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The Effects of Alkali Ions on Gas-Solid
Adsorption in an Electric Field

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M.S. degree in CHE

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**THE EFFECTS OF ALKALI IONS ON GAS-SOLID ADSORPTION
IN AN ELECTRIC FIELD**

By

Gregory Earl Stevens

A THESIS

**Submitted to
Michigan State University
in partial fulfillment of the requirements
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ABSTRACT

THE EFFECTS OF ALKALI IONS ON GAS-SOLID ADSORPTION IN AN ELECTRIC FIELD

By

Gregory Earl Stevens

The primary objective of this thesis was to investigate the effects enhanced alkali ion surface concentrations have on water vapor adsorption onto silica gel in the presence of an electric field. Fly ash collection efficiency in electrostatic precipitation is known to be reduced by high particulate electrical resistivities. Increased water vapor concentrations in the flue gas, as well as some conditioning agents such as alkali metal ions or sulfur trioxide, have been found to significantly decrease ash resistivity. (18) In this study, silica gel was chosen to model the fly ash in order to determine the effects of surface alkali metal ions, surface treatment methods, and non-uniform DC electric fields on water vapor adsorption rates. Listed in order of decreasing effect, potassium, magnesium, and sodium deposited on the surface of silica gel enhanced the water vapor adsorption rates. A non-uniform DC electric field enhanced the adsorption rates for both the untreated and alkali ion treated silica gel samples.

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I wish to express my appreciation to Dr. Bruce Wilkinson for his guidance and assistance throughout the course of this work, and for his patience during the completion of the final thesis. I would also like to thank my wife, Rebekah, for her motivation and unwavering support.

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Chapter I

Introduction

A. Motivation for Research

Electrostatic precipitation collection efficiency is known to be reduced due to high particulate electrical resistivities. These high resistivities, primarily attributable to the burning of low sulfur coal, cause "back corona" or "spark-over" which can lead to severe collection problems. The fly ash or dust electrical resistivity is not only sensitive to the composition of the coal itself, but to the flue gas as well. An increased water vapor concentration in the gas has been found to significantly decrease ash resistivity. Also, the addition of small amounts of conditioning agents which bind the water more tightly to the particulate surface has been known to have similar effects. (16)

Someshwar and Wilkinson have studied the effects of electric fields on gas-solid adsorption. They have found that water vapor adsorption rates onto silica gel are enhanced in the presence of D.C. electric fields. (17) A gravimetric method was used to examine the adsorption kinetics. Field-induced effects on adsorption involving silica gel containing Na^+ surface ions were reduced when the gel was treated with concentrated HCl to remove all surface ions. Surface ions seem to play a significant role in the field-induced mass

transport phenomena. However, the reduction in field-induced effects could be the result of a change in surface characteristics of silica gel due to HCl treatment. The effects of strong electric fields on silica gel with significantly enhanced surface alkali ion concentrations have not been investigated in the literature.

It was the goal of the present research to determine the effects HCl sample pretreatment has on the gas-solid adsorption characteristics of silica gel. Also investigated were the effects enhanced alkali ion surface concentrations have on water vapor/silica gel adsorption kinetics both in absence of and in the presence of non-uniform D.C. electric fields.

B. Research Objective and Outline

The initial emphasis of this research work was to establish the effect HCl pretreatment has on the surface structure and adsorption characteristics of silica gel. Following this, a method for treating the silica gel surface with sodium ions while retaining its original internal surface area and porosity was developed. Neutron activation analysis was utilized to determine surface ion concentrations present in the silica gel. Finally, the effects of surface alkali ion concentrations on the water vapor adsorption kinetics of silica gel both with and without non-uniform electric fields were examined.

This report is organized in the following manner. A summary is located in Chapter 2. The theoretical basis and

background for this work is presented in Chapter 3. Chapter 4 illustrates and describes the silica gel treatment methods, the experimental apparatus, and experimental procedures. Chapter 5 presents the experimental results and a discussion of these results. The conclusions and recommendations follow in Chapter 6.

Chapter II

SUMMARY

A. Introduction

Fly ash collection efficiency in electrostatic precipitation is known to be reduced by high particulate electrical resistivities. Increased water vapor concentrations in the flue gas, as well as some conditioning agents such as alkali metal ions or sulfur trioxide, have been found to significantly decrease ash resistivity. In order to study gas-solid adsorption on a porous solid more closely, silica gel was chosen to model the fly ash in a number of gas-solid adsorption experiments.

The experiments were designed to determine the following:

- The effect of silica gel wash methods on the surface sodium ion concentrations, water vapor adsorption capacity, and rate of adsorption,
- The best method for treating the silica gel surface with sodium ions,
- The effect of the alkali metal ions sodium,

potassium, and magnesium on the water vapor adsorption rates on silica gel, and

- The effect of non-uniform D.C. electric fields on the water vapor adsorption rates on silica gel with and without surface alkali metal ions.

B. Experimental Results and Conclusions

The experimental procedure is based on the exothermal water vapor adsorption process and the temperature rise associated with the adsorption. Qualitative information about the water vapor adsorption rates can be obtained by comparing the temperature history of the samples during adsorption. Approximately 50 to 70 mg of silica gel was placed in a 25°C, 90 percent saturated water vapor environment, and the temperature of the sample was recorded using a miniature thermocouple temperature sensing device. The concentration of surface alkali ions was measured using neutron activation analysis, and the water vapor capacity was determined using gravimetric techniques.

The Sigma Chemical Company S-2509 silica gel was found to contain 0.06 wt.% sodium "as received", of which 85% was removed by simply rinsing with deionized water, and 90% was removed by first soaking in concentrated HCl, followed by rinsing with deionized water. The water adsorption capacity was unaffected by the HCl pretreatment; however, the

temperature rise associated with the adsorption was less for the HCl pretreated and water rinsed samples than for the "as received" silica gel. Since the sodium was so easily removed from the silica surface, its form is believed to be an oxide of sodium, which has a noticeable heat release when it reacts with water. The lower water vapor adsorption temperature rise for the washed samples may then be a result of the absence of the reactive sodium oxide. The HCl pretreated, or ion-free, silica gel was used for the remaining tests involving alkali ion treatment.

The best method for treating the silica gel surface with sodium ions was to soak the samples in saturated NaCl solution for several hours. This was followed by rinsing with de-ionized water. This method resulted in over twice the sodium concentration as compared to the "as received" silica gel. In addition to depositing twice the number of ions, the ions were more securely bound to the silica gel surface since they could not be rinsed away with water.

All of the alkali metal ions tested resulted in the enhancement of water vapor adsorption rates on silica gel. For a given ionic concentration, potassium and magnesium enhanced the water vapor adsorption rates greater than sodium. It is difficult to make quantitative evaluations of adsorption rates on silica gel treated with magnesium, since its surface concentration was 60 to 70 percent less than that of sodium or potassium. (The divalent magnesium ion did not adsorb to the silica gel surface as readily as potassium or sodium because

it requires two adjacent active silanol groups, SiOH , for adsorption to occur.)

A 6 kV D.C. electric field enhanced the adsorption rates for all of the samples. The order of enhancement from greatest to least was Na, ion-free, K, and finally Mg. The sodium treated and ion-free samples, which exhibited the lowest non-field adsorption rates, were more affected by the electric field than the potassium and magnesium treated samples which had the highest non-field rates.

In comparing the temperature rise associated with the water vapor adsorption rates on the silica gel samples in a 6 kV D.C. electric field, the sodium treated sample experienced the highest initial adsorption rate. This was followed closely by the potassium, ion-free, and magnesium treated samples. The initial adsorption rate (which is defined as the rate during the first ten minutes of adsorption) is assumed to be primarily monolayer adsorption coverage. Multilayer adsorption occurs after that time. The magnesium treated sample appeared to have the highest multilayer adsorption rate, even though the magnesium molar concentration was much less than the sodium or potassium treated samples. This was due to either the higher charge density of the divalent ion (which reaches beyond the first few monolayers of adsorbed water) or the greater driving force for adsorption during the latter part of the experiment for the sample which adsorbed the least during the initial part.

Chapter III

Theory

A. Particulate Resistivity in ESP Performance

The electrical resistivity of fly ash is one of several important factors to be considered in the design of an electrostatic precipitator for the dry collection of particulates.

(5) High ash resistivity causes operating problems such as back corona and sparkover. (4) Since resistivity adversely influences the allowable electrical parameters in a precipitator, high resistivity necessitates the design of large precipitators for a given collection efficiency. The relationship between size, performance, and cost makes the knowledge about resistivity mandatory.

Fly ash resistivity is a function of the chemical composition of the coal burned, ash particle characteristics (particle size distribution, porosity), flue gas composition, chemical composition of the fly ash, temperature, and field strength. The combustion of low sulfur coal is a major source of high resistivity ash. (17)

Fly ash resistivity has been found to be inversely proportional to its surface area, which is a function of porosity and particle size. (3) This is due to the surface ionic conduction that exists on the fly ash particle. This surface conduction is affected by the chemical composition of the fly

ash surface. Chemical treatment of fly ash particles can directly influence the surface conduction and fly ash resistivity.

Surface conduction occurs by an electronic or ionic migration which is dependent on the physical and chemical adsorption of certain species on the ash surface to produce a conducting film. (19) This implies that conduction is governed by the ionization of the adsorbed species and that the component ions serve as charge carriers.

Since the principle component of fly ash is a glassy aluminosilicate particulate, surface conduction most likely occurs in a manner similar to that of glass. If this is the case, conduction takes place via an ionic mechanism in which alkali metal ions serve as the principal charge carriers. The flue gas composition plays an important role in providing the mobilizing environment for the carrier ions. (5) Flue gas composition will affect resistivity by providing a means for surface alteration of the fly ash. Flue gas water vapor content has a pronounced effect on fly ash resistivity (especially at lower temperatures). (4) The ash surface conductivity is directly dependent on the interaction between the surface and the water vapor. Water vapor, when adsorbed on the fly ash surface, acts as a mobilizing medium for the charge-carrying surface species. Alkali metal ions are also known to increase the surface conductivity (thus decreasing resistivity) by acting as charge carriers. Flue gas conditioned with both sodium compounds and water vapor has been

shown to lower ash resistivity. (19) Other conditioning agents, such as lithium and sulfur trioxide, have also been used with successful results. (6) There is a general observation that greater average electrical field stress across an ash layer decreases the resistivity. This is most likely a result of the increased mobility of charge-carrying ions. (19)

Since the effects of adsorbed water vapor and surface ions on fly ash resistivity can be so significant, it is important to understand the effects of certain surface constituents on the water vapor adsorption rates on fly ash in the presence of a DC electric field. This study investigates these effects using silica gel as the dielectric adsorbent to model the fly ash particles.

B. Gas-Solid Adsorption

There are two classifications of gas-solid adsorption as determined by the types of bonds that are formed between the adsorbate and the solid surface. Physical adsorption is a result of Van der Waals' forces between the adsorbate molecules and the solid surface. Chemical adsorption involves the sharing of electrons between the adsorbent and adsorbate. Both of these processes liberate heat which is associated with the type of bonds involved. The heat of adsorption evolved from physical adsorption is approximately equal to the heat of condensation. This is why physical adsorption is often thought of as a condensation process. Chemical adsorption, however, generates heat equal to the heat of reaction between

the adsorbate and the solid material. Due to the nature of the bonds, physical adsorption may occur in multiple molecular layers, whereas chemical adsorption is limited to one monolayer. (9)

The effect of temperature on the rate of adsorption can indicate the adsorption type. Since physical adsorption is typically a condensation process, the adsorption rate increases with decreasing temperature. Conversely, chemisorption undergoes a rate decrease with decreasing temperature. This is due to the exothermic nature of the molecular bonds involved in chemical adsorption and the activation energy of the reaction taking place.

C. Water Adsorption on Silica Gel

Silica Gel is a known adsorbent for water vapor and is commonly used as a drying agent. Other commercial applications include use as a catalyst component and support, refractory, finely divided filler and reinforcing agent. (20)

Silica gel was chosen as an adsorbent for this study because it can be produced with well-defined pore sizes and it has a high capacity for water vapor adsorption. The silica gel used in these experiments was chromatographic grade Sigma Chemical silica gel S-2509. Someshwar showed this silica gel to have a maximum water capacity of 70% by weight of dry gel.

(17)

Table 3.1. Physical Properties of Silica Gel S-2509 (18)

Source:	Sigma Chemical Co.
Particle size:	63-200 μm
Mean pore radius:	30.7 Angstroms
Bulk density:	0.461 g/cm^3
Specific surface area:	456.1 m^2/g
Total void fraction:	0.794
Internal void fraction:	0.323
Monolayer adsorbed water:	6.49 wt. %

Experimental evidence has been presented suggesting that water vapor adsorption (physical) is initially restricted to silanol sites on the silica surface. (2,11,20) The silanol sites are surface Si-OH groups which act as a weak acid, leaving the polar oxygen atom available as a bonding site for polar water molecules. The remainder of the silica surface, which does not adsorb water vapor, is composed only of silicon and oxygen atoms in approximately the same general arrangement of the bulk structure but subject to displacements normally expected in a surface layer. The silicon-oxygen surface bonds are essentially non-polar. This explains why water vapor does not adsorb on surfaces void of silanol groups.

