3 Future work

The experiments had shown that adding desiccant salts to kaolin will produce a solid mixture with a behavior similar to silica gel. The long time it takes for specimens to reach steady state and the special care needed to keep a container with a saturated salt solution for long time limited the number of experiments. For future investigations, curves with different ratios of lithium chloride should be tested. Another parameter that can be investigated is the highest relative humidity a specimen can be subjected to without losing its solid state. Also, other properties of these salt-clay mixtures could be measured. Properties such as density and specific heat can be measured as a function of ratio of salt to clay in the mixture.
Figure 6-4 Behavior of mixture of kaolin with lithium chloride with ratio 10:1 under different imposed relative humidity levels

Whether the observed phenomenon is worth implementing or not can be decided by modeling the material as a solid desiccant in a typical solid desiccant system such as a desiccant wheel. Such analyses have been reported by several investigators (Pesaran and Mills, 1987) using silica gel.
Chapter 7. Conclusions

The main accomplishment of this research is proving the concept of combining the electroosmotic phenomenon with the desiccant effect to achieve dehumidification using low voltage DC sources. A variety of activities were performed including generalized air conditioning analysis (Chapter 2), analytical modeling of the electroosmotic flow, EOF (Chapter 3), bench top experiments (Chapter 4), and simulation of a system that incorporates an electroosmotic dehumidifier, EOD with a conventional A/C system (Chapter 5). Studying the electroosmotic process closely, we gained some insights that are translated into conclusions or suggestions for future research.

To judge how efficient an air conditioning system may be, it is useful to define an ideal limit of operation. The traditional Carnot expression for the reversible limit of heat engines is helpful only in case of dry air. A more general COP was developed in this work based on a second law analysis for humid air. The general COP treats the air condition system as a black box. Only the exit and inlet conditions as well as the ambient conditions (temperature and humidity ratio) are required for determination of the ideal limit of operation. The difference in exergy between the inside and outside of the conditioned space determines whether the system needs work in order to change the state of the air, or if work can be produced as a result of the conditioning process.

The simulation of the electroosmotic process has shown that the phenomenon depends on the pore diameter. While small capillary diameters may not be easy to manufacture, they do exist in certain porous materials that have the required electrokinetic characteristics. Small pores have the advantage of having a higher dependence on the electric field than on the pressure gradient. This enables a membrane with small pores (less than 100 nm in diameter) to operate using small electric potentials, which make the process suitable to batteries, photovoltaic cells, fuel cells, and other low voltage sources. The use of low voltage also makes the use of EOD less dangerous which opens more opportunities to implement it.

Experiments with plaster membranes covered with a desiccant layer succeeded in moving water vapor against a pressure gradient using a small DC voltage. A setup for estimating the zeta potential was constructed based on measuring the streaming potential. The zeta potential of diatomaceous earth and fiberglass were measured and showed promising values for potential use.

Many issues were raised by the experimental activities of the research. All of them revolve around making the electroosmotic dehumidifier more efficient and more reliable. For example, incorporation of the desiccant layer onto the electroosmotic membrane and the connection of electrode surfaces on either side of the electroosmotic membrane are significant problem areas.

The flow resistances of the vapor across an EOD were studied and it was found that the flow of vapor to the desiccant surface is a primary resistance in that flow. The mass transfer coefficient of vapor from the room air to the surface of the desiccant affects the area needed for the membrane. It also affects the mass flux of water through the membrane and consequently the voltage required.

The incorporation of an EOD into an A/C system does not reduce the overall cooling load. However, decoupling the moisture conditioning from the sensible conditioning system converts the latent load into a sensible load. Dealing with a sensible load, the evaporator of the A/C system does not have to be as cold. This reduces the
load on the compressor and increases its isentropic efficiency as well. On the other hand, pumping water through the EOD needs additional power that the analysis showed that it depends on the configuration of the EOD and the efficiency of electroosmotic pump. In most cases, incorporating the EOD yields some savings.
Appendix

This appendix describes a method undertaken to measure the zeta potential of membranes. The results obtained were not consistent enough to pursue it further. The setup used, shown in Figure A-1, consists of a plastic container open from both sides, with the membrane cast in its bottom. A constant head of water acts on one side of the membrane, and the voltage across the membrane sides is measured. Because each membrane is expected to be different than the other, several membranes are manufactured and the flow experiment is repeated several times on each membrane. The value of the flow rate of water is observed also. Figure A-2 presents the data collected in one of the experiments.

Figure A-1 Setup to measure the streaming potential

Figure A-2 Mass accumulated on the scale and the voltage read across the membrane (streaming potential) for a plaster membrane. The black line shows a linear best fit of the voltage. The best fit is used to determine the average value of the streaming potential.
The voltage across the membrane was expected to be the same every time the experiment is repeated. But this value varied for the same membrane from experiment to another. The following table gives the average values of the streaming potential measured for some of the runs. That discrepancy in results is due to the non homogeneity of the material as well as the effect of water on the plaster. Water is thought to cause the ions in the membrane (which contribute in the charge carrying process) to deplete. The presence of water on the surface of the membrane caused small holes to appear on the surface.

Table A.1 Streaming potential for different runs on different specimens

<table>
<thead>
<tr>
<th>Specimen/run</th>
<th>Voltage [mv]</th>
<th>Pressure [kPa]</th>
<th>Flowrate [gram/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/1</td>
<td>153</td>
<td>0.4</td>
<td>0.323</td>
</tr>
<tr>
<td>½</td>
<td>64</td>
<td>0.4</td>
<td>0.455</td>
</tr>
<tr>
<td>1/3</td>
<td>100</td>
<td>0.4</td>
<td>0.356</td>
</tr>
<tr>
<td>2/1</td>
<td>35</td>
<td>0.4</td>
<td>0.336</td>
</tr>
<tr>
<td>2/2</td>
<td>0-3</td>
<td>0.4</td>
<td>0.350</td>
</tr>
<tr>
<td>2/3</td>
<td>~0</td>
<td>0.4</td>
<td>0.390</td>
</tr>
<tr>
<td>3/1</td>
<td>50</td>
<td>0.4</td>
<td>0.032</td>
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Bibliography