Figure 3.1 shows the water-silica gel surface bonds. Klier et. al.'s infrared study indicates that the silanol groups provide a donor hydrogen bond to the adsorbing water molecules. (11) Bassett et. al. found that the adsorption

heat (at less than monolayer coverages) was as low as 6 kcal/mole, and that the water molecules tend to form clusters in which the energy per molecule is close to the heat of condensation (10.6 kcal/mole) long before all adsorption centers are occupied.

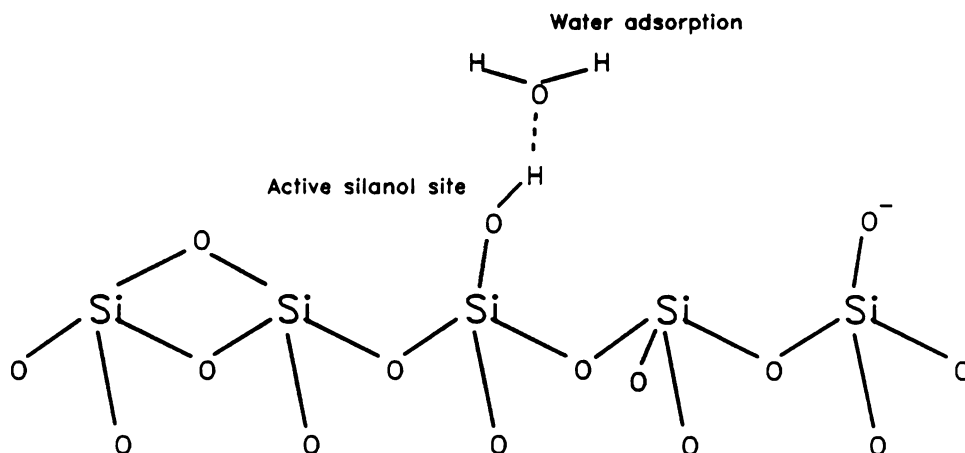


Figure 3.1. Chemical Structure of Silica Gel Surface.

D. Silica Surfaces Treated with Alkali Metals

Nishioka and Schramke conducted a study on the effect of adsorbed cations on the interaction of water with the silica surface. (13) They used a P_2O_5 electrolytic cell for detecting water desorption rates. This method was reported to possess the sensitivity to detect water thermodesorbed from samples with specific areas as small as $0.1 \text{ m}^2/\text{g}$. The detection limit was $0.1 \text{ }\mu\text{g}$ of water desorbed from a 1 g sample.

The cations Na^+ and Ca^{2+} were found to chemically adsorb only onto the silanol groups existing as the base SiO^- . Since the surface silanol groups are weakly acidic, only a small fraction exist as the conjugate base, SiO^- . Because of this, Nishioka and Schramke noticed little adsorption of the Na^+ and Ca^{2+} cations onto the silica gel surface. However, silica gel treated with aluminate ion had a higher affinity for cation adsorption. This is due to the more strongly acidic behavior of the surface group aluminol, AlOH . Each sodium ion is held by one aluminate site, and each calcium ion is held by two aluminate sites. Water vapor was attracted to the cation treated surface more readily than to the non-treated surface, and much more readily to the aluminate-cation treated silica surface.

An earlier study by Panchenko et. al. yielded similar results. They attributed the water vapor sorption rate increase on metal cation-treated silica gel to the lower potential barrier which a water molecule must overcome in order to move from one location to another. (15) Panchenko also noted an increase in the sorption capacity of silica gel when treated with the metal cations. The difference in sorption capacities indicated the presence of additional sorption centers located at the inner surface of the micropores. In addition, the bivalent ions appeared to produce a closer packing of sorbed water molecules, inasmuch as two monovalent ions occupy more surface area than one bivalent ion.

In Someshwar's thesis, which focused on the field-induced effects on water vapor adsorption, the results were similar. (18) The industrial gel samples used for the experiments were found to contain small impurities of sodium ion. These samples were soaked overnight in concentrated HCl and then washed repeatedly with deionized water to reduce the sodium ion concentration. The samples were dried in a 120°C oven overnight. The samples with reduced Na⁺ ion concentrations exhibited a smaller field-induced enhancement in water vapor adsorption rates compared with the as-received silica gel. The author attributed this to a possible "activation" of the silica surface from the HCl treatment leaving a more energetically favorable surface for adsorption. Several other investigators have found, however, that heating the silica gel samples to temperatures as low as 110°C may cause a reduction in the number of surface silanol groups. (10, 11, 20) They have also seen, however, an increase in silanol groups following treatment of the gel in boiling water. This study investigated the effect of HCl treatment on water vapor adsorption rates on silica gel in an attempt to determine whether the resultant loss in field-induced enhancement is due to the loss of surface Na⁺ ions, a reduction in the surface silanol groups, or a change in the surface area and structure of the silica gel.

E. Adsorption of Water Vapor on Silica Gel in an Electric Field

Much work has been done to date on mass transfer processes in an electric field. Griffiths and Morrison (7), and Harker and Ahmadzadeh (8) have studied the effects of electric fields on mass transfer from falling drops. They studied both steady (direct) and alternating electric fields and concluded that increases in mass transfer rates are due to the increase in Reynolds' numbers rather than enhanced interfacial turbulence and internal circulation.

A related study by Lincoln and Olinger investigated the adsorption of hydrogen and ethylene on both a porous nickel catalyst and on nickel foil in the presence of a D.C. electric field. (12) They concluded that surface interactions of a fluid and solid could be affected through application of an appropriate electric field. The evidence suggested that adsorption rate and capacity can be increased for some gases due more to a chemical phenomenon rather than physical. This conclusion was based on the observations that accompanying the altered adsorption results was a shift in the heat of adsorption and, thus, in the mechanism of adsorption. Furthermore, as adsorbate diffusion became important at the higher pressures, the effects of the imposed voltage on adsorption diminished.

The effect of electrostatic fields on adsorption of polar vapors on a dielectric surface has received limited attention in the literature. Panchenko et. al. conducted an

experimental study on the effect of surface cations on the internal mass transfer of water vapor within the silica gel structure. (15) Enhanced adsorption rates in the D.C. electric field were attributed to the polarizing effect on the water vapor, adsorbed water, and adsorbent.

The greatest effect was seen on silica treated with K^+ and Ca^{2+} ions. This was supposedly due to a redistribution of moisture toward higher densities accompanied by a drop in concentration of hydrated ions in regions of a capillary-porous body where the electric or the magnetic field gradient and intensity are highest. Panchenko theorized that a rise in the alkali ion surface concentration causes a change in the rate and degree of water polarization. This is followed by the stronger effect of a constant non-uniform field on the moisture transfer rate.

A study by Panasyuk et. al. also found that the application of inhomogeneous magnetic and D.C. electric fields accelerates the attainment of equilibrium through the enhancement of internal mass transfer in the sample. (14) This effect was not seen with nonpolar vapors, such as CCl_4 . From the adsorption rate curves in Panasyuk's study, it is seen that, in the initial stages (when the pressure gradient and adsorption rate are large) the fields accelerate the process only slightly.

Someshwar and Wilkinson investigated the possible influence of D.C. electrical fields on the conditioning of coal fly ash with water vapor. (18) Silica gel was used as

the model for the fly ash. One of the major conclusions was that the presence of a non-uniform D.C. field surrounding the solid particles causes an increase in the rate of adsorption but not the total amount adsorbed. The presence of alkali metal ions on the silica surface had a strong enhancing effect on the adsorption rate. The key variable in the field effects was found to be the local, internal electric field gradient in the pores rather than the external applied field.

Chapter IV

Experimental Equipment and Procedures

A. Introduction

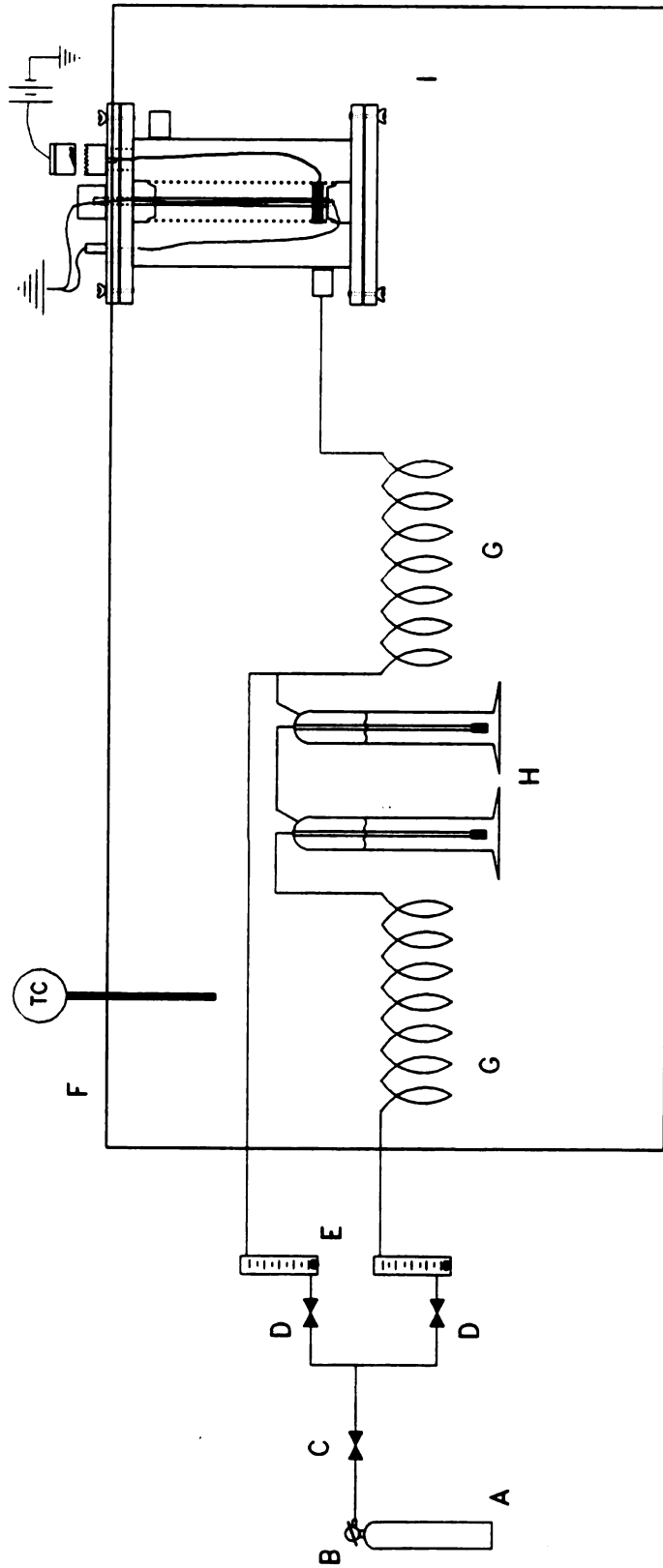
The experimental apparatus and procedures are presented in this section. The experimental method chosen was based on the thermodynamics of gas-solid adsorption. Silica gel experiences an increase in temperature as water vapor is adsorbed onto its surface. This is due to the heat evolved at the silica gel - water vapor interface during the exothermic adsorption process. Consequently, the temperature of a silica gel sample in the presence of water vapor can be monitored to indicate the extent of adsorption. With an adequate energy balance for the system, the temperature rise over a period of time can provide quantitative information regarding the adsorption kinetics. In this particular study, however, the thermal properties of the sorption process are evaluated such that only qualitative generalizations can be made for the silica gel - water vapor system and the various factors governing the adsorption kinetics. The modeling and mathematic computations involved in a more quantitative study would be too rigorous for a work of this scope.

This chapter will provide a description of the flow scheme for the adsorption experiments. Next, a detailed description of the experimental apparatus, including the

adsorption chamber and temperature monitoring equipment, will be discussed. Finally, the experimental procedures will be outlined.

B. Flow Scheme

A flow diagram is presented in Figure 4.1. The air flow originated in the pressurized air cylinder containing medical grade breathing air. The total air flowrate of 250 cc/min was controlled by two precision pressure regulators. The air was dried as it passed through a holding tank containing CaSO_4 dessicant particles. This dry stream was channeled into two separate streams controlled by precision needle valves and measured by Lab Crest Century flowmeters. The first of these streams entered a 25°C constant temperature water bath at a rate of 225 cc/min and passed through a copper coil heat exchanger before being saturated with water in two glass sintered water bubblers in series. The second stream, which was dry air at 25 cc/min, entered the water bath and combined with the first saturated air stream to produce 90% saturated ($P/P_g = 0.9$) water vapor. This vapor passed through another copper coil heat exchanger before entering the adsorption chamber containing the silica gel sample. The adsorption chamber was also submerged in the 25°C constant temperature water bath. Finally, the gas stream exited the adsorption chamber as system effluent.



- A. Pressurized air cylinder
- B. Pressure regulator
- C. Low pressure regulator
- D. Precision needle valves
- E. Calibrated rotameters
- F. Temperature controlled water bath (25° C)
- G. Copper tubing heat exchangers
- H. Glass scintered bubbler (two in series)
- I. Adsorption Chamber
- J. Drying Chamber

Figure 4.1. Experimental flow diagram.

C. Experimental Equipment

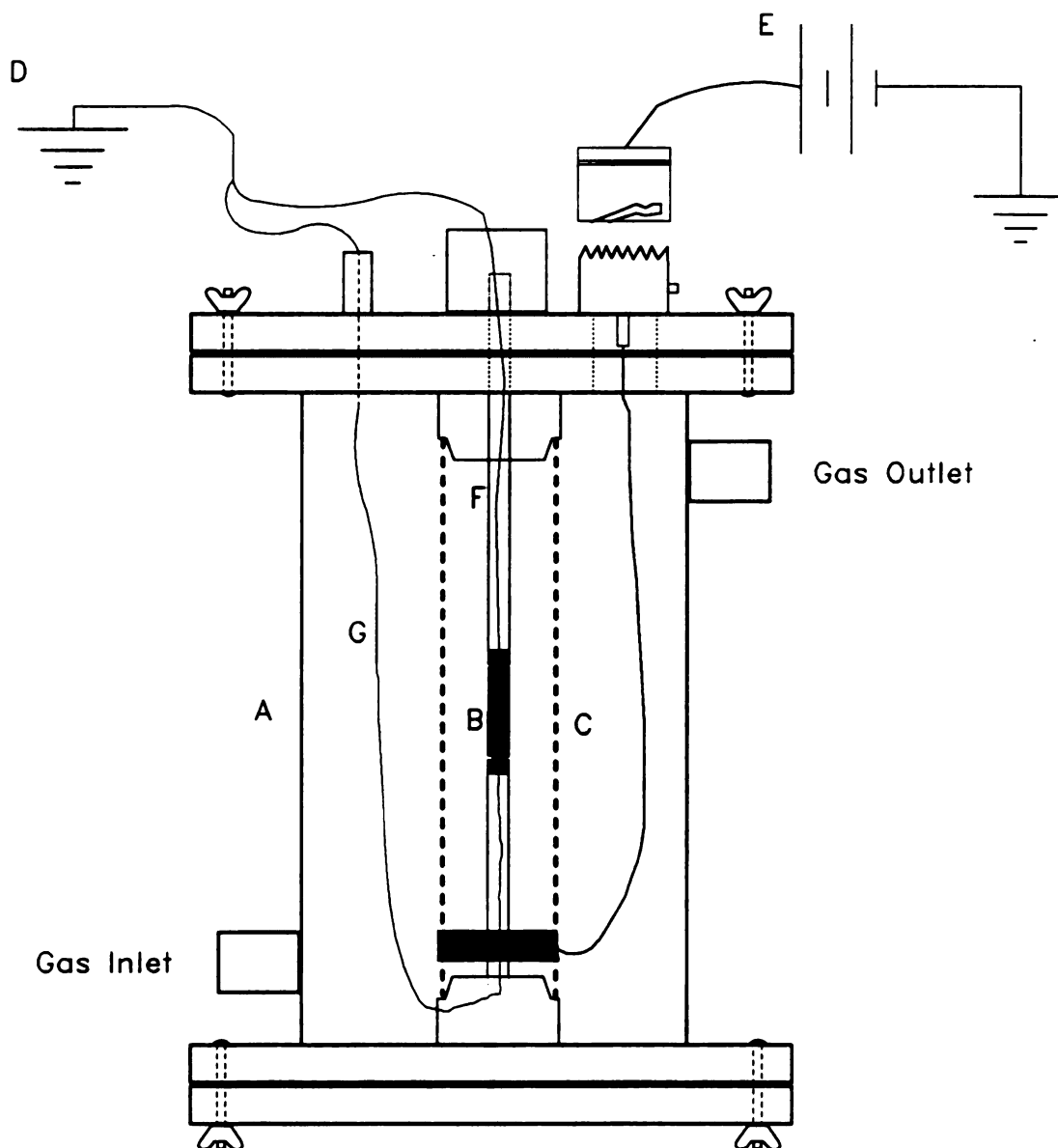
1. Adsorption Chamber

The adsorption chamber, shown in Figure 4.2, was an airtight plexiglass cylinder with an inlet for moist air flow and an outlet for the effluent air stream. The cylinder is flanged at each end to accommodate the flat plexiglass bottom and lid, which are secured by bolts with wing nuts and kept airtight via two rubber gaskets. The chamber was designed for easy entrance and self-centering of the sample within a cylindrical wire mesh screen which acts as the positive electrode for the D.C. electric field. The lid contains a coaxial connector for input of the positive electrode from a Spellman high voltage D.C. power supply.

The copper mesh screen (2.5 centimeters in diameter) was installed concentrically within the plexiglass chamber. The silica gel sample container was a fine mesh copper cylinder 0.35 centimeters in diameter and 1.3 centimeters in length. This container was held concentrically inside the copper screen by two plexiglass cylindrical inserts. The electric field ground wire was constrained longitudinally in the center of the silica gel sample and exits through the lid of the adsorption chamber.

2. Temperature Monitoring Equipment

The temperature of the silica gel sample was monitored using an iron/constantan (type J) thermocouple. The thermocouple wire was also used as the ground wire for the



- A. Adsorption chamber
- B. Sample container
- C. Cylindrical wire mesh for electric field
- D. Ground
- E. 6 kV D.C. Power Supply
- F. Sample support tubes
- G. Thermocouple/ground wire

Figure 4.2. Adsorption chamber for silica gel experiments.

electric field and consequently was chosen to be 0.005 inches in diameter to provide a large potential field gradient in the silica gel sample. The thermocouple wire passes axially along the center of the adsorption chamber, with the joint of the iron and constantan leads halfway along the axial length of the silica gel sample. The thermocouple bead was formed by bringing the iron lead in through the top of the cell, twisting it to the constantan lead and soldering the connection. The joint was approximately 0.015 inches in diameter.

The temperature readings are obtained by determining the millivolt output of the thermocouple and utilizing thermocouple - millivolt reference tables. A cold junction compensator from Omega Engineering, Model CJ-J, was used to avoid the problems and inaccuracies associated with maintaining an ice bath thermocouple reference. The cold junction compensator provides a steady electrical thermocouple reference corresponding to zero degrees celcius and outputs an accurate thermocouple signal on copper leads to be read by a potentiometric device.

D. Experimental Procedure

The preparation of silica gel samples, neutron activation analysis techniques, and the procedures for evaluating the temperature changes in silica gel are presented below.

1. Silica Gel Samples

Silica gel S-2509 from Sigma Chemical Company was used

for all of the experiments. Four different treatment methods were used to either clean or modify the silica gel surface. The "as received" silica gel was dried in the oven at 120°C overnight before being used.

a. HCl Pretreatment: 400 mg of silica gel was placed in 100 ml concentrated hydrochloric acid for 12 hours. The slurry was then diluted with 150 ml distilled water and filtered with an aspirated buchner funnel. The sample was filtered and washed with an additional 200 ml distilled water. The filtrate was discarded and the silica gel was placed in 200 ml distilled water for four hours before the final filtration. The washed silica gel was placed in a 120°C oven overnight for drying.

b. Sodium Treatment: Following HCl treatment, the silica gel was placed in a solution of 5 N NaCl (saturated) solution overnight (approximately 12 hours). This slurry was filtered and washed with distilled water. A four hour distilled water soak preceded the final filtration and the sample was dried overnight in a 120°C oven.

c. Potassium Treatment: This was similar to the sodium treatment, with the exception that a saturated potassium chloride solution was used for the treatment.

d. Magnesium Treatment: This was also similar to the sodium treatment, with the exception that a saturated magnesium chloride solution was used for the treatment.

2. Neutron Activation Analysis

The basic principle of activation analysis consists of

placing the sample to be analyzed in a flux of thermal neutrons for a sufficient time to produce enough radionuclide product to measure with the desired statistical precision. The Michigan State University Reactor Laboratory's TRIGA nuclear reactor served as the source for the neutron flux. The comparative method was used for quantitative determinations of alkali ions present in the prepared silica gel samples. Standard samples of alkali hydroxides were prepared at various concentrations as comparators which were positioned in parallel with the silica gel samples for neutron activation. Consequently, both the experimental samples and the comparator samples were irradiated under the same flux conditions. A Ge-Li detector was used to analyze the samples. A multi-channel analyzer allowed the measurement of the gamma peaks.

3. Thermal Analysis of Adsorption

The experimental procedure for studying water vapor adsorption rates on silica gel via thermal analysis is presented below in outline form:

- a. Following pretreatment with HCl and treatment with alkali metal salts (as described in section D.1 above), the silica gel sample was placed in a 120°C oven for approximately 12 hours to desorb any surface moisture.

- b. The thermocouple wire was threaded through the sample chamber and into the sample container. The wire was brought out through the lid of the chamber.

c. One hour prior to loading the sample, 100 cc/min dry air was passed through the adsorption system to purge any moisture in the gas lines or adsorption chamber.

d. The sample was loaded from the oven immediately into the sample container, which was then lowered into the sample chamber and centered within the cylindrical copper mesh electrode via the two plexiglass inserts. The plexiglass inserts were used both to hold the sample in place within the electric field, and to guide the ground/thermocouple wire through the center of the sample.

e. The system was allowed to reach equilibrium temperature for approximately two hours in the constant temperature water bath at 25°C. The dry air continued to flow through the system during this time.

f. If the experiment was to be run with an applied electric field, the positive electrode from the high voltage D.C. power supply was connected to the BNC coaxial connector located on the lid of the adsorption chamber.

g. The initial temperatures of the water bath and that of the sample were noted and the thermocouple wire was connected to ground for the electric field experiments.

h. At the initiation of the experiment 90% of the 250 cc/min air stream was channeled to the water bubblers and, for the electric field experiments, the 6 kV D.C. electric field was activated.

i. The temperature of the sample was recorded at various intervals during the adsorption process. For the

experiments using an electric field, the power supply was momentarily turned off and the thermocouple wire was disconnected from the ground and connected to the data acquisition equipment for a temperature measurement.

j. Temperature data was usually taken at 4, 6, 8, 10, 15, 20, 25, 30, 40, 50, and 60 minutes into the adsorption process. The temperature data was plotted to indicate adsorption rate differences for the various test conditions.

E. Experimental Reproducibility

The experimental reproducibility of the thermal analysis tests is illustrated in figure 4.3. This graph represents the data from three identical tests involving silica gel that had been treated with concentrated HCl (see D.1.a above for the treatment procedure). The standard deviation for the peak temperature rise was approximately 0.05°C .

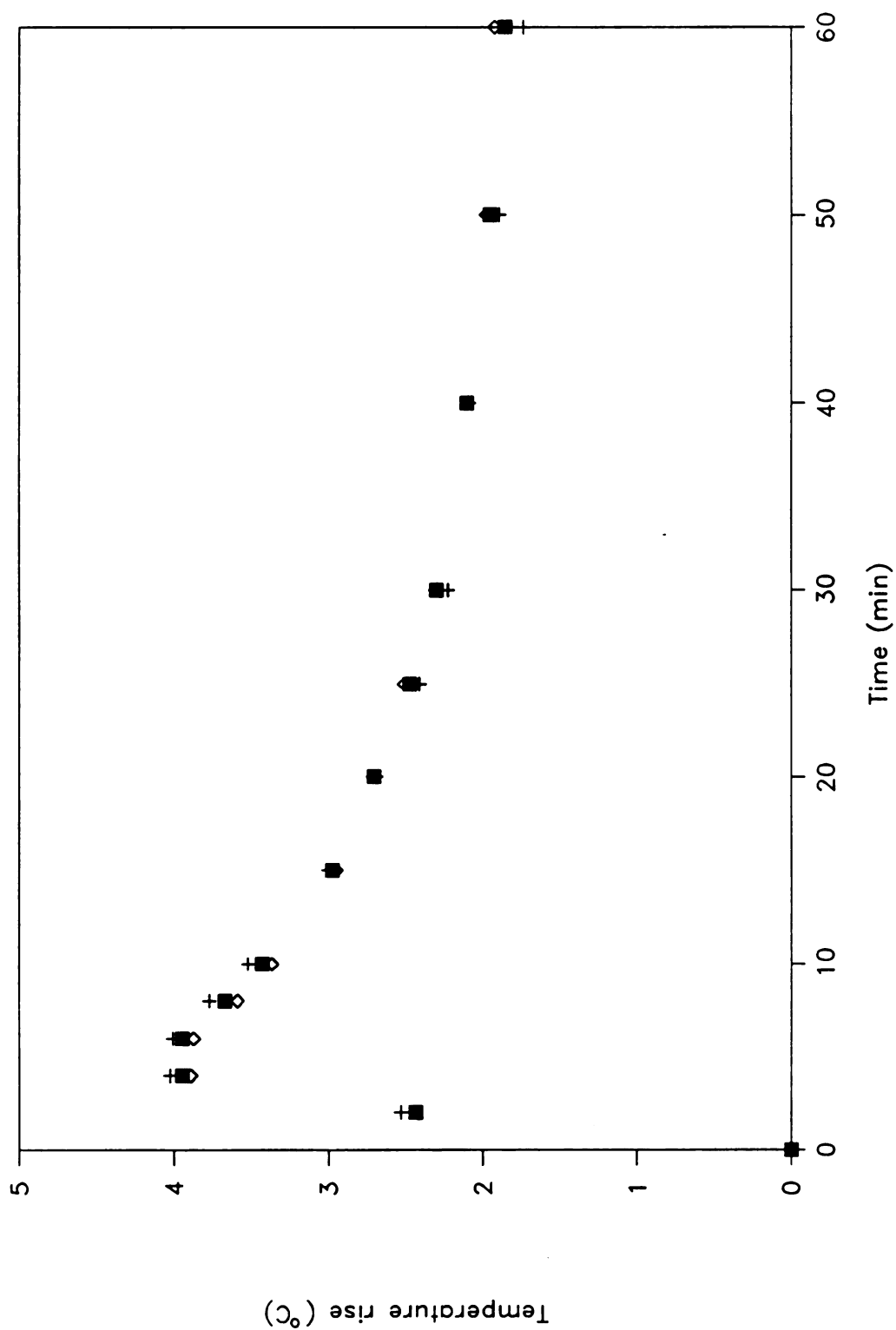


Figure 4.3. Reproducibility of data for thermal experiments involving water vapor adsorption on HCl treated (ion-free) silica gel. ($P/P_s = 0.9$, $T = 25^\circ\text{C}$)

Chapter V

Experimental Results and Discussion

This section presents the results for the experiments involving water vapor adsorption on silica gel in the presence of a D.C. electric field and the various methods of treating the silica gel surface. Chapter IV presented the experimental procedure for these tests. The first section discusses the results of tests which established the effect HCl pretreatment had on the surface characteristics and adsorption kinetics of silica gel. The second section presents the results for the determination of a method for treating the silica gel surface with mono- and bi-valent alkali ions while retaining its original water vapor adsorption capacity. Finally, test results for water vapor adsorption on silica gel with surface alkali ions in the presence of a D.C. electric field are presented.

A. HCl Pretreatment of Silica Gel

The method of HCl pretreatment of Sigma silica gel S-2509 for these tests was conducted similarly to the HCl pretreatment method in Someshwar's tests. (17) Two other S-2509 silica gel samples were compared with the HCl treated samples. The first sample was untreated, dried silica gel

The second sample was simply rinsed with deionized water and placed in a 120°C oven overnight for drying.

Three variables were used to evaluate the effect of HCl pretreatment on silica gel: Water vapor adsorption capacity, sodium concentration in the silica gel, and water vapor adsorption rates.

1. Effect of HCl Pretreatment on Adsorption Capacity.

In Someshwar's experiments, silica gel that was to be treated with alkali ions was first pretreated with concentrated HCl to remove any foreign ions and then washed with deionized water. The effect of this pretreatment on the silica gel, however, has never been clearly determined. The question is, does treatment of silica gel with concentrated HCl alter the internal structure or surface chemistry of the silica? Since the surface of the silica gel contains the active, slightly acidic silanol groups, it would seem that the presence of a strong acid would contribute to the number of these active sites. However, the strong acid also has the potential to change the pore structure, thereby actually decreasing the capacity for water vapor adsorption within the silica gel. These questions can be answered in part by observing the effect of pretreatment on the water vapor adsorption capacity of the gel.

The maximum water vapor capacity of various silica gel samples was determined by placing the sample in a saturated water vapor stream for 12 hours and comparing the saturated

Table 5.1. Effect of Pretreatment on Water Vapor Adsorption Capacity for Silica Gel S-2509.

<u>Pretreatment Method</u>	<u>H₂O Capacity g H₂O/g dry gel</u>
Untreated	0.650
H ₂ O Rinse	0.642
HCl Treatment	0.667

sample weight with that of the dry sample. Table 5.1 shows the capacity test results for three silica gel samples. The first sample was untreated or "as received", the second was rinsed with deionized water and dried, and the third was treated with HCl, rinsed, and dried (see Chapter IV for specific treatment methods).

The two pretreatment methods had very little effect on the total adsorption capacity of the silica gel. The HCl treatment may have enhanced the adsorption somewhat, but the magnitude of the experimental enhancement was too small to draw general conclusions.

2. Effect of HCl Pretreatment on Surface Sodium Concentration.

Silica gel S-2509 received from Sigma Chemical contains a residual amount of sodium on its surface. The form of this

sodium is not known. However, from the previous section it appears to have a significant effect on the water vapor adsorption rate and the temperature rise associated with that rate.

Neutron activation analysis was conducted on the three silica gel samples that were studied in the previous section: untreated gel, H₂O rinsed gel, and HCl treated gel. Table 5.2 lists the results of these analyses.

Table 5.2 Effect of Pretreatment on Surface Sodium Concentration.

<u>Pretreatment Method</u>	<u>Wt.% Na</u>
Untreated	0.060
H ₂ O Rinse	0.009
HCl Treatment	0.006

The water rinse decreased the silica gel sodium content by 85%, and the HCl treatment resulted in a 90% decrease. The ease of dissociation of sodium indicates either a weak bond between the surface silanol groups and sodium, or that sodium is present in a residual form (perhaps as an oxide) which is easily rinsed away with water.

3. Effect of HCl Pretreatment on Water Vapor Adsorption Rates.

Temperature studies were conducted to determine the effect of HCl pretreatment on the water vapor adsorption rate on silica gel. The procedure for the tests is described in Chapter IV. The temperature rise associated with the water vapor adsorption is shown as a function of time in Figure 5.1 for the three silica gel samples. All of the tests were conducted with $P/P_g = 0.9$ and at 25°C and with no imposed electrical field. From this data it appears that both the water rinse and the HCl pretreatment have an adverse effect on the water vapor adsorption rates.

The decrease in adsorption rates for the pretreated samples may be due to the effect of drying the silica gel samples in the oven following the water rinsing. The effect of temperature on the concentration of surface silanol groups is well documented. (10,16,20) Iler found that rapid heating of wet silica gel contributes to the loss of internal surface area and adsorption capacity as a result of sintering. He also found that repeated wetting and drying of the silica gel with heat at temperatures as low as 120°C caused a reduction in the surface hydroxyl group concentration.

Since the samples were shown to retain their adsorption capacity when pretreated, the reduction in adsorption rates is not likely due to sintering of the silica surface. One possible explanation is the loss of surface hydroxyl groups and the resulting decrease in water vapor adsorption rates due

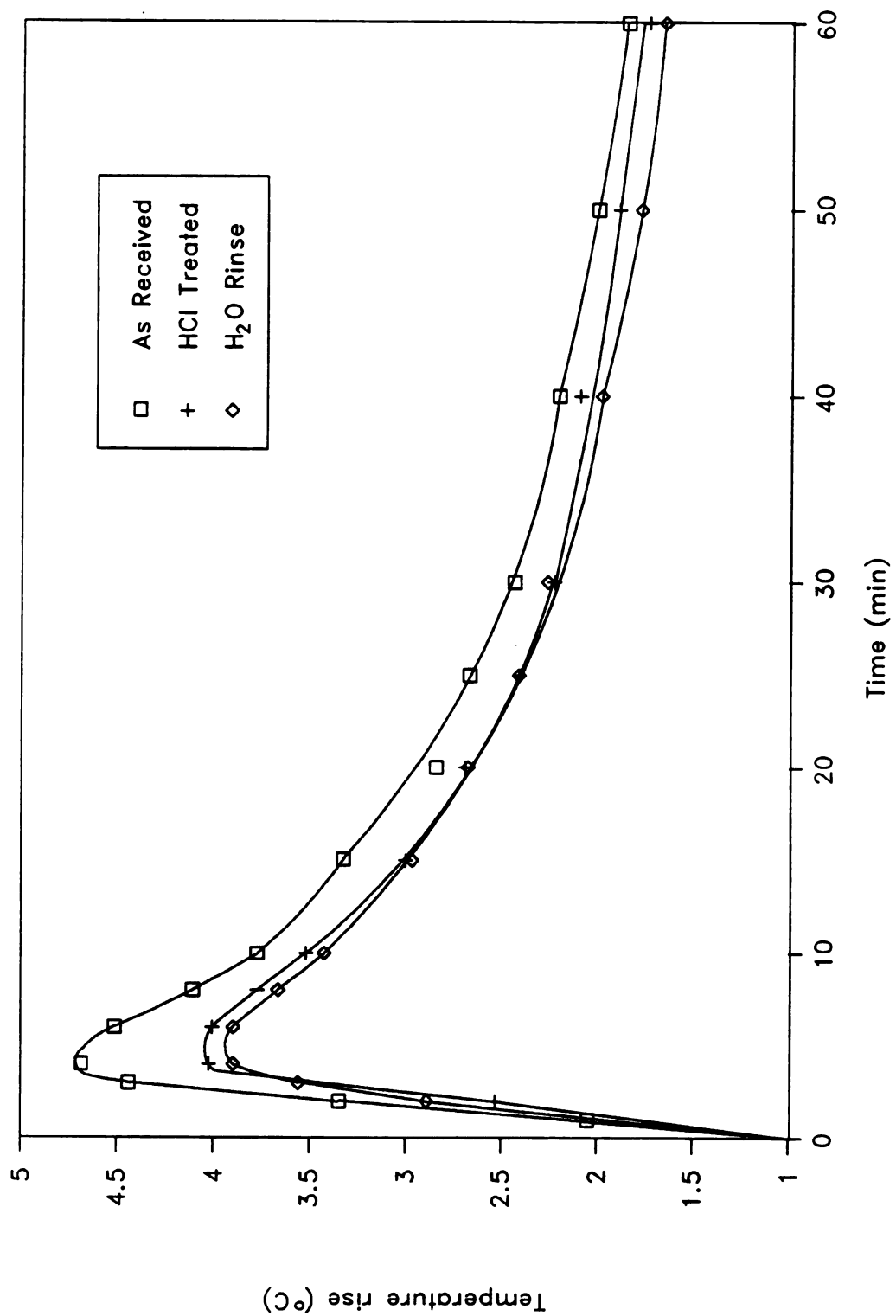


Figure 5.1. Effect of HCl treatment on the temperature rise associated with water vapor adsorption on silica gel.

to the decrease in active sorption sites. This decrease in sorption sites would not necessarily affect the total adsorption capacity, since capacity is dependent on total void fraction rather than the surface chemistry.

Another possible explanation for the higher adsorption rates in untreated silica gel is the presence of trace amounts of sodium. Neutron activation analysis revealed that the untreated silica gel "as received" contained approximately 600 ppm sodium. If the sodium is present as surface sodium oxide which reacts exothermally with water, the higher temperature rise during the water vapor adsorption tests may be due to the added energy released by this reaction during the initial stages of the adsorption process. The reaction occurs as follows:



A simple energy balance yielded an adiabatic temperature rise of approximately 9°C if all of the sodium on the "as received" sample reacted with water vapor. This would account for the the greater temperature rise for the untreated samples in these experiments.

B. Silica Gel Surface Treatment Method

Someshwar and Wilkinson (18) reported an enhancement in water vapor adsorption rates when the surface of the silica

gel was treated with alkali metal ions. The optimum method of surface treatment was not determined, however. Thus, the following tests were conducted.

Two methods of treating the silica gel surface with sodium ions were investigated. Both methods used silica gel that had first been pretreated with HCl and water. The first method involved soaking the sample in a solution of sodium chloride salt for several hours, followed by rinsing and soaking the sample in deionized water. The sample was then dried in a 120°C oven overnight. The second method was similar to the first, except that a solution of sodium hydroxide was used instead of the salt. The NaOH concentrations used were .001, .005, .01, and 0.1 N.

Three parameters were used to evaluate the sodium treatment methods. They were: a) the concentration of sodium in the solid silica gel samples following treatment, b) the water vapor adsorption capacity of the treated silica gel, and c) the water vapor adsorption rate on the sample.

1. Sodium Concentration by Neutron Activation Analysis

Several concentrations of sodium salt and base were used in the experiments to treat the silica gel samples. The concentrations of sodium adsorbed onto the silica gel for the various treatment methods is listed in Table 5.3. Also included are the concentrations of sodium in the "as received" silica gel and the pretreated samples.

The samples with greater than .001 N NaOH contained considerably more sodium than the samples treated with the salt solutions. This can be attributed to the chemical nature of the silica surface. Since it is weakly acidic, it would

Table 5.3. Effect of Silica Gel Treatment Method on Sodium Ion Concentration.

<u>Treatment Method</u>	<u>Wt.% Na</u>
Untreated	.060
H ₂ O Rinse	.009
HCl Treatment	.006
5 N NaCl	.122
4 N NaCl	.128
.10 N NaOH	2.31
.01 N NaOH	.580
.005 N NaOH	.373
.001 N NaOH	.006

readily react with a base such as NaOH. However, the chemical reactions taking place may not be occurring exclusively on the surface of the silica gel. The NaOH may also be reacting with the gel structure itself, thus altering the pore diameter and internal surface area. This can be determined using the adsorption rate and capacity studies. The samples treated

with saturated NaCl solution contained approximately twice the amount of sodium as the untreated samples.

In Section A.2 of this chapter the effect of HCl pretreatment on the surface concentration of sodium was investigated and it was shown that 90% of the sodium which was present in the "as received" S-2509 silica gel was removed following a water rinse. Table 5.3 indicates that the sodium which is deposited on the silica gel surface following treatment with NaCl is more strongly bound and can not be removed with just a water rinse. This would indicate that the sodium in the "as received" sample is just a residual form which is easily removed.

2. Effect of Sodium Treatment Method on Water Vapor Adsorption Capacity.

Since the water vapor adsorption capacity is a good indicator of porosity and void fraction for a porous adsorbent, it was used to determine the effect, if any, of sodium treatment methods on the silica gel structure. The adsorption capacities for silica gel samples that were pretreated with HCl and water, followed by either saturated NaCl or .005 N NaOH treatment are presented in Table 5.4. (All samples were rinsed with distilled water and dried for 12-18 hours before testing).

The sodium hydroxide concentration of .005 N was chosen because it was the lowest concentration used which resulted in a significant increase in the amount of sodium deposited onto

Table 5.4. Effect of Sodium Treatment Method on Water Vapor Adsorption Capacity.

<u>Treatment Method</u>	<u>Capacity (Wt. %)</u>
Concentrated HCl	67
5 M NaCl	69
.005 N NaOH	52

the silica gel. The adsorption capacity of the sample treated with NaOH decreased by approximately 22 percent, whereas the capacity of the sample treated with the salt increased by three percent.

The reduction in water vapor adsorption capacity for the sample treated with the base is most likely due to the reaction of NaOH with the slightly acidic silica gel structure.

3. Effect of Sodium Treatment Method on Water Vapor Adsorption Rates.

Changes in surface structure of the silica gel due to reaction with NaOH or NaCl may also be evident in the water vapor adsorption rates. Temperature studies were conducted on the samples to determine these effects using the procedures described in Chapter IV.

Figure 5.2 shows the temperature rise associated with the water vapor adsorption on the silica gel samples treated

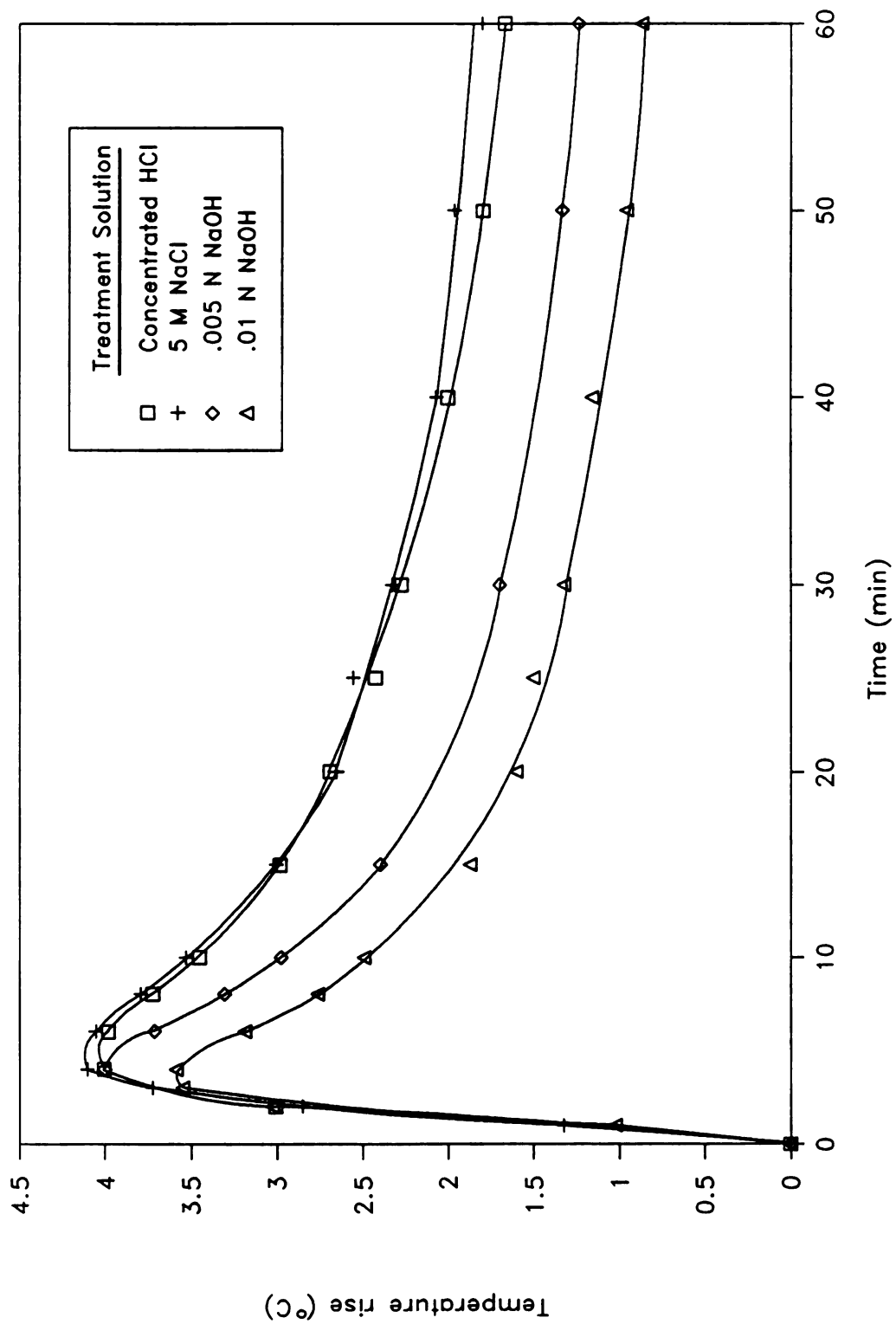


Figure 5.2. Effect of sodium treatment method on the temperature rise associated with water vapor adsorption on silica gel.

with both NaOH and NaCl. Two different concentrations of NaOH were used, .005 and .01 N. All of the tests were conducted with $P/P_g = 0.9$ and at 25°C.

The temperature study results indicate that the adsorption rate for the samples treated with NaCl were unaffected, whereas the samples treated with NaOH experienced a decrease in water vapor adsorption rates. The decrease in temperature rise, or adsorption rate, for the samples treated with NaOH was proportional to the concentration of base used. The reduced rate with the NaOH treated silica gel was observed in spite of the fact that higher sodium concentrations were present on the silica gel.

C. Water Vapor Adsorption on Silica Gel with Surface Alkali Ions.

Sigma Chemical S-2509 silica gel was treated with the alkali metal ions sodium, potassium, and the divalent magnesium. The treatment methods are discussed in Chapter IV. All of the samples were first pretreated with HCl to remove any residual surface species that may have been present on the "as received" sample. The concentration of alkali metal ion adsorbed onto the silica gel surfaces following the various treatments is listed in Table 5.5 as both percent by weight and molar concentration. The molar concentration is useful for comparing the number of silanol sights which were occupied.

On a mass basis there was 35 percent more potassium

Table 5.5. Alkali Ion Concentration on Treated Silica Gel.

<u>Sample</u>	<u>Wt. % alkali</u>	<u>mmole/g</u>
5 M NaCl Treated	.122	53.1
4 M KCl Treated	.165	42.2
4 M MgCl ₂ Treated	.04	16.5

adsorbed onto the silica gel than sodium; however, on a molar basis there was approximately 20 % less. This effect is probably due to the size of the potassium atom, restricting the amount that can adsorb onto a given area on the silica gel surface and also restricting the diffusion of potassium into the silica gel micropores.

The magnesium did not adsorb to the same extent as sodium and potassium because it is a divalent atom which requires two adjacent active silanol sites on the silica gel surface for adsorption to occur.

The effect of monovalent and divalent alkali metals on the water vapor adsorption rates on silica gel is illustrated in Figure 5.3. The temperature rise associated with the water vapor adsorption rates was highest for the sample treated with potassium, then magnesium, followed by sodium and HCl (no surface alkali ions present). It is interesting to note that even though there was almost 70 percent less magnesium deposited onto the silica gel surface, the water vapor

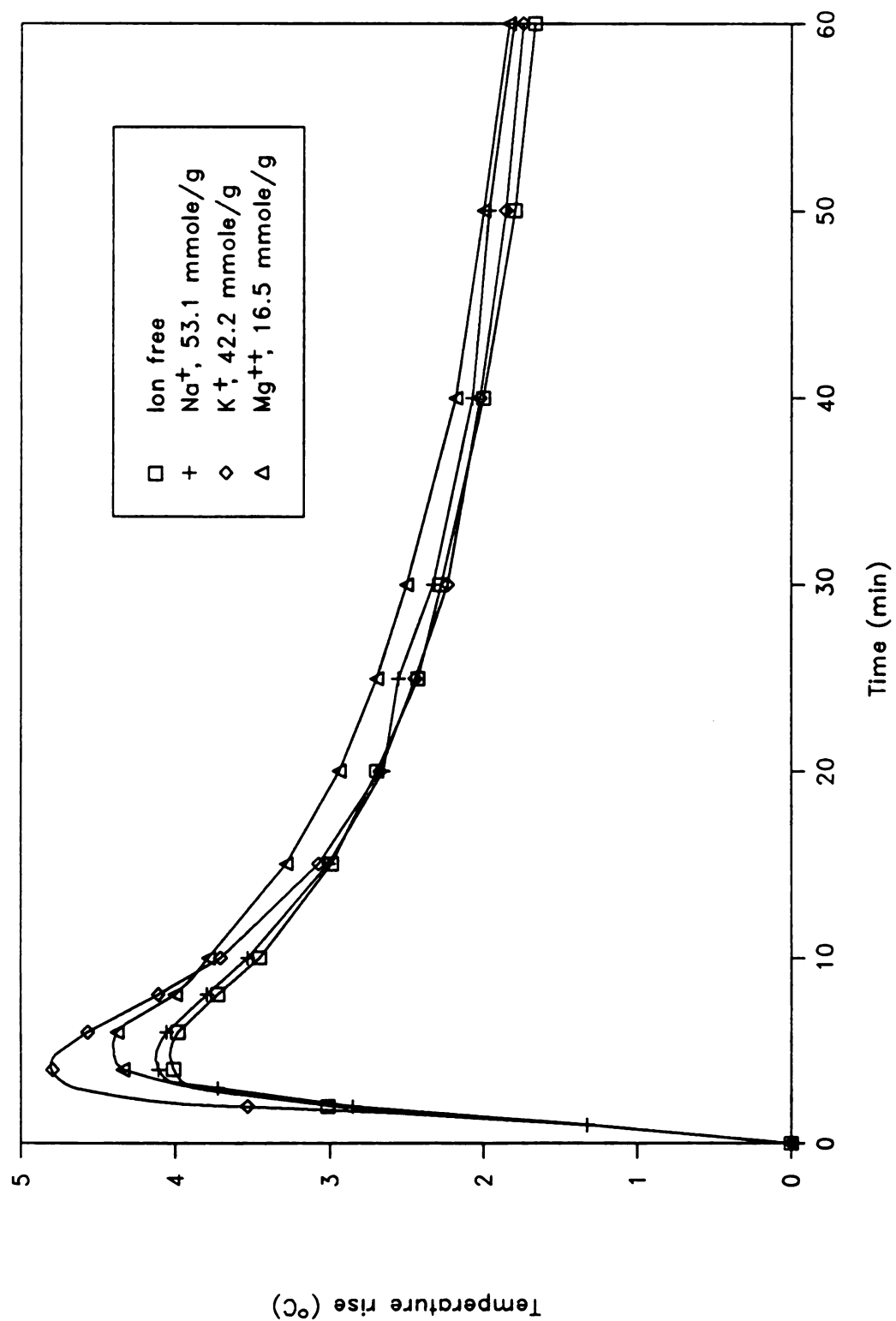


Figure 5.3. Effect of surface alkali metal ions on the temperature rise associated with water vapor adsorption on silica gel. ($P/P_s = 0.9$, $T = 25^\circ\text{C}$)

adsorption rate appeared to be greater than the adsorption rate for the sample treated with sodium. Also, the sample appeared to continue to adsorb water at a faster rate than the other samples beyond the first ten minutes, when adsorption rate differences are more noticeable. This may be an effect of the greater charge density of magnesium which enhances water adsorption beyond the first or second molecular layer of adsorbed water.

The water vapor adsorption rate is clearly a function of the concentration and electronegativity of the deposited alkali ion on the silica gel surface.

D. Effect of Electric Fields on Water Vapor Adsorption Rates

The results of the temperature study experiments involving water vapor adsorption on silica gel treated with alkali metals in the presence of a D.C. electric field are presented in this section. The experiments were performed using a cylindrical non-uniform D.C. electric field of 6 kV. The water vapor stream was 90 percent saturated ($P/P_g = 0.90$). Comparisons are made between the field and non-field experiments for the base case (HCl pretreatment) and each alkali metal treated sample. Also, the results for all of the adsorption studies in an electric field are compared.

Figures 5.4-5.7 show the effect of a 6 kV non-uniform electric field on the temperature profile associated with the water vapor adsorption rates on the ion-free, sodium, potassium, and magnesium treated silica gel samples. The

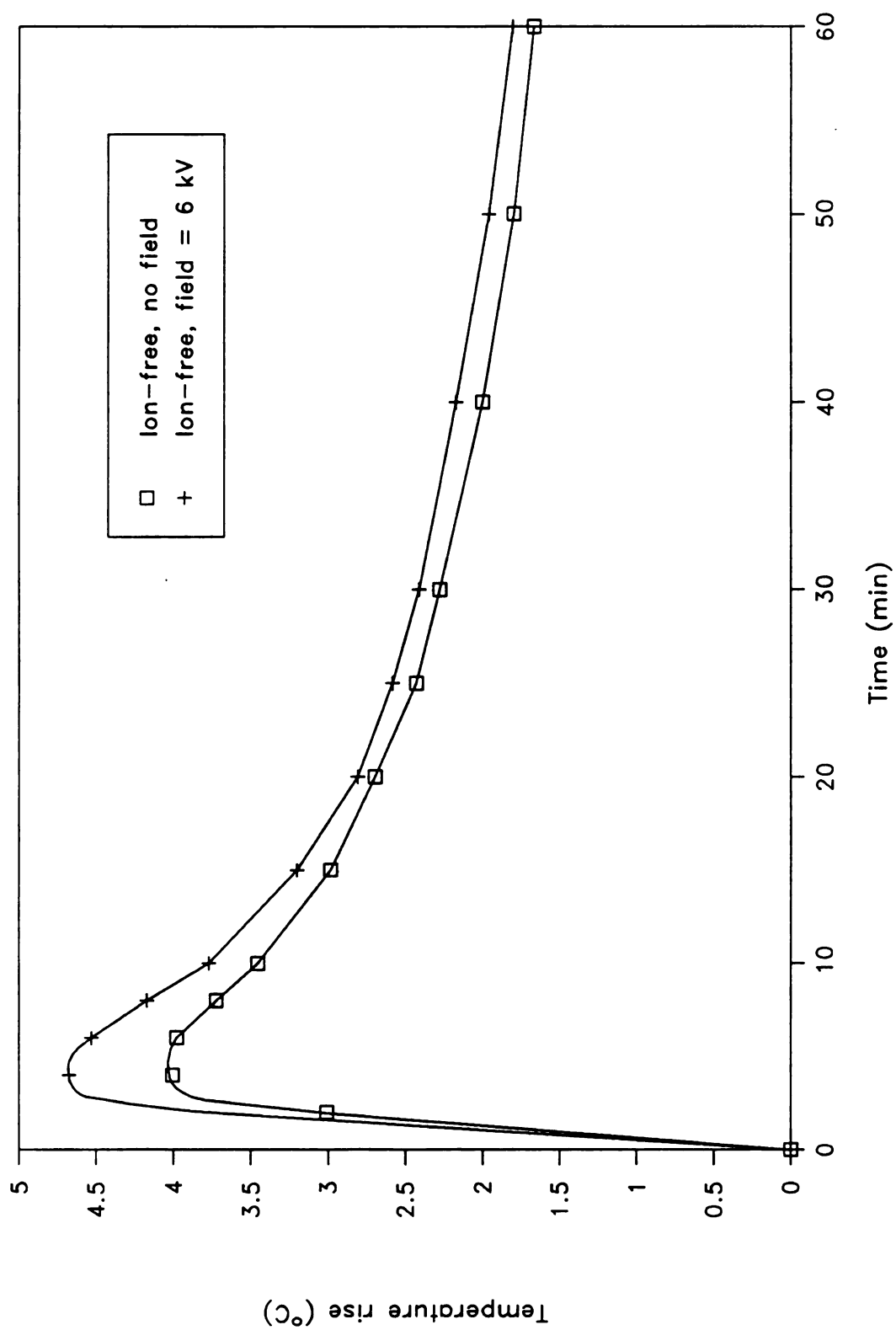


Figure 5.4. Effect of 6 kV non-uniform D.C. electric field on the temperature rise associated with water vapor adsorption on silica gel pretreated with HCl. ($P/P_s = 0.9$, $T = 25^\circ\text{C}$)

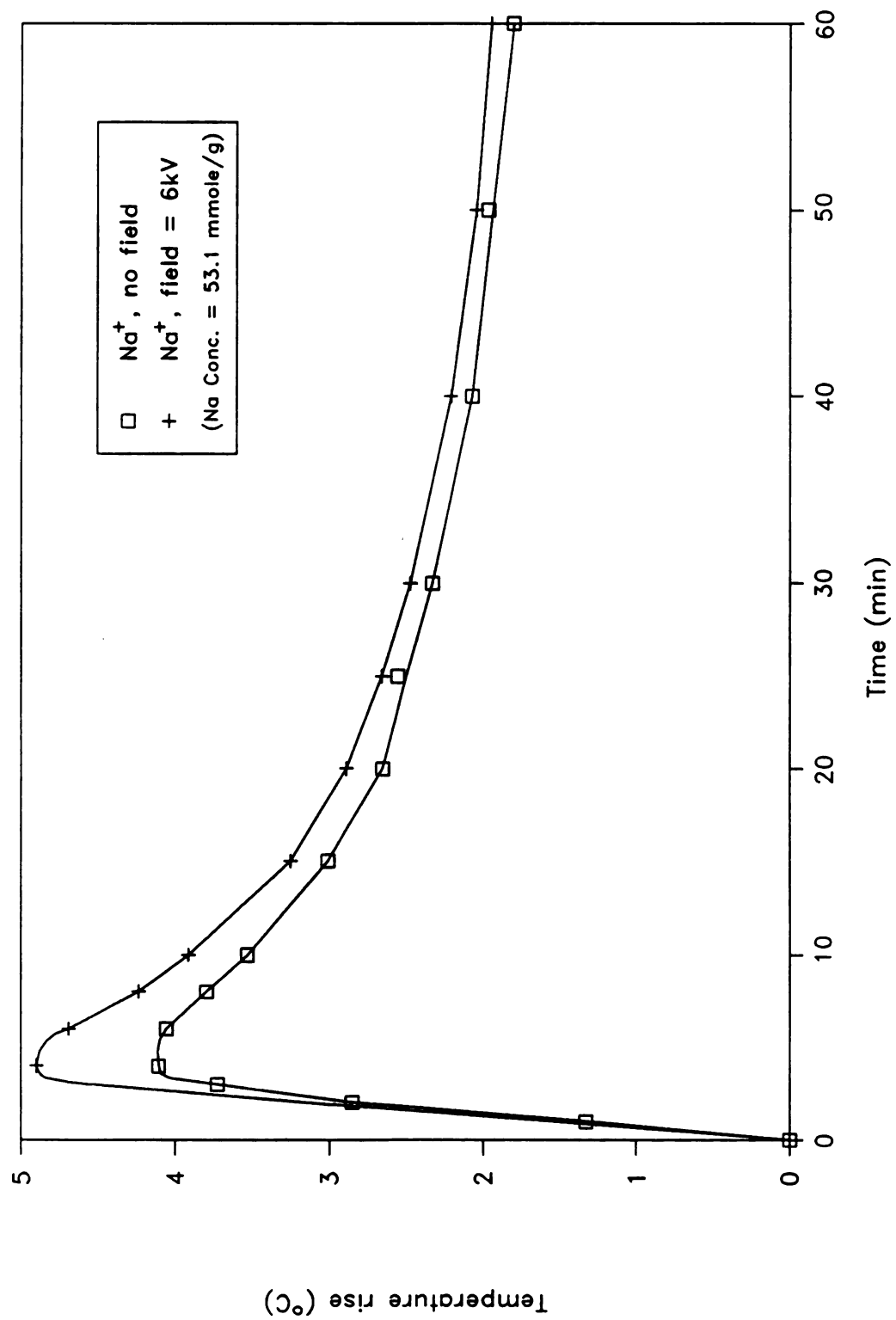


Figure 5.5. Effect of a 6kV non-uniform D.C. electric field on the temperature rise associated with water vapor adsorption on silica gel treated with sodium ions. ($P/P_s = 0.9$, $T = 25^\circ\text{C}$)

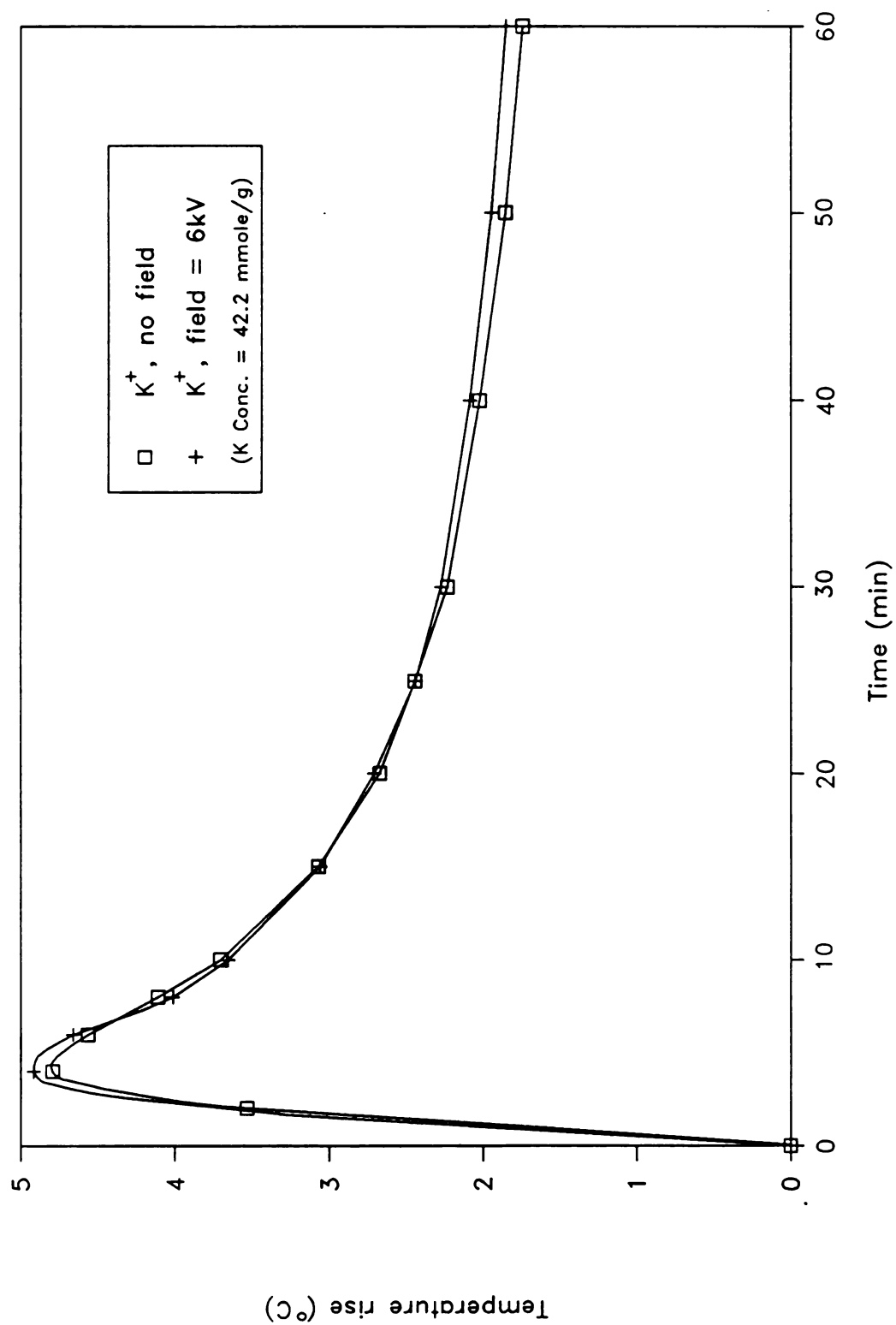


Figure 5.6. Effect of a 6 kV non-uniform D.C. electric field on the temperature rise associated with water vapor adsorption on silica gel treated with potassium ions. ($P/P_s=0.9$, $T=25^\circ\text{C}$)

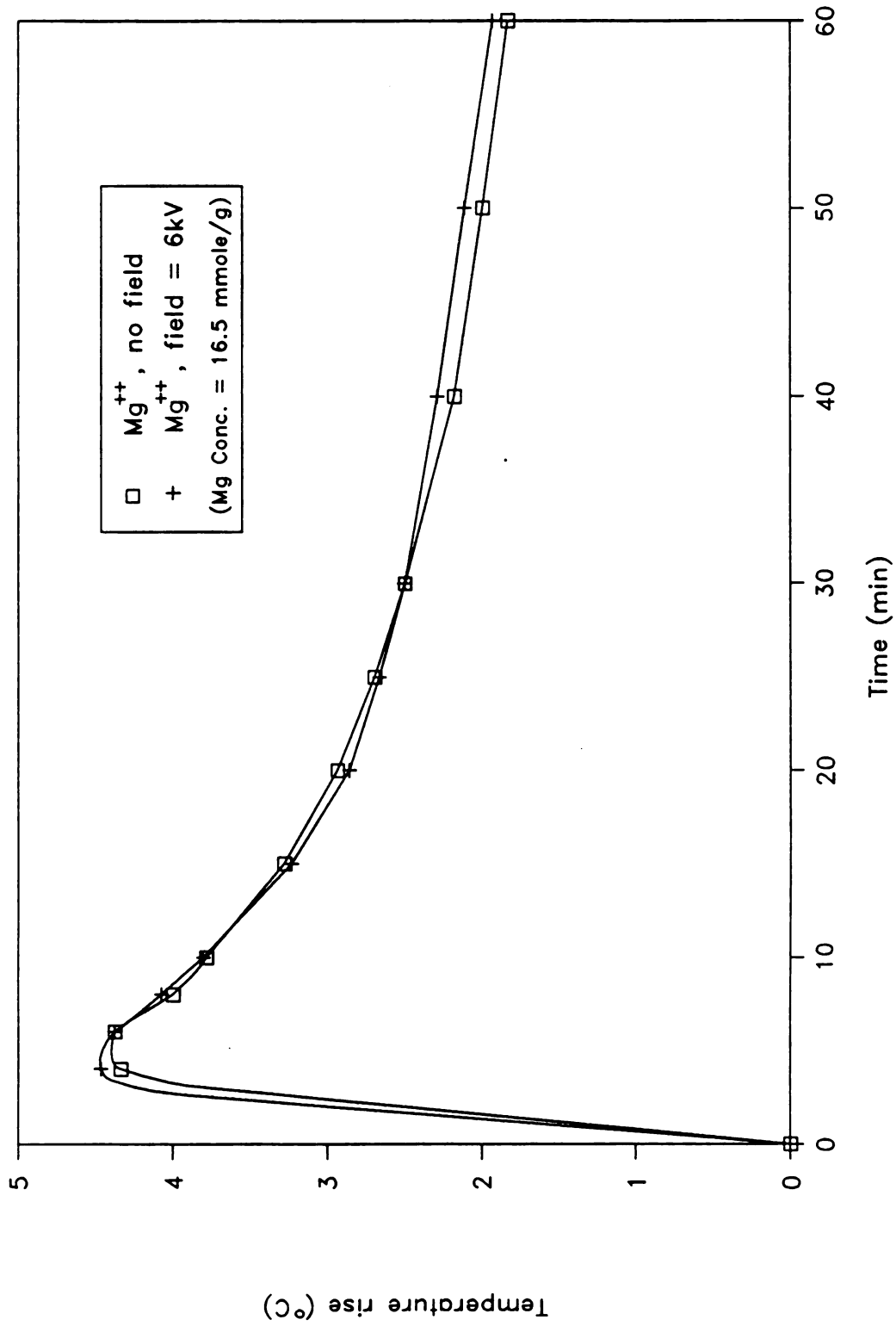


Figure 5.7. Effect of a 6 kV non-uniform D.C. electric field on the temperature rise associated with water vapor adsorption on silica gel treated with magnesium ions. ($P/P_s = 0.9$, $T = 25^\circ\text{C}$)

ion-free and sodium treated samples exhibited definite field-enhanced adsorption rates throughout the first sixty minutes of the adsorption experiment, whereas the samples treated with potassium and magnesium were affected very little by the electric field.

It is interesting to note that the silica gel samples which showed the lowest non-field adsorption rates (see figure 5.3) exhibited the greatest field-enhancement effects (see figures 5.4-5.7). This may be due to the overriding effect of the stronger cations during the initial stages of adsorption when monolayer water vapor adsorption is primarily taking place. Later during the adsorption process, when multilayer adsorption and capillary condensation are occurring, the electric field has a more noticeable effect.

This can be seen by looking at the electric field enhancement beyond the initial ten or twenty minutes of adsorption. All of the samples exhibited slight adsorption enhancement from thirty minutes onward. This continued enhancement was most noticeable for the ion-free sample that was pretreated with HCl and rinsed with water. The temperature rise associated with the water vapor adsorption appears to remain elevated beyond the initial thirty minute time period. However, this apparent adsorption enhancement may be due to the higher initial temperature which results from the initial adsorption rate enhancement.

Figure 5.8 compares the temperature rise for water vapor adsorption rates on alkali metal treated silica gel in the

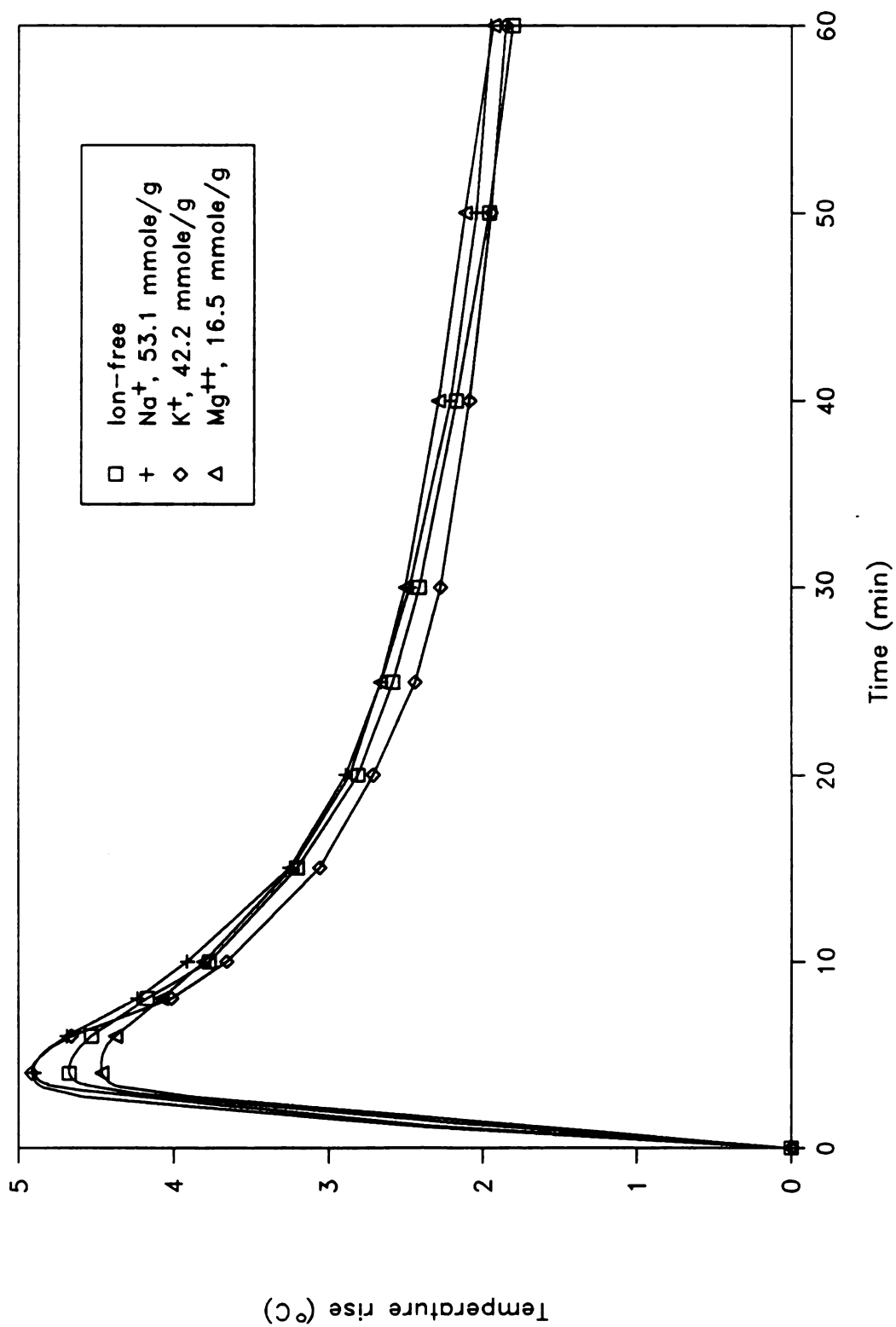


Figure 5.8. Effect of various alkali metal ions on the temperature rise associated with water vapor adsorption on silica gel in the presence of a 6 kV non-uniform D.C. electric field. ($P/P_s = 0.9$, $T = 25^\circ\text{C}$)

presence of a 6 kV D.C. electric field. The potassium and sodium treated samples experienced the greatest temperature rise at the beginning of the experiment; however, the potassium treated sample temperature dropped off more sharply than the other samples, and even had the lowest temperature after ten minutes. The magnesium treated sample behaved oppositely by yielding the lowest initial adsorption rate temperature rise followed by the highest adsorption temperature enhancement past the first twenty minutes. This may be a result of the decrease in the driving force for adsorption as the silica gel becomes more filled with water. In other words, the samples which exhibit a higher initial adsorption rate will become saturated faster and thus will show a greater adsorption rate decrease than the samples which exhibited a slower initial adsorption rate.

Chapter VI

Conclusions and Recommendations

A. Conclusions

Aqueous HCl pretreatment of Sigma Chemical S-2509 silica gel removes essentially all of the surface sodium ions without altering the silica surface chemistry. Neutron activation analysis revealed that approximately 90% of the sodium ions were removed following pretreatment with concentrated HCl and rinsing with water. The "as received" silica gel contained .06 wt.% sodium compared to .006 wt.% sodium measured on the HCl pretreated sample.

The total water vapor adsorption capacity of the silica gel was unaffected by the hydrochloric acid pretreatment. This was evidence that the gel surface area, surface activation, and porosity had remained unchanged. The adsorption capacity of the "as received" and HCl pretreated silica gel samples were 65 and 67 percent respectively (defined as grams H₂O/grams silica gel).

The "as received" silica gel contains sodium which may be in the form of an oxide, Na₂O, which reacts exothermally with water as follows:



The adiabatic temperature rise of the "as received" silica gel sample, if all of the sodium were present as Na_2O , would be 9°C . The amount of water that would react with this sodium is 0.03 mg/100 mg silica gel (0.03 wt.%). This represents only 0.15 percent of the total water adsorbed during a typical one hour experiment. Thus, even a small amount of residual sodium oxide on the "as received" silica gel could have caused the unusually high initial temperature rise for the water vapor adsorption experiments compared with the HCl pretreated sample.

Alkali metal ions deposited on the surface of silica gel enhance the water vapor adsorption rates. The three alkali metals tested were sodium, potassium, and magnesium. Since the metals were deposited on the silica gel at different concentrations, it is difficult to compare the magnitude of the rate enhancement. However, it is clear that potassium and magnesium enhanced the adsorption rates to a greater extent than sodium. The deposited ions are not present as the oxides since they are not soluble. The number of potassium ions deposited on the silica gel surface was less than the number of sodium ions, yet the temperature rise associated with the adsorption on the potassium treated samples was higher than that of the sodium treated samples.

One factor that could contribute to the enhanced adsorption rates for the potassium treated samples is the larger ionic radius, providing more surface area for adsorption. Potassium has an ionic radius of 1.33 angstroms,

compared with 0.96 angstroms for sodium.

Magnesium deposited on the silica gel surface also enhanced the water vapor adsorption rates, but not to the same extent as potassium. This is because the magnesium treated samples contained 60 to 70 percent less ions than the sodium or potassium treated samples. The divalent magnesium ion requires two active adjacent surface silanol groups for adsorption to occur, whereas the monovalent ions require only one. The ionic radius of Mg (0.65 angstroms) is smaller than sodium or potassium. This translates to a smaller surface area for adsorption of the polar water molecules.

A non-uniform D.C. 6 kV electric field was shown to enhance the water vapor adsorption rates on silica gel. Adsorption enhancement was evident during the entire sixty minutes of the adsorption experiments for the ion-free and sodium treated silica gel samples, but only during the final thirty minutes for the potassium and magnesium treated samples. Interestingly, the silica gel samples which showed the lowest initial non-field adsorption rates exhibited the greatest field-enhancement effects. This may be due to the overriding effect the stronger cations have during the initial stages of adsorption when monolayer water vapor adsorption is primarily taking place. Later, during multi-layer adsorption and capillary condensation, the electric field has a more noticeable effect.

B. Recommendations

In light of the qualitative results from this study, a more thorough, quantitative evaluation of the effects of alkali ions on water vapor adsorption rates on silica gel needs to be conducted. Several methods are available for studying low water vapor adsorption rates on silica gel. These include a thermal conductivity cell (19), a P_2O_5 electrolytic cell (11), and a gravimetric method (1).

An investigation of the monolayer adsorption kinetics and the effects of alkali ions should be included by subjecting the silica gel to water vapor streams with $P/P_g = 0.3$ rather than $P/P_g = 0.9$ for this study. These conditions are more typical of coal burning facilities. Also, from results seen in this study, monolayer adsorption may be affected by the alkali surface ions to a greater extent than multilayer adsorption. This can be concluded by looking at the more drastic temperature rise differences during the initial stages of adsorption for the $P/P_g = 0.9$ tests in this study.

The temperature profiles for times greater than 60 minutes should be investigated to study the multilayer and capillary condensation phenomena more closely. One of the drawbacks in this type of study, however, is that the dissipation of energy due to conductive and convective heat losses may be so large that the temperature differences due to adsorption may be indistinguishable between the various silica gel samples.

Methods need to be developed for activating the silica

gel surface so that more active silanol groups can be made available for alkali metal chemisorption. Suggestions would include treatment with boiling water (11), steam, or various acids.

A sufficient energy balance needs to be developed for the silica gel-water vapor system in order to quantitatively evaluate the adsorption rates by observing the temperature rise associated with the adsorption. These energy balances could then be applied to the data for this study to obtain a more quantitative evaluation of the results.

Adsorption experiments using fly ash and alkali ion treated fly ash need to be conducted to verify the applicability of using silica gel as a model for the fly ash - water vapor system. Fly ash composition and structure is highly dependent on the type of coal burned and on the particulate removal devices used to collect the fly ash. Therefore, high variability will exist with different fly ash samples from different sources tested. Various fly ashes should be tested to observe the effects of alkali metal content, sulfur content, fly ash particle size, etc.

APPENDICES

APPENDIX A

Appendix A
Neutron Activation Analysis Data

Sodium Analysis #1

<u>Sample Description</u>	<u>Sample Size, mg</u>	<u>Na-24 Integral</u>	<u>Na, mg</u>
Untreated S.G.	100	836	0.057
Untreated S.G.	150	1208	0.084
HCl, Water Treated	100	114	0.005
1 M NaCl, Water	100	454	0.030
1 M NaCl, Water	80	360	0.023
Standard		29231	2.30
Standard		16255	1.15
Standard		10987	0.69
Standard		6216	0.46 (r=.996) ¹
Distilled Water	1 ml	63	0.0

Sodium Analysis #2

<u>Sample Description</u>	<u>Sample Size, mg</u>	<u>Na-24 Integral</u>	<u>Na, mg</u>
Untreated S.G.	100	6029	0.068
HCl, Water Treated	100	455	0.007
4 M NaCl, Water	100	11360	0.128
0.1 N NaOH	81	145699	1.876
Standard		90201	1.15
Standard		40550	0.46
Standard		24365	0.23
Standard		10452	0.115 (r=.998)
Distilled Water	1 ml	0	0.0
Empty Vial		0	0.0

¹_r - Correlation Coefficient

Sodium Analysis #3

Sample Description	Sample Size, mg	Na-24 Integral	Na, mg
.01N NaOH Treated	0.5	4048	0.05
.01N NaOH Treated	89.1	43492	0.52
.01N NaOH Treated	99.1	418	0.006
.001N NaOH Treated	99.8	376	0.006
.0001N NaOH Treated	99.0	510	0.007
Standard		109347	1.15
Standard		38614	0.46
Standard		19000	0.23 (r=.9994)
Distilled Water	1.0		

Sodium Analysis #4

Sample Description	Sample Size, mg	Na-24 Integral	Na, mg
Standard		86214	0.460
Standard		45082	0.230
Standard		23563	0.115 (r=.9999)
Untreated S.G.	95	9263	0.050
Water Rinsed	100	1778	0.009
.005N NaOH Treated	95.3	67432	0.355
5M NaCl Treated	97.8	23019	0.122
Distilled Water	1 ml	0	0

Potassium Analysis

<u>Sample Description</u>	<u>Sample Size. mg</u>	<u>K Integral</u>	<u>K. mg</u>
Sat'd KCl Treated	100	2528	0.168
Sat'd KCl Treated	100	2400	0.161
Standard		6195	0.43
Standard		3184	0.215
Standard		1701	0.108
Standard		925	0.054 (r=.9999)

Magnesium Analysis

<u>Sample Description</u>	<u>Sample Size. mg</u>	<u>Mg Integral</u>	<u>Mg. mg</u>
Sat'd MgCl ₂ Treated	200	37537	0.08
Standard		191960	0.40
Standard		94656	0.20
Standard		50694	0.10 (r=.9997)

Magnesium half life = 10 minutes. Numbers are corrected for half life error.

APPENDIX B

Appendix B
Adsorption Experimental Data

Silica Gel Water Vapor Adsorption Capacity Data
(P/Ps = 0.9, adsorption time = 8 hrs.)

<u>Treatment</u>	<u>Dry Weight</u>	<u>Saturated Weight</u>	<u>Wt.% Water Capacity</u>
As Received	48.6	80.2	65.0
Water Rinse	43.5	71.4	64.2
HCl, Water	58.3	97.2	66.7
.005 N NaOH	65.8	100	52.0
Sat'd NaCl	54.9	92.8	69.0

Temperature Study Results (temperature rise, deg. C)

Treatment: None, "as received"
Field: 0 kV

TIME MIN	Test 31	Test 35	Test 39	Average	Std. Dev.
0	0	0	0	0.00	0.00
1	2.050			2.05	0.00
2		3.346		3.35	0.00
3	4.623		4.255	4.44	0.18
4	4.836	4.545	4.681	4.69	0.12
6	4.642	4.429	4.468	4.51	0.09
8	4.178	4.101	4.043	4.11	0.06
10	3.772	3.83	3.714	3.77	0.05
15		3.327		3.33	
20			2.843	2.84	0.00
25	2.573	2.766		2.67	0.10
30	2.398	2.514	2.398	2.44	0.05
40		2.263	2.147	2.21	0.06
50	1.934	2.07		2.00	0.07
60	1.799	1.934	1.818	1.85	0.06

Treatment: H2O
Field: 0 kV

TIME MIN	Test 46	52	53	Average	Std. Dev.
0	0	0	0	0.00	0.00
1					
2	2.437	2.532		2.48	0.05
3					
4	3.946	4.023	3.891	3.95	0.05
6	3.946	4.006	3.875	3.94	0.05
8	3.675	3.772	3.589	3.68	0.07
10	3.433	3.521	3.367	3.44	0.06
15	2.978	3.002	2.951	2.98	0.02
20	2.708	2.692	2.714	2.70	0.01
25	2.476	2.411	2.508	2.47	0.04
30	2.302	2.228	2.312	2.28	0.04
40	2.108	2.094	2.1	2.10	0.01
50	1.954	1.895	1.981	1.94	0.04
60	1.857	1.74	1.923	1.84	0.08

Temperature Study Results (temperature rise, deg. C)

Treatment: HCl
Field: 0 kV

TIME MIN	Test 16	Test 17	Test 18	Test 25	Test 45	Average	Std. Dev.
0	0	0	0	0	0	0	0.00
1							
2	3.114	3.249	2.668			3.01	0.25
3		4.023	3.559				
4	4.236	4.321	3.887	3.802	3.793	4.01	0.23
6	4.119	4.313	3.926	3.694	3.851	3.98	0.22
8	3.771	3.963	3.733	3.501	3.657	3.73	0.15
10	3.462	3.578	3.539	3.269	3.425	3.45	0.11
15	2.920	3.056	3.075	2.882	3.000	2.99	0.08
20	2.591	2.766	2.862	2.572	2.690	2.70	0.11
25	2.340	2.495	2.475	2.379	2.458	2.43	0.06
30	2.185	2.34	2.359	2.224	2.284	2.28	0.07
40	1.895	2.089	2.011	1.973	2.052	2.00	0.07
50	1.721	1.876	1.702	1.799	1.897	1.80	0.08
60	1.586	1.721	1.605	1.663	1.762	1.67	0.07

Treatment: None, "as received"
Field: 6 kV

TIME MIN	36	37	38	40	41	42	Average	Std. Dev.
0	0	0	0	0	0	0	0	
2								
4	4.778	4.178	4.507	4.758	4.197	4.391	4.47	0.24
6	4.526	4.101	4.294	4.487	4.081	4.255	4.29	0.17
8	4.197	3.830	3.926	4.081	3.830	4.004	3.98	0.13
10	3.810	3.598	3.636	3.714	3.617	3.694	3.68	0.07
15	3.346	3.172	3.172	3.191	3.191	3.230	3.22	0.06
20	2.921	2.805	2.805	2.843	2.843	2.901	2.85	0.04
25	2.727	2.631	2.611	2.631	2.514	2.688	2.63	0.07
30	2.592	2.456	2.437	2.456	2.244	2.514	2.45	0.11
40		2.205	2.205	2.244	2.070		2.18	0.07
50		2.031	2.012	2.031	1.934	2.108	2.02	0.06
60	2.186	1.954	1.818	1.838		1.973	1.95	0.13

Temperature Study Results (temperature rise, deg. C)

Treatment: HCl
Field: 6 kV

TIME MIN	26	27	28	29	30	Average	Std. Dev.
0	0	0	0	0	0	0	0
1							
2							
3							
4	4.468	4.99	4.333	4.545	5.029	4.67	0.28
6	4.216	4.719	4.236	4.468	5.010	4.53	0.30
8	3.849	4.255	3.927	4.236	4.584	4.17	0.26
10	3.578	3.888	3.637	3.636	4.120	3.77	0.20
15	3.114	3.288	3.114	3.056	3.443	3.20	0.14
20	2.804	2.882	2.708	2.514	3.133	2.81	0.20
25	2.611	2.592	2.495	2.360	2.863	2.58	0.17
30	2.437	2.437	2.321	2.244	2.631	2.41	0.13
40	2.205	2.166	2.050	2.128	2.321	2.17	0.09
50	1.857	1.992	1.876	1.895	2.186	1.96	0.12
60	1.760	1.857	1.760	1.779	1.876	1.81	0.05

Treatment: NaCl
Field: 0 kV

TIME MIN	20	21	47	49	50	51	54	AVG	Std. Dev.
0	0	0	0	0	0	0	0	0	0
1	1.16	1.489						1.32	0.16
2	3.056	2.959	2.882	3.288	2.863	2.205	2.708	2.85	0.31
3	3.791	3.656						3.72	0.07
4	4.061	3.888	4.236	4.352	4.159	3.946	4.101	4.11	0.15
6	3.984	3.810	4.159	4.216	4.101	4.004	4.12	4.06	0.13
8	3.675	3.559		3.946	3.888	3.868	3.83	3.79	0.13
10	3.404	3.346	3.424	3.714	3.617	3.636	3.578	3.53	0.13
15	2.862	2.940	2.901	3.114	3.133		3.095	3.01	0.11
20	2.572	2.514			2.766		2.766	2.65	0.11
25		2.379		2.592	2.592	2.689	2.534	2.56	0.10
30	2.224	2.263	2.224	2.379	2.398	2.476	2.360	2.33	0.09
40	1.992	2.050	1.973	2.108	2.186		2.128	2.07	0.08
50				1.953	1.992		1.954	1.97	0.02
60			1.721	1.818	1.838		1.838	1.80	0.05

Temperature Study Results (temperature rise, deg. C)

Treatment: .005 N NaOH
Field: 0 kV

TIME MIN	34
0	0
1	
2	
3	
4	4.004
6	3.714
8	3.308
10	2.979
15	2.398
20	
25	
30	1.702
40	
50	1.335
60	1.238

Treatment: .01 N NaOH
Field: 0 kV

TIME MIN	15	19	Average	Std. Dev.
0	0	0	0	0.00
1	0.657	1.393	1.025	0.37
2	3.057	2.998	3.028	0.03
3	3.597	3.501	3.549	0.05
4	3.597	3.579	3.588	0.01
6	3.210	3.172	3.191	0.02
8	2.746	2.786	2.766	0.02
10	2.514	2.476	2.495	0.02
15		1.876	1.876	
20		1.606	1.606	
25	1.508		1.508	
30	1.373	1.277	1.325	0.05
40	1.160	1.161	1.160	0.00
50	0.928	0.987	0.958	0.03
60	0.831	0.909	0.870	0.04

Treatment: 5 N NaCl
Field: 6 kV

TIME MIN	52	55	56	57	Average	Std. Dev.
0	0	0	0	0	0	0
1						
2						
3						
4	4.990	4.739	4.913	4.952	4.90	0.10
6		4.623	4.700	4.739	4.69	0.05
8	4.313	4.217	4.275	4.139	4.24	0.07
10	3.946	3.888	3.907	3.907	3.91	0.02
15	3.288	3.288	3.191	3.249	3.25	0.04
20	2.921	2.940	2.824	2.882	2.89	0.04
25	2.689	2.689	2.592	2.669	2.66	0.04
30	2.514	2.495	2.398	2.495	2.48	0.05
40	2.224	2.263	2.07	2.282	2.21	0.08
50	2.070	2.128	1.857	2.128	2.05	0.11
60	1.954	2.012	1.818	2.012	1.95	0.08

Temperature Study Results (temperature rise, deg. C)

Treatment: KCl
Field: 0 kV

TIME MIN	58	59	60	61	AVG	STD
0	0	0	0	0	0	0
1						
2	3.482	3.965	3.501	3.191	3.53	0.28
3						
4	4.719	4.971	4.797	4.681	4.79	0.11
6	4.487	4.623	4.565	4.584	4.56	0.05
8	4.043	4.139	4.101	4.159	4.11	0.04
10	3.656	3.752	3.656	3.772	3.71	0.05
15	3.017	3.037	3.114	3.114	3.07	0.04
20	2.669	2.650	2.669	2.708	2.67	0.02
25	2.437	2.379	2.495	2.476	2.45	0.04
30	2.282	2.166	2.263		2.24	0.05
40	2.050	1.973	2.050	2.031	2.03	0.03
50	1.876	1.818	1.876	1.857	1.86	0.02
60	1.760	1.683	1.779	1.760	1.75	0.04

Treatment: KCl
Field: 6 kV

TIME MIN	62	64	65	66	Average	Std. Dev.
0	0	0	0	0	0	0
1						
2						
3						
4	4.832	4.932	5.064	4.836	4.92	0.09
6	4.543	4.732	4.801	4.559	4.66	0.11
8	4.059	4.023	4.081	3.888	4.01	0.07
10	3.615	3.703	3.741	3.567	3.66	0.07
15	3.016	3.092	3.092	3.034	3.06	0.03
20	2.629	2.744	2.764	2.706	2.71	0.05
25	2.301		2.512	2.512	2.44	0.10
30	2.029	2.358	2.338	2.377	2.28	0.14
40	1.913	2.165	2.107	2.165	2.09	0.10
50	1.855	2.029	1.836	2.068	1.95	0.10
60	1.836	1.894	1.701	1.971	1.85	0.10

Temperature Study Results (temperature rise, deg. C)

Treatment: MgCl₂
Field: 0 kV

TIME MIN	70	71	Average	Std. Dev.
0	0	0	0	0
1				
2	3.420	2.937		
3				
4	4.579	4.096	4.34	0.24
6	4.521	4.231	4.38	0.14
8	4.077	3.922	4.00	0.08
10	3.864	3.710	3.79	0.08
15	3.381	3.188	3.28	0.10
20	2.995	2.879	2.94	0.06
25	2.744	2.647	2.70	0.05
30	2.531	2.473	2.50	0.03
40	2.280	2.087	2.18	0.10
50	2.106	1.894	2.00	0.11
60	1.913	1.758	1.84	0.08

Treatment: MgCl₂
Field: 6 kV

TIME MIN	68	69	Average	Std. Dev.
0	0	0	0	0
1				
2				
3				
4	4.541	4.386	4.46	0.08
6	4.444	4.309	4.38	0.07
8	4.115	4.038	4.08	0.04
10	3.787	3.826	3.81	0.02
15	3.227	3.246	3.24	0.01
20	2.879	2.840	2.86	0.02
25	2.686	2.647	2.67	0.02
30	2.512	2.492	2.50	0.01
40	2.280	2.299	2.29	0.01
50	2.087	2.145	2.12	0.03
60	1.893	1.971	1.93	0.04

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